

**METHODOLOGY FOR ASSESSING HEALTH RISKS
ASSOCIATED WITH MULTIPLE PATHWAYS OF EXPOSURE
TO COMBUSTOR EMISSIONS**

**Update to EPA/600/6-90/003
Methodology for Assessing Health Risks
Associated With Indirect Exposure
to Combustor Emissions**

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PREFACE

The National Center for Environmental Assessment has prepared this methodology in response to the 1993 Combustion Strategy for Hazardous Waste Incinerators released by the Administrator of EPA. Among other mandates regarding the regulation of this industrial sector, the strategy involved the requirement of EPA and/or the regulated community to conduct indirect exposure assessments to evaluate the impact of stack emissions. Although this mandate was specific to hazardous waste incinerators, the importance of the indirect pathways has extended to all combustors. The available methodologies at that time to conduct an indirect risk assessment were a 1990 ORD document titled, "Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions" (IEM) and the 1992 NCEA dioxin exposure reassessment document, "Estimating Exposure to Dioxin-Like Compounds". In order to develop a response to the Administrator's strategy, a workgroup comprised of ORD, OSWER, OAQPS, and others, convened. The result of this workgroup was an "Addendum" document to the 1990 Indirect Exposure document, released in November of 1993. This document described updates and other changes to the 1990 document; the two documents, together with other relevant information such as that from the dioxin exposure document or the Exposure Factors Handbook, would provide guidance on conducting indirect risk assessments.

The purpose of this document is to update the 1990 IEM. Most of the revisions provided in this document are based on SAB and public comments to the 1993 Addendum. Earlier versions of this document have undergone internal Agency and external peer review.

FOREWORD

The Cincinnati Office of the National Center for Environmental Assessment, in partnership with NCEA offices in Washington, DC and Research Triangle Park, is a center for leadership in the evolution of risk assessment research, conducting key risk assessments, and providing expert advice and support. We strive to provide our clients with the highest quality information and methods, resulting in the protection of human health and preservation of ecological integrity on a social cost-effective basis.

This methodology has been developed by NCEA scientists and engineers in Cincinnati and Washington. In addition, significant contributions to the methodology were provided by Office of Research and Development's National Exposure Research Laboratory in Athens, Georgia. The purpose of this methodology is to provide a set of procedures for estimating exposures resulting from atmospheric pollutants that are emitted from a stationary combustion source, transferred through the atmosphere, and deposited downwind to environmental media and biota.

Moreover, the methodology provides procedures to estimate indirect exposures that may result from uptake and transfer of atmospheric agents through the terrestrial or aquatic food chains. This multiple pathway exposure approach to environmental stressors facilitates reaching goals for aggregate exposure and estimates of cumulative risks.

This document is dedicated to our pursuit to improve exposure assessment as it relates to combustion risk assessment and other multiple pathways of exposures within the environment.

We commend all contributors and reviewers for creating this improved tool for completing risk assessments that result in more informed risk intervention decisions and improved communications for all.

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ABBREVIATIONS AND ACRONYMS

| | |
|--------|--|
| ADT | Average Daily Traffic |
| APCD | Air Pollution Control Devices |
| AQUIER | Aquatic Toxicity Information Retrieval |
| BAF | Bioaccumulation Factor |
| B(a)P | Benzo(a)pyrene |
| BCF | Bioconcentration Factor |
| BEF | Bioaccumulation Equivalency Factor |
| BSAF | Biota Sediment Accumulation Factor |
| BW | Body Weight (kg) |
| CDEP | Connecticut Department of Environmental Protection |
| DBAPE | Data Base Analysis and Parameter Estimation |
| DDT | 1,1'-(2,2,2-Trichloroethylidene)bis[4-chlorobenzene] |
| DI | Daily Intake (mg/kg-day) |
| DOC | Dissolved Organic Carbon |
| DOI | United States Department of Interior |
| DW | Dry Weight |
| EPA | United States Environmental Protection Agency |
| ER | Extra risk (unitless) |
| FCMs | Food Chain Multipliers |
| FDA | United States Food and Drug Administration |
| FGETS | Food and Gill Exchange of Toxic Substances |

ABBREVIATIONS AND ACRONYMS cont.

| | |
|--------|--|
| FW | Fresh Weight |
| GEMS | Graphical Exposure Modeling System |
| GI | Gastrointestinal Tract |
| H | Henry's Law constant (atm-m ³ /mol) |
| ha | Hectacre |
| HEM | Human Exposure Model |
| HI | Hazard Index |
| HSDB | Hazardous Substances Data Bank |
| IRIS | Integrated Risk Information System |
| ISC | Industrial Source Complex |
| ISCEV | Industrial Source Complex - Short Term EVENT Dispersion Model. |
| ISCST | Industrial Source Complex - Short Term Dispersion Model. |
| ISCLT | Industrial Source Complex - Long Term Dispersion Model. |
| IUR | Inhalation Unit Risk (per [mg/m ³]) |
| LOAEL | Lowest-Observed-Adverse-Effect Level |
| LST | Local Standard Time |
| MF | Modifying Factor |
| MSW | Municipal Solid Waste |
| MWC | Municipal Waste Combustor |
| NATSGO | National Soil Geographic Data Base |
| NCEA | National Center for Environmental Assessment |

ABBREVIATIONS AND ACRONYMS cont.

| | |
|--------|--|
| NFCS | National Food Consumption Survey |
| NOAA | National Oceanic and Atmospheric Administration |
| NOAEL | No-Observed-Adverse-Effect Level |
| NRMRL | National Risk Management Research Laboratory |
| NSSAD | National Soil Survey Area Data Base |
| NWS | National Weather Service |
| OPTS | Office of Pesticides and Toxic Substances |
| OSW | Office of Solid Waste |
| PAH | Polyaromatic Hydrocarbons |
| PCB | Polychlorinated Biphenyls |
| PCDD/F | Polychlorinated Dibenzo-p-dioxins/Polychlorinated Dibenzofurans |
| pH | - log [H ⁺] |
| POC | Particulate Organic Carbon |
| RCF | Root Concentration Factor |
| RCRA | Resource Conservation Recovery Act |
| RfC | Reference Concentration for Chronic Inhalation Exposure (mg/m ³) |
| RfD | Reference Dose for Chronic Oral Exposure (mg/kg-day) |
| SCS | Soil Conservation Service |
| SEAM | Superfund Exposure Assessment Manual |
| SIRS | Soil Interpretations Data Base |
| SOC | Semivolatile Organic Compounds |

ABBREVIATIONS AND ACRONYMS cont.

| | |
|-----------|--|
| SOILSF | GEMS Soil Data Base |
| SSURGO | Soil Survey Geographic Data Base |
| STATSGO | State Soil Geographic Data Base |
| $t_{1/2}$ | Environmental half-time (days) |
| T | Temperature (K) |
| TBI | Total Background Intake |
| TCB | 3,3',4,4'-Tetrachlorobiphenyl |
| TCDD | 2,3,7,8-Tetrachlorodibenzo-p-dioxin |
| TCE | Trichloroethylene |
| TDI | Total Daily Intake |
| TEF | Toxic Equivalent Factor |
| TEQ | Toxic Equivalent Concentration |
| TSP | Total Suspensible Particulate |
| TSS | Total Suspended Solids |
| UF | Uncertainty Factor |
| USDA | United States Department of Agriculture |
| USGS | United States Geological Survey |
| USLE | Universal Soil Loss Equation |
| VKT | Vehicle Kilometer Traveled |
| VOC | Volatile Organic Compound |
| WATSTORE | Water Data Storage and Retrieval Data Base |

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EXECUTIVE SUMMARY

INTRODUCTION

The “Methodology for Assessing Health Risks associated with Multiple Pathways of Exposure to Combustor” (MPE) document was developed by the Office of Research and Development’s National Center for Environmental Assessment (NCEA) - Cincinnati and Washington offices with the assistance of National Exposure Research Laboratory (NERL) -Athens, Georgia.

Purpose

The intent of this methodology is to 1) provide a set of algorithms for assessing human exposures to atmospheric pollutants emitted from stationary combustors, and 2) provide information on how to apply the methodology.

Historical Perspective

The inception of multiple pathway assessment occurred in the late 1980's and was first applied to rule-making in the evaluation of multiple pathways of exposure to air pollutants emitted from municipal waste incinerators in 1987. At the time, the U.S. Environmental Protection Agency (EPA) was undertaking risk assessments specific to exposures to a single chemical through a single pathway. For example, the Office of Air and Radiation would evaluate risks from inhalation exposures to single airborne toxicants; Office of Water would evaluate only ingestion of individual contaminants in drinking water.

The EPA published a document in 1990 entitled, “ Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions: Interim Final” (IEM), which charted new territory, and was a catalyst for change within the Agency. In May of 1993, the Administrator released the “Hazardous Waste Minimization and Combustion Strategy.” Among other recommendations regarding the regulation of this industrial sector, the strategy urged that the EPA and/or the regulated community

conduct indirect exposure assessments to evaluate the impact of stack emissions. To respond to the Administrator's request, a workgroup comprising several EPA offices was convened. In November of 1993, the Addendum to the IEM document was released by the cross-Agency workgroup. The IEM: Addendum was reviewed by the EPA's Science Advisory Board and the public. Subsequently, the peer review comments have been incorporated into this document. In addition, this MPE document contains information from the 1990 IEM and the IEM: Addendum as well as, the Dioxin Reassessment Document (1994), the Mercury Report to Congress (1997) and the Utility Boiler Report to Congress (1997). Therefore, this document supersedes the IEM and the IEM: Addendum.

Scope

The MPE methodology represents the state-of-the-science with respect to providing reliable guidance in the proper conduct of assessments of human health risks that may result from multimedia and multiple pathways of exposure. It includes analytical procedures and models for estimating exposures through direct and indirect pathways and risks resulting from atmospheric pollutants (excluding incinerator ash) that are emitted from a stationary combustion source. Direct exposures normally result from inhalation of combustor products. Indirect exposures result when the products of the combustor are transferred through the atmosphere and deposited downwind to environmental media (soil and water) and biota. Humans are secondarily exposed to multiple media (multimedia) by dermal contact, direct ingestion and/or ingestion of foods grown in the contaminated soil or water.

Intended Audience

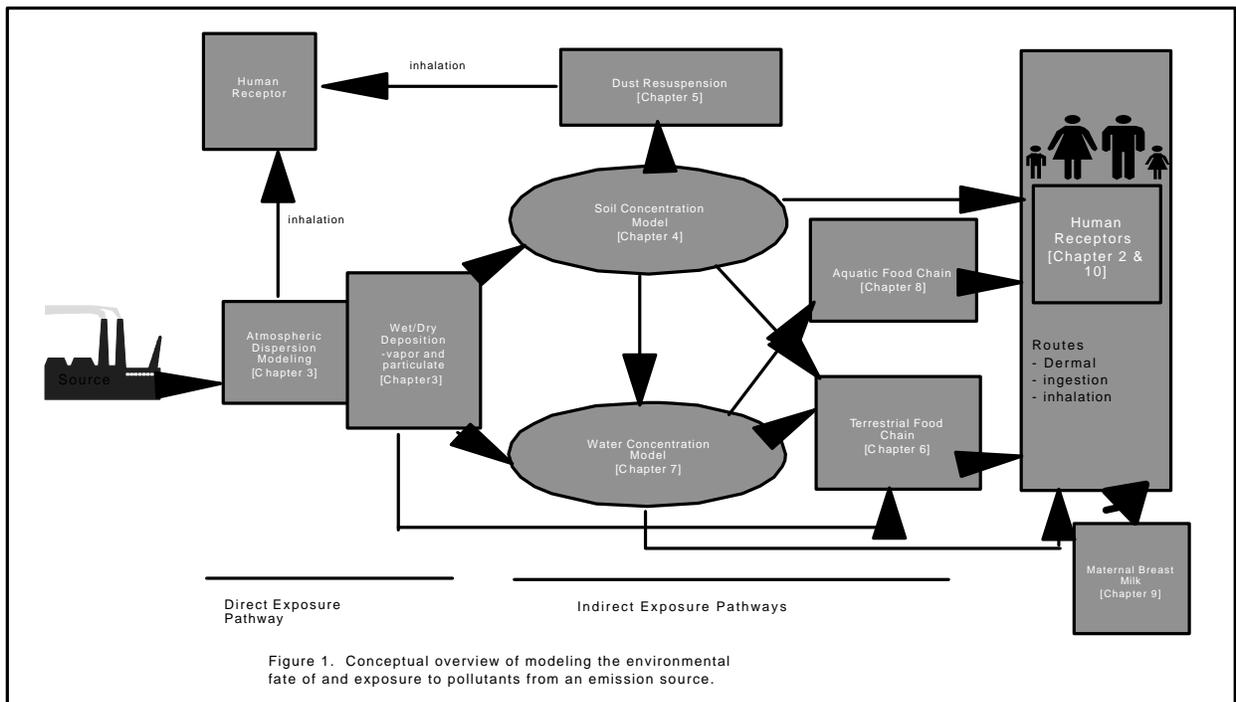
This methodology has broad application in the field of environmental science. It can be used by risk assessors, permit writers, scientists and engineers to estimate human exposures for various types of waste sites. The audience is anyone who is conducting a site assessment and needs to calculate pollutant concentration in

environmental media. It should be noted that this methodology is descriptive in nature, and other appropriate documents should be consulted when performing tasks that require step-by-step guidance. For example, this methodology does not provide default values for parameters, instead it describes the parameters and provides the algorithms for calculating media concentrations. A companion document, "Parameter Guidance" will provide a range of parameter values and direct the user to the source of information.

METHODOLOGY

This document is organized into chapters that reflect the components of the MPE process, as presented in Figure 1. The methodology begins with designing an exposure scenario and ends with a presentation of risk characterization. Aspects of this process significantly involve:

- ! Delineating the details of human exposure (Chapter 2);
- ! Determining the concentrations of pollutants emitted from the source utilizing air dispersion modeling (Chapter 3);
- ! Estimating media concentrations and exposure dose (Chapters 4 through 9);
 - ✓ Estimating cumulative soil concentration and exposure dose (Chapter 4)
 - ✓ Estimating dust resuspension (Chapter 5)
 - ✓ Evaluating exposure through terrestrial systems (Chapter 6)
 - ✓ Estimating water concentration and exposure dose (Chapter 7)
 - ✓ Evaluating exposure through aquatic systems (Chapter 8)
 - ✓ Estimating infant exposure to contaminants in breast milk (Chapter 9)
- ! Discussion of toxicity assessment and risk characterization as they relate to MPE (Chapter 10).



Chapter 2: Human Exposure

The main purpose of this chapter is to present a brief overview of exposure assessment as it relates to combustor emissions. This chapter presents the key elements and general approaches to developing an exposure scenario. In addition, a brief discussion on the different descriptors of exposure is provided.

Human exposure (contact of the chemical with the outer boundary of a human receptor) can occur by various pathways including dermal contact with pollutants in soil or water, inhalation of contaminated air, ingestion of contaminated soil, water, or biota; or consumption of breast milk contaminated by one or more of the other pathways. Development of exposure scenarios involves specification of: the time course of exposure; the exposure pathways (physical source or medium (e.g., soil), route, magnitude, duration); and the exposed individuals or populations.

Human exposure scenarios are developed using the following steps:

- ! identify emission source
- ! define source characteristics
- ! define the study area
- ! identify potential exposure pathways (environmental media and the possible routes of exposure)
- ! identify factors related to human exposures
- ! identify study populations, and/or individuals that could be exposed

Numerous exposure scenarios are therefore possible. The assessor has the responsibility to determine which reasonable scenario poses the greatest threat to human health.

In determining the exposure scenarios, land use, meteorological conditions, and topographic features are considered. After defining the scope of the assessment, other sources of exposure (background), defined as exposures to specific contaminants not the result of the combustor source in the particular assessment may also be considered.

The study area is characterized generally at a circular maximum distance of 50 km from the source (when the ISC3 air dispersion model is utilized.) Isopleths of concentrations, including air concentrations, wet deposition and dry deposition values within this region) are estimated. Each isopleth area can be examined individually and/or in conjunction with areas that pose the greatest health risk. If the outer isopleth is of concern, the study area must be enlarged. Assessment of the latter would require use of long-range transport models and would add uncertainty in the assessment.

Following delineation of the study area, the pathways of exposure are defined. They may include food ingestion, soil ingestion, dermal exposure to soil, inhalation of resuspended, contaminated dust, groundwater exposure pathways (bathing or

inhalation of volatilize contaminants, crop irrigation, livestock watering, etc.), surface water exposure pathways from deposition of emissions and runoff, consumption of fish and other aquatic organisms, accidental ingestion during recreational activities, collected precipitation (used as a water source), and maternal milk. The pathways may be selected based on knowledge of pollutant chemistry or factors associated with the exposed population.

Exposure factors which vary among exposed individuals and populations include biological characteristics such as age, and personal preferences (e.g., diet and cultural practices). Age can be a significant factor, especially when considering pollutants for which children are highly susceptible. Normal default assumptions include: the life span of adults, approximate average of 70 years, and adult body weight is 70kg. Residence time is a key factor and is best determined by site-specific information rather than national averages. Other factors include: recreational activities (fishing, hunting, outdoor exercise, sports), hobbies (home gardening), cultural practices (subsistence hunting and fishing, rituals), occupational activities (especially if the individual works for the combustor facility), lifestyle and habits (smoking, alcohol and drug use).

The approach to defining human exposure can be an in-depth analysis or a screening framework. With the latter, a maximally exposed individual is defined (99th + percentile involving all pollutants, pathways and exposure routes). If this individual does not have a significant risk, other analysis may be unnecessary. Also, it may be possible to eliminate some pollutants or pathways from a more detailed analysis.

Risks can be computed as point estimates (usually central tendencies and high end estimates (90th percentile)) or risk distributions. They may, for example, be presented as the potential number of cancer cases in an affected population or for noncancer effects, the number of persons whose exposure exceeds a specific risk level or reference dose (RfD). Risks can be defined for the population or specific sub-groups.

Chapter 3: Air Dispersion and Deposition Modeling

Estimation of health risks associated with exposure to air releases of contaminants from stationary industrial and combustion sources requires estimates of the atmospheric concentrations and annual wet and dry deposition rates of the emitted contaminants in the areas around those facilities. When atmospheric concentrations and deposition rates cannot be measured in the vicinity of operating sources, the U.S. EPA customarily uses air dispersion/deposition models to estimate the atmospheric transport, the surface deposition flux, and the ambient air concentrations of specific compounds attributable to smokestack emissions from an industrial combustion source. Air dispersion models are mathematical constructs that approximate the physical and chemical processes occurring in the atmosphere that directly influence the dispersion of gaseous and particulate emissions from the stack of a combustion source. These models are computer programs encompassing a series of partial differential and algebraic equations that calculate the dispersion and deposition of the emissions. Concentration and deposition estimates of the contaminants discharged from the stack are computed at specified distances from the source. These quantities are used to estimate the magnitude of potential exposures to receptors, and to estimate the potential health risks in populations living and working in the vicinity of the stationary combustion source.

The Industrial Source Complex 3 (ISC3) model is recommended, recognizing that improvements in this type of model are continuous and future recommendations may vary. Using this model involves: selection of air pollutants that are measured in stack emissions; estimation of the stack emission rate; estimation of increases in emissions during malfunctions, startup and shutdown; modeling of the fate of stack emissions, including wet and dry deposition; estimation of the size distribution of particulate matter, and estimation of exposure through inhalation of dispersed pollutants.

The assessor must define the contaminants that may be emitted from the source combustor. This information can be obtained from feed material, stack emission rate and operational circumstances and time factors of operation. A time frame of reference

must be determined, such as over the lifetime of the facility. Additionally, start-up, upset conditions, transitory meteorologic situations (inversions, etc.) need to be considered although for indirect exposure considerations, these may not be important.

The ISC3 model predicts ground-level concentrations directly proportional to the emissions rate. For operating facilities, stack emission analytical measurements are recommended; for planned facilities, stack tests may be used. Before modeling, the physical geography within 50 km of the combustor location must be systematically examined to include surrounding terrain elevation and dimensions of structures that may impact dispersion of the plume.

The **Critical Inputs** of the ISC3 are as follows: control, source, meteorological data (hourly stability class, wind direction, wind speed, and receptor).

The **Key Outputs** from the ISC3 include program control parameters, source data, receptor data, tables of hourly meteorological data for each specified day, average concentrations or total deposition calculated at each receptor for any desired source combination. Model outputs include both pollutant concentration and wet and dry atmospheric deposition over a given receptor area.

Sources of uncertainty and variability are always present and must be considered in all analyses and are inherent in transport variables (wind speed, mixed layer height, surface heat flux, emission characteristics, etc.) Even with a perfect model (which doesn't exist) there will be deviations (residuals) from the observed concentrations due to unknown conditions. Available evidence suggests that this source of uncertainty alone may be responsible for a typical range of variation in concentrations as much as 50%. Reducible uncertainty is caused by: uncertainties in the input values, errors in measured concentrations, and inadequate model physics and formulation. Regarding the latter, model verification is based on comparison of the model predictions and actual air concentration measurements. However, model limitations and database limitations are often confounded.

Limitations related to the ISC3 model are include: 1) model predictions are better for long-term averages than short-term and 2) beyond 50km the model utility diminishes.

After concentrations in air are estimated for receptor sites, the human exposure and dose are determined. Exposure is measured by the intensity and duration of contact at the external boundary of the organism and can be represented by a time-dependent profile of the environmental concentration at the point of contact. The biologically significant measure is the amount of contaminant that crosses the external boundary. This occurs by inhalation, ingestion or absorption through the skin.

Chapter 4: Soil Concentration and Exposure Pathways

Contaminants emitted from combustors either deposit onto surfaces in the vicinity of the facility or travel downwind. Deposition to soils through the processes of wet or dry deposition occurs in the particle or the vapor phase. Following deposition, contaminants may be incorporated into the upper layers of soil where crops or other vegetation are grown. This chapter focuses on estimating the concentration of a given contaminant in the soil following deposition from a combustor. The cumulative soil concentrations (C_s) are used to estimate the risk to humans who may have dermal contact with contaminated soil, ingest soil or household dust directly, or consume vegetation or animals that have been exposed to contaminated soil.

The **Key Inputs** include soil loss constant, bulk density, and wet and dry deposition rates of the contaminant to soil. When available, an overall environmental dissipation rate can be used as the soil loss constant. Otherwise, the soil loss constant can be determined by summing the applicable contaminant losses due to the individual environmental processes of leaching, degradation, volatilization, soil erosion, and surface water runoff. Losses due to degradation are chemical-specific and must be obtained from published field studies; availability of such data is a fundamental limitation on the application of the soil incorporation model. The other losses can be modeled from data on the underlying environmental processes if specific loss-rate

constants are not available. Such modeling, however, introduces considerable uncertainty in the overall dissipation rate estimate, as several of the inputs to the individual loss-rate models are difficult to estimate and model uncertainty may be high.

Another **key input parameter** that appears in several equations, on which the entire soil incorporation model is dependent, is the soil-water partition coefficient (K_{ds}). K_{ds} reflects the equilibrium sorption/desorption of chemicals to soil particles and is chemical specific. Some values for K_{ds} can be found in the literature but are central tendency estimates. Variations in soil properties greatly affect K_{ds}, which for inorganic chemicals can vary up to 3 orders of magnitude depending on soil pH. K_{ds} for organics may be estimated as a function of organic carbon in soil; model and parameter uncertainty is high in such cases. Therefore, it is advisable to use site-specific data for K_{ds} when available.

Key assumptions for soil concentration calculations are:

- ! Trace metal contaminants are assumed to be conserved indefinitely in the upper layer of soil unless loss constants are available;
- ! Degradation of organic contaminants is first-order; and
- ! If soil incorporation of contaminant is assumed, incorporation depth is 20 cm.

Contaminants on soil can be ingested incidentally by hand-to-mouth transfer or intentionally by eating soil. Human exposure to contaminants from soil ingestion is a simple function of soil-contaminant concentrations and estimated ingestion rates. A

Key Assumption is as follows:

- ! Deposited contaminants are assumed to be distributed within the uppermost 1 cm of soil (which is assumed to be the ingested layer). The incorporation depth is likely to be somewhat variable depending on local conditions; field studies are needed to define the variability in this parameter.

A primary limitation to this model is the general lack of data on the bioavailability of contaminants in soil, which is presumed to be much lower than bioavailability in food.

The daily intake for this pathway is compared with the RfD (reference dose for chronic oral exposure, mg/kg-day) for systemic toxicants to determine if the contaminant adversely affects human health. If the chemical is a carcinogen, the daily intake is used with the human cancer potency to determine excess risk.

A model is presented that estimates human exposure from skin contact with contaminants in the soil using a simple linear absorption fraction approach. The model relates absorbed dose to contaminant concentration in soil and depends on soil adherence properties, the frequency and duration of soil contact, the area of exposed skin, and the chemical-specific absorption fraction. The limited bioavailability of soil contaminants from combustor emissions, however, may significantly reduce the overall importance of this exposure pathway. In addition, the general lack of adequate data for estimation of at least one key parameter further limit the applicability of this model. Nevertheless, there is still the potential for human exposure from this pathway. The **key parameters (inputs)** of the model are absorption fraction, adherence factor, and exposure frequency. Variability in all of these key inputs can be an order of magnitude or more.

The absorption fraction (ABS) is particularly difficult to estimate. ABS is a chemical-specific quantity that depends on the physicochemical properties of the contaminant, but may also be affected by soil characteristics, skin characteristics, physical environmental factors, and extent of exposure. Most of these factors are not incorporated into the model, but may have significant impact on exposure. Predictive procedures for ABS are generally very limited, with most providing upper bound, rather than central tendency, estimates for ABS. The more robust approach based on permeability coefficients has not been tested adequately.

Chapter 5: Dust Resuspension

Contaminated particles deposited on soil may become aggregated with soil particles, which can be resuspended into the air by wind erosion and mechanical disturbances such as tilling or vehicular traffic. The risk assessor must identify

potential sources of dust generation within the study area and assess the potential for exposure. The contaminant resuspension flux can be calculated for agricultural soils and unpaved roads by multiplying the dust emission rate and the concentration of contaminant in the soil. Therefore the **Key Inputs** are dust emission rate, concentration of contaminant in the soil (C_s) and the enrichment ratio.

Key assumptions are as follows:

- ! Resuspended dust can add to exposure by the direct inhalation and by indirect routes;
- ! Transport is important in determining whether the resuspension changes the impact of the dust.

Factors which influence resuspension are: moisture content, presence of nonerodible surfaces, wind velocity, particle size, surface crust stability, and soil roughness height. Aspects of soil movement by wind are suspension (small particles that are kept airborne by wind forces), saltation (particles bounced over surfaces by wind, surface creep, and resuspension (re-entry of previously deposited contaminants back to the atmosphere). Wind erosion of open, plowed fields is considered to be a potentially significant source. Factors affecting this are soil erodibility, surface roughness, climate, unsheltered field width, and vegetative cover.

Chapter 6: Terrestrial Food Chain

The terrestrial food chain includes plants that animals consume, plants that humans consume, and animals that humans consume. Plants take up contaminants directly from the soil or from the atmosphere. Animals are exposed to contaminants by ingestion of plants and soils. The algorithms for estimating terrestrial food chain impacts are relatively simple screening-level models.

Key Input parameters in these fate algorithms fall into three categories. The first category includes media concentrations, specifically the soil and air concentrations and the atmospheric deposition fluxes presented in Chapters 3 and 4. A second category of parameters includes those that are specific to the contaminant. Included here, for example, are the bioconcentration/biotransfer factors used to translate an animal diet of the contaminant into an animal tissue concentration. The final category of parameters are the general physical parameters not related to the contaminants, such as plant yields and animal diet descriptors.

The analysis procedures for plants and animals are similar. First, the fate pathways are analyzed (transfer of contaminants from air to plant, or the bioaccumulation of ingested contaminants in animal tissue). Following this, human daily intake is determined, given the food concentrations.

The **Key Assumptions** are:

- ! The source strength remains constant throughout the period of exposure,
- ! Plant concentrations are modeled as a function of the deposition of contaminants that have been emitted from the combustion source and traversed to where the plants are growing (also considered is a component due to root uptake and translocation),
- ! Exposure of terrestrial animals to bioaccumulating contaminants is primarily through ingestion of food and soil.

Human daily contaminant intake from consumption of contaminated plants is calculated by multiplying the concentration of contaminant in each plant group by the amount of contaminated plant group consumed daily. Similarly, daily contaminant intake from the consumption of meat, dairy products, or eggs is determined from the concentration of contaminant in the animal tissue and the amount of each contaminated animal tissue that is consumed daily.

Chapter 7: Water Concentration and Exposure Pathways

To determine exposures to combustor-emitted contaminants in water, a model is presented for estimating surface water concentrations resulting from contaminant deposition. To proceed from concentrations to exposures, water consumption rates are presented, and then a model for estimating dermal absorption is given. Modeling the concentrations in surface waters requires determining the flows of water and sediments into a water body (such as a lake or river near the combustor), within the water body (especially between the water column and the bottom sediments) and out of the water body. These are normally determined only on a long-term basis, but for some contaminants it may be important to determine these flows during storm events, and a procedure for doing this is also presented. Superimposed on these flows are the partitioning characteristics of the contaminant, which determine how it will be distributed between the respective soil, water, sediment and air compartments of the watershed and water body, and environmental dissipation characteristics.

Besides the contaminant deposition rates and air and soil concentrations, which are calculated earlier, the **Key Inputs** to this model fall into the categories of watershed, hydrologic, partitioning and degradation. The key watershed and hydrologic parameters are those used to estimate sediment runoff yields in the Universal Soil Loss Equation (USLE) and its storm-event companion, the Modified USLE. Problems may be encountered in determining these yields over large watershed areas or for large water bodies; the complex hydrodynamics of estuaries makes them particularly difficult to model. The needed partitioning and degradation parameters are chemical-specific and sometimes are unavailable or entail large uncertainties.

Deposited contaminants may directly enter precipitation collection systems, but attention must be given to the synchrony of stack emissions and precipitation events, and to the behavior of contaminants within the collection system itself. Contamination of potable ground water is ruled out unless unusual conditions of contaminant emission or aquifer vulnerability exist.

Dermal absorption of contaminants, such as during bathing, depends on knowing a contaminant's permeability coefficient and other parameters related to the

dynamics of uptake. For fat-soluble (lipophilic) contaminants, uptake through the skin into the body occurs slowly and in stages, and may not reach steady state during brief exposure episodes. Modeling procedures for this nonsteady-state process are recently developed and are still under review within the scientific community.

Key assumptions are as follows:

- ! Soil concentrations within a depositional area are assumed to be uniform;
- ! Distribution of contaminants between the soil and water can be described by partition coefficients;
- ! Routes of entry are direct deposition, dissolution in annual surface runoff, soil erosion;
- ! For the steady-state surface water solution algorithm the assumption of equilibrium is maintained between contaminants within the water column and contaminants in bed sediments;
- ! The rate of contaminant burial in bed sediments is estimated as a function of the rate at which sediments deposit from the water column onto the surficial sediment layer;
- ! Separate water column and benthic decay rate constants allow for consideration of decay mechanisms that remove contaminants from the water body.

Chapter 8: Determining Exposure from Intake of Aquatic Organisms

The goal of chapter 8 is to present mathematical models that estimate human exposure to chemicals that occur in the tissues of aquatic organisms. Aquatic tissue concentrations of these chemicals are estimated from concentrations in either the water column or the sediment. In the pathway model described in this MPE, concentrations of chemicals in these two abiotic media are the result of the atmospheric and terrestrial transport of combustor emissions (Models described in Chapters 3 and 6, respectively). Chemicals that are known or suspected to bioaccumulate in aquatic food chains should be evaluated with these models. These may include organic compounds that could

accumulate in adipose tissues or metallic compounds that bioaccumulate in other fish tissues.

The **key inputs** to this model are chemical-specific medium concentration (in the water column or aquatic sediments), a bioaccumulation factor, and a fish consumption rate divided by human body weight.

A **key assumption** is this model assumes a steady-state concentration of pollutant in the abiotic medium.

The models presented evaluate bioaccumulation of chemicals through the aquatic food chain; several sources of such data as well as several alternative models which estimate the bioaccumulation are presented. The bioaccumulation factor (BAF) is defined as the equilibrium concentration of a chemical in a biological medium (as a result of all environmental sources of exposure) divided by the equilibrium concentration of a chemical in an environmental medium. Many environmental factors may affect bioaccumulation in an aquatic system. The uncertainty in this model parameter (BAF) is the typically the greatest source of uncertainty when the model is applied. The variability in individual human fish consumption rates also contributes to uncertainty in the modeled exposure estimate, although less substantially than the uncertainty in the bioaccumulation factor. Daily human fish consumption rates are known to range from 0 to well over 100 grams per day; it is important to know or estimate the distribution of local fish consumption rates in the study population. Body weight is also known to vary in the population; the variability in this factor generally affects model results less substantially than either bioaccumulation or consumption rate. Several large fish consumption rate surveys express the quantity of fish consumed on a body weight basis. These two parameters may be related, correlated, survey of this type account for such correlations. Other factors such as dilution of pollutants through growth in children are not modeled in this chapter.

Chapter 9: Infant Exposure to Contaminants in Breast Milk

Residues of organohalogen, organometallic and inorganic contaminants, many of which are found in emissions from combustion sources, have been detected in human breast milk. The contaminant concentrations in the milk, which in turn can be estimated on the basis of the contaminant intake by the mother, is used to estimate the average daily dose to the infant ingesting breast milk. Linear pharmacokinetic models are used to predict levels of contaminants in both the fat and aqueous phases of breast milk from maternal intake. Both phases are considered in order to estimate exposures from lipophilic compounds (dioxins, dibenzofurans, PCBs, etc.) and nonlipophilic compounds (metals, organo-metallics, etc.) alike.

The infant exposure model predicts contaminant concentrations in breast milk based on values for absorption, distribution to fat or within blood compartments, biological half lives, and plasma to milk partition coefficients. The **Key Inputs** to the breast milk model are the biological elimination constants for lactating (k_{elac}) or nonlactating (k_{elim}) women, and the red blood cell to plasma partition coefficient ($P_{\text{C}_{\text{RBC}}}$) for aqueous-phase compounds. There are no default values for the elimination constants, so existing data must be sufficient for estimation of these parameters in order to use the breast milk model. Also, lacking data for lactating women, breast-feeding losses must be modeled directly and combined with k_{elim} for nonlactating women. This approach may potentially overestimate k_{elac} , as the kinetic component for breast-feeding losses is much larger than k_{elim} itself. $P_{\text{C}_{\text{RBC}}}$ is a key parameter because it can dramatically influence the concentration of contaminant in the plasma, which is presumed to be the sole mode of transfer of contaminant to the aqueous phase of breast milk. Although the default for $P_{\text{C}_{\text{RBC}}}$ is set at 1.0, values higher than 20 have been reported for a least one compound (MeHg).

The breast milk model is structured to allow for consideration of both steady state and nonequilibrium conditions, the latter being of particular importance for shorter-term maternal exposure to highly lipophilic compounds. The model also allows for consideration of breast-feeding dynamics, in which the contaminant concentration in breast milk declines over the duration of breast feeding.

The **Key Assumptions** related to the breast milk model are as follows:

- ! The incorporation of time dynamics in the model is designed to avoid over prediction of infant exposure for some exposure scenarios if steady state were assumed;
- ! In order for the dynamic model to be accurate. First, linear (first-order) kinetics must be a reasonable approximation of the true kinetic behavior of these compounds. The simple linear models are unlikely to be accurate across a wide range of chemical properties and physiological processes, but the accuracy of this assumption remains to be tested.
- ! Maternal fat content and metabolism for both body fat and milk fat must remain in equilibrium; this assumption is very likely to be inaccurate, but a demonstrable bias in any given direction has not been established.

Available data are insufficient for adequate assessment of model performance. If the dioxin data are consistent with all models, then they are just another example of insufficient data, as described in the last bullet.

The incorporation of time dynamics is necessary in order to overcome a demonstrable (mathematical) bias towards over prediction of infant exposure, but errors in estimates of breast-feeding loss rate could over compensate for that bias resulting in under prediction of infant exposure. The utility of the infant exposure model is limited by the general lack of dose-response information for nursing infants. The model can still be used, however, to estimate contribution to lifetime cancer risk and for comparing exposure with the RfD for screening purposes. Potential risk to the infant from exposure to contaminants in breast milk must be balanced against the well-documented benefits of breast feeding.

Chapter 10: Risk Assessment

Chapter 10 provides an overview of human health risk assessment as practiced at the U.S. EPA and discusses specific risk characterization issues that may arise while conducting an assessment of risks posed by combustor emissions. This chapter shows how to use information from the previous 9 chapters that discuss various aspects of

exposure assessment in the larger context of human health risk assessment. Human health risk assessment has been defined as a four-step process, viz., hazard identification, dose-response assessment, exposure assessment, and risk characterization.

Hazard Identification The problem and the potential toxic effects are defined and the data needs are determined.

Exposure The exposure scenarios modeled may include exposure by multiple pathways and routes. Models designed to estimate chemical concentrations in environmental and biological media and, ultimately, human exposure are presented. In the MPE, daily pollutant intake has been calculated independently for the following routes and pathways: oral via produce, livestock, fish, breast milk, soil, and water; dermal via soil and water; and inhalation. A given individual or population may experience exposure by one or more of these pathways or routes.

To calculate total exposure to an individual, exposure estimates must be combined across pathways and routes. Ideally, internal measures of exposure to chemicals in question will be available. In the absence of measuring exposures or in cases where the facility has not yet been constructed, chemical-specific pharmacokinetic models should be used to estimate the internal doses that may result from exposures through different routes. In the absence of data to the contrary and if the risk assessor judges it to be appropriate, this methodology describes models capable of summing chemical exposures across both pathways and routes. The total daily intake (TDI) of a chemical attributable to indirect exposure to emissions from a combustor for a particular exposure scenario is estimated by summing the oral equivalent daily doses.

The MPE describes sources of exposure to chemicals other than from incinerator emissions. Background levels are defined as the concentration of a substance in an environmental media that (1) occurs naturally or (2) the concentration of a substance in a defined area from the period of time before the introduction of a specific anthropogenic source. Models are presented that describe how an assessor

could include background levels into a human health risk assessment. Models are presented that illustrate other approaches to assessing issues such as exposure duration.

Dose-Response The dose-response assessment defines the relationship between the exposure to a chemical and the associated health effects. The most common approaches used by the Agency, the reference dose (RfD-oral, dermal exposure) and reference concentration (RfC-inhalation) for noncarcinogens and the slope factor and unit risk for carcinogens, are presented.

Risk Characterization The risk characterization step provides both a quantitative and a qualitative evaluation and integration of the three previous steps; this evaluation and integration is translated into an overall conclusion about the likelihood of one or more adverse health effects occurring due to chemical exposure.

A component of the risk characterization is an assessment of uncertainty in the risk assessment. The uncertainty may arise from a lack of knowledge (i.e., uncertainty) or actual variability of a particular parameter. Sources of uncertainty include uncertainties related to the model predictions (physical construction of the model and uncertainties in inputs). Variability may include factors such as specific consumption rates. Approaches for evaluating uncertainty in the assessment, such as Monte Carlo analysis, are presented.

FUTURE RESEARCH NEEDS

Further development in the area is expected as new information becomes available and is interpreted and integrated. A few topic areas related to MPE development which were identified by external peer reviewers are as follows:

- ! Evaluation of “background” conditions and contribution to risk.
- ! Evaluation of degradation/transformation of chemicals (e.g., mercury, chromium, arsenic, dioxins, PCBs).
- ! Evaluation of multi-pollutant stressors.

- ! Evaluation of cumulative risk.
- ! Evaluation of fetal and infant exposure; evaluation of child sensitivity.

INTRODUCTION

1.1. BACKGROUND

In 1990, the National Center for Environmental Assessment (formerly known as the Office of Health and Environmental Assessment) released *Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions* (IEM) (U.S. EPA, 1990). The document provided risk assessors with a methodology to assess health risks that result from exposures to toxic pollutants in combustor emissions by pathways other than inhalation. Procedures for assessing human health risks through inhalation of combustor emissions were well established; the 1990 IEM provided procedures for estimating the indirect human exposures and health risks that can result from the transfer of emitted pollutants to soil, vegetation, and water bodies.

In May of 1993, the Administrator of the Environmental Protection Agency (EPA) released the "Hazardous Waste Minimization and Combustion Strategy." Among other recommendations regarding the regulation of this industrial sector, the strategy urged that EPA and/or the regulated community conduct indirect exposure assessments to evaluate the impact of stack emissions. Although this strategy was specific to hazardous waste incinerators, the importance of all exposure pathways, including indirect pathways, is logically extended to all combustors. The available methodologies were the 1990 IEM and the 1992 "Estimating Exposure to Dioxin-Like Compounds." To develop a response to the Administrator's strategy, a workgroup comprising several EPA offices was convened. The result was an "Addendum" document to the 1990 IEM, released in November 1993. The EPA's Science Advisory Board (SAB) and the public reviewed the Addendum. The SAB and public comments have been incorporated into this document. Therefore, this document supersedes the IEM and the Addendum (U.S. EPA, 1990, 1993).

1.2. PURPOSE

The intent of this methodology is to provide a set of algorithms for assessing human exposures to toxic atmospheric pollutants emitted from stationary combustors. The document describes procedures and models that can be used to estimate exposure and risk using a variety of environmental pathways. In addition, it serves as a preliminary source of data for carrying out the risk estimations. The degree of scientific support, or uncertainty attendant to each calculation, varies widely. Therefore, the appropriate use of these procedures and the discussion of uncertainties surrounding the results remain an important responsibility of the risk assessor, leading to effective risk characterizations.

Although the focal point of this effort is exposure assessment, Chapter 10 describes the other three steps of risk assessment (hazard identification, dose-response assessment, and risk characterization) initially described by the National Research Council (NRC, 1983). Several EPA documents are available that provide details on other components of the risk assessment paradigm. In this document, however, exposure assessment is presented before the other steps, as we believe the four-step process is not necessarily sequential (Harvey et al., 1995). Exposure assessment encompasses a determination of the pathways leading to exposure, the contact media, estimates or measures of contaminant concentration in these media, and the routes by which exposure occurs, including the time, frequency, and duration. The U.S. EPA (1992) describes exposure as “the condition of a chemical contacting the outer boundary of a human”. For humans and other animals, the outer boundary includes openings into the body such as the mouth, the nostrils, and the skin, including skin damage by punctures and lesions. Most of the time, the chemical occurs in air, water, soil, or biota. The exposure concentration is the chemical concentration at the point of contact.

1.3. STATIONARY COMBUSTORS

Since this document deals primarily with the accumulation of pollutants in the environment, this methodology is limited to stationary combustors. Stationary

combustors are combustors built on a site and expected to operate for several years. This methodology does not address exposure and health effects from incinerator ash. A document from the National Center for Environmental Assessment (U.S. EPA, 1991) entitled *Methodology for Assessing Environmental Releases and Exposure to Municipal Solid Waste Combustor Residuals* considers incinerator ash exposure.

The most common types of stationary combustors are those used to treat municipal solid waste, hazardous waste, medical waste, and sewage sludge. Other anthropogenic sources of atmospheric emissions identified in the Mercury Report to Congress are utility boilers, commercial/industrial boilers, residential boilers and wood combustors. In addition, the draft Dioxin Reassessment Report (U.S. EPA, 1994) describes various types of combustors and other high temperature sources, including coal combustion and metal smelting/refining.

1.4. SCOPE

The scope of this methodology has been expanded to include a multiple pathway exposure assessment that includes both direct and indirect routes of exposure to combustor emissions. Since this methodology is primarily focused on combustors, the direct route of exposure is inhalation. On the other hand, indirect exposures results from atmospheric pollutants which are transferred and deposited onto environmental media.

Pollutants from stack emissions can be incorporated into soil or water and, from there, can accumulate in the terrestrial or aquatic food chains. Humans are exposed to these pollutants in various media (multimedia) by dermal contact, direct ingestion, and/or ingestion of foods grown in the contaminated soil or water.

This methodology guides risk assessors through the four steps of risk assessment to characterize the exposure and risk posed by pollutants in various pathways. The document starts by presenting guidelines on human exposure scenarios (Chapter 2). After discussing air dispersion models appropriate for analyzing combustor emissions (Chapter 3), the document describes assessment of exposure through terrestrial and aquatic systems.

For terrestrial systems, Chapter 4 presents methods for calculating pollutant concentration in soil, ingestion of soil, and dermal absorption from soil. Exposure through inhalation of resuspended dust is evaluated (Chapter 5). A method for calculating daily intakes through ingestion of food can be found in Chapter 6.

For aquatic systems, Chapter 7 presents methods for calculating pollutant concentration in surface water, rainwater, and groundwater. A method for calculating daily intakes through ingestion of water and dermal absorption from water is also provided. A method for calculating daily intake through ingestion of fish is presented in Chapter 8.

Methods for calculating daily intake by infants through ingestion of breast milk are discussed in Chapter 9. Chapter 10 discusses toxicity assessment and risk characterization. A validation exercise is shown in Appendix A. Appendix B contains an equation for estimating breast feeding losses. A list of definitions is provided in Appendix C.

The U.S. EPA recognizes that there are limitations inherent in the methods presented. For example, the methodology can be applied only to the finite number of chemicals that have actually been identified in combustor emissions. There are potentially hundreds of pollutants that may be emitted but have not been measured or identified.

This document uses emission rates that were, for the most part, measured during good operations of the incinerator. Methods for assessing emissions resulting from perturbations, mechanical failures, and shutdown of the plant are presented in Chapter 3.

There are other data limitations that ultimately constrain the methodology. This document frequently relies on default input values based on current national monitoring data. Readers should consider that many of the factors affecting exposure vary according to region, climate, or local habits. Risk assessors should use local data to conduct a community or site-specific assessment whenever possible to reduce the uncertainty associated with applying national data to a local community.

The methodology, therefore, is not a comprehensive environmental tool, but is best regarded as an evolving and emerging process. However, these methods move the U.S. EPA beyond the analysis of potential effects on only one medium (air) and exposure pathway (inhalation) to the consideration of other media and exposure pathways.

1.5. USE

This methodology is not intended to be prescriptive; that is, it provides a set of procedures that the risk assessor can draw upon, where applicable, for an assessment. It does not comprise a set of guidelines or recommended approaches that the U.S. EPA believes should be applied in all circumstances. For example, the methodology does not give a set default value for parameters; instead a range of default values will be provided in the

companion “Parameter Guidance” document. Because this methodology is descriptive, it is suggested that the user consult other EPA documents for additional information and/or prescriptive guidance. Guidance information related to combustion risk assessment can be obtain in the “Human Health Risk Assessment Protocol for Hazardous Waste Combustion

EPA documents related to MPE

- ! Mercury Study Report to Congress
EPA/452/R-97-0003
- ! Estimating Exposure to Dioxin-Like Compounds
EPA/600/6-88/005 (External Review Draft)
- ! Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities
EPA/530-D-98-001A (External Review Draft)
- ! Air Quality Criteria for Particulate Matter
EPA/600/P-95/001
- ! Exposure Factors Handbook
EPA/600/P-95/002
- ! Dermal Exposure Assessment: Principles and Application :
EPA/600/8-91/001
- ! Region 6 Risk Management Addendum - Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities.
EPA-R6-98-002
- ! Guidance on Collection of Emissions Data to Support Site-Specific Risk Assessments at Hazardous Waste Combustion Facilities (Review Draft)
EPA/530-D-98-002

Facilities” document and its addendum document. An accompanying document which focuses on ecological assessment is under development.

Although this methodology focuses on providing appropriate site-specific procedures for conducting exposure assessments of emissions from combustion sources, it can be used to develop assessment on issues other than combustors. The material also includes some information on individual parameter assumptions and other specific factors to consider. However, several of the assumptions needed to complete an exposure assessment may vary, depending on the specific application or program involved. Therefore, decisions are still required in applying this methodology to different situations.

This document provides some generalized information on limiting the scope of an assessment (Chapter 2). It is very important that the exposure assessment include a detailed description of all of the uncertainties involved and how they may affect the final results.

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HUMAN EXPOSURE ASSESSMENT

2.1. INTRODUCTION

Pollutants emitted to the atmosphere from stationary combustion facilities are transported through the atmosphere and may subsequently impact environmental media (i.e., soil, water, and vegetation) near the combustor. Human exposure to the emitted pollutants may occur by various pathways such as dermal contact with the pollutants in soil or water; inhalation of contaminated air; ingestion of contaminated soil, water, or biota; or consumption of breast milk contaminated via one or more of the previously mentioned pathways.

The main purpose of this chapter is to present a brief overview of exposure assessment as it relates to combustor emissions. This chapter presents the key elements and general approaches to develop an exposure scenario. In addition, a brief discussion on the different descriptors of exposure is also provided.

2.2. OVERVIEW OF EXPOSURE ASSESSMENT

Exposure is defined as the condition of a chemical contacting the outer boundary of a human (U.S. EPA, 1992a). Exposure assessment involves characterizing the magnitude, duration, and frequency of human contact with the contaminant of concern. The exposure assessment process consists of identifying potential exposure pathways, estimating chemical intakes, and identifying exposed individuals or populations. This chapter deals with all three components of the exposure assessment process. An exposure pathway usually includes the physical source or medium (e.g., soil) of the pollutant, the route of exposure (e.g., ingestion), and the receptor (e.g., humans). For example, a typical exposure pathway statement might be: ingestion of contaminated soil by humans. Exposure scenarios are real (provable) or hypothetical situations that define the source (e.g., hazardous waste combustor), characteristics of the human receptor (e.g., age, gender), pathway(s) of exposure, exposure duration, frequency, and exposure dose. The significant difference between an exposure pathway and exposure scenario is the inclusion of time, source

information, and exposure dose. U.S. EPA (1988) states, "In exposure scenario evaluation, the assessor attempts to determine the concentration of chemicals in a medium or location and link this information with the time that individuals of populations contact the chemical."

Figure 2-1 presents a schematic of possible emission sources, contact media, and routes of exposures which lead to the exposure pathways being defined or the development of exposure scenarios.

2.3. CREATING EXPOSURE SCENARIOS. Successful application of this method depends on the judgment of the risk assessor. The exposed individual(s) must be defined in terms of age, location relative to the combustion source, and length of time spent at that location. Although the age of the individual will affect exposure routes and pathways, defining age in general terms such as child or adult generally suffices for exposure assessment. In most cases, location will refer to the residence of the individual. The length of time (i.e., number of years) that the individual spends at the defined location influences potential pathways of both exposure and duration levels. Choices of appropriate exposure scenarios and study area are essential elements of a multiple pathway exposure assessment. Human exposure scenarios are developed from the following:

- ! identify emission source (*section 2.3.1.*)
- ! define source characteristics (*section 2.3.2.*)
- ! define the study area (*section 2.3.3.*)
- ! identify potential exposure pathways (environmental media and the possible routes of exposure) (*section 2.3.4.*)
- ! identify factors related to human exposures (*section 2.3.5.*)
- ! identify study populations, and/or individuals that could be exposed (*section 2.4.1.*)

Chapter 2
 Human Exposure Assessment

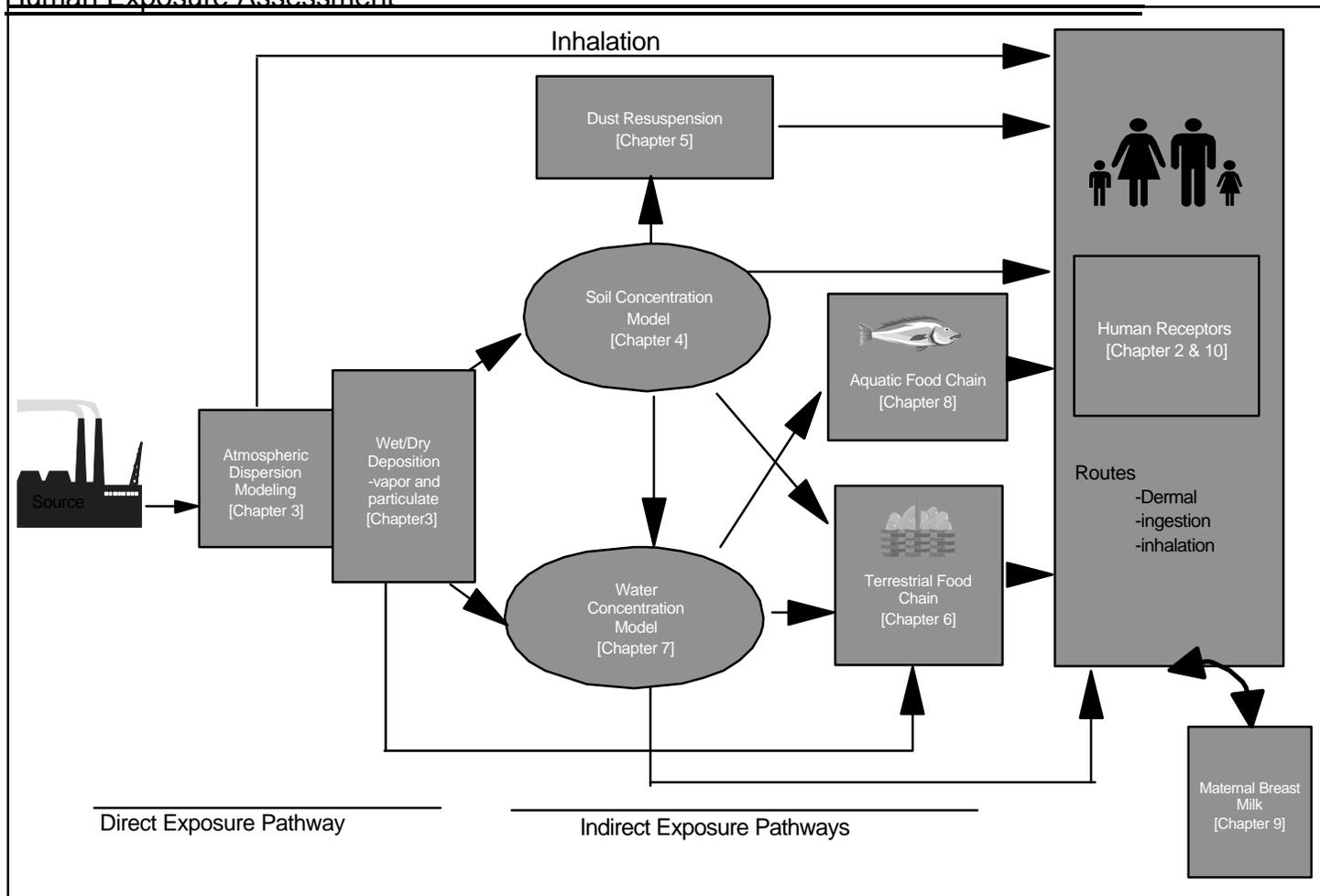


FIGURE 2-1. Conceptual Overview of Modeling the Environmental Fate of and Exposure to Pollutants from an Emission Source.

- ! determine exposure point and media concentrations (*chapters 4,5,6,7,8, and 9*)
- ! estimate exposure dose (*chapter 10*)

The assessor has the responsibility to determine which exposure scenarios pose the greatest threat to human health.

The environmental media likely to be impacted by combustor emissions should be defined because the area surrounding the source is used to evaluate exposure pathways. The land use, meteorological conditions, and topographic features in the area of concern can help identify the possible pathways of exposure (see discussion above). Sources of these data may include USGS maps and county land-use maps.

2.3.1. Identify Emission Source. This methodology is specifically written for combustor emissions which are discussed in Chapter 3. If other waste management options such as waste piles, landfills, recycling or composting are identified as the emission source, more suitable source and transport models should be selected. Regardless of the emission source, the same fundamental approach would be used to develop an exposure scenario.

2.3.1.1. Identification Other Sources of Exposures — Other sources of exposures to humans exist that may not be definitively associated with combustor or other waste management options. This would be the case if the chemical existed naturally in the local environment, or if the chemical were ubiquitous in the environment although it may not be natural to the environment. In this document, the term “background exposure” will be used to describe the exposures to specific chemicals that were not the result of combustor source emissions in a site-specific assessment. A more detailed description of approaches to estimate background exposures is provided in Chapter 10.

2.3.2. Defining Source Characteristics. For combustor exposure assessment, the first step in the analysis is the identification and selection of contaminants that may be emitted to the air during the combustion process. Several factors influence what

chemicals are being released to the environment and their emission rates. Chapter 3 provides a description of important characteristics related to combustor facilities. These characteristics include feed material being combusted, stack emission rate of toxic air pollutants, and operational specifications. For multiple pathway exposure (specifically, indirect exposure assessment to combustor emissions), the length of time of operation is an important issue.

2.3.2.1. Defining the Length of Time of Emissions — Estimates of annual average air concentration and average deposition rate over defined areas is a requirement. These concentrations may depend on a particular time frame of interest. For example, one may want to consider the impact of emissions over the lifetime of a facility. Some facilities are designed to last 30 years or more. Facilities may be replaced or upgraded periodically extending the period of emissions even longer.

This methodology primarily addresses long-term exposure to contaminants in environmental media resulting from long-term combustor emissions. However, upset conditions and intermittent emissions (e.g., combustor startup or shutdown conditions) are considered in Chapter 3. Such occasional short-term releases are generally not an issue for the indirect exposure analyses component of multiple pathway exposures because long-term buildup in the food chain is the principal concern for indirect exposure. The accumulation of short-term releases can be averaged and added to the continuous emissions if data are available to do so. It is suggested that studies using acute exposures be used in the assessment of potential acute effects as part of the direct exposure assessment. The highest inhalation exposures are associated with periods of highest air concentrations. Other meteorologic conditions (i.e., inversions) cause stable air and may minimize dispersion and lead to unusually high air concentrations, as can increases in emission rates. As discussed in Chapter 3, the air model can estimate the highest daily air concentration expected to occur during a year. The model output is normalized by emission rate. Combining the highest expected emission rate with daily high model output can estimate the highest short-term exposure level, which in turn can be compared with acute exposure guidelines.

2.3.3. Defining the Study Area. In defining the study area, the main objective is to determine where the study area begins and ends (U.S. EPA, 1992a). For this methodology, the spatial concern is the area around the combustor that is impacted by the emissions. As discussed in Chapter 3, the recommended air dispersion/deposition model (ISC3) is designed to provide air concentration and deposition estimates to a maximum distance of 50 km from the source. Accordingly, the recommended approach for establishing the study area is to initially assume that the study area is described by a 50 km radius around the facility. Figure 2-2 presents a simple representation of defining the study area using isopleth rings. This procedure can result in the inclusion of minimally exposed persons in the study population or may exclude relevant population. When detailed land-use and population-activity data are collected, it is important to avoid collecting information for wide geographical areas where little or no exposure occurs. The dispersion/deposition models provide air concentration, wet deposition and dry deposition values over a polar grid (see Chapter 3 for a more detailed description of the air modeling output). It is assumed that each polar grid junction point represents a block of land surrounding the point, so that every point within 50 km has associated with it an air concentration, wet deposition and dry deposition value. Next, is the evaluation of the exposures at each area block, using the site-based exposure scenario (contaminant, pathway and activity patterns) that poses the highest potential for risk.

It is possible that the risks at the outer edge of the study area may be considered insignificant and a smaller study area would be appropriate. Alternatively, the risks at the outer edge may still be of concern, suggesting that the study area should be expanded. In this case, use of long-range atmospheric transport models would be needed, adding considerably to the uncertainties inherent in the methodology.

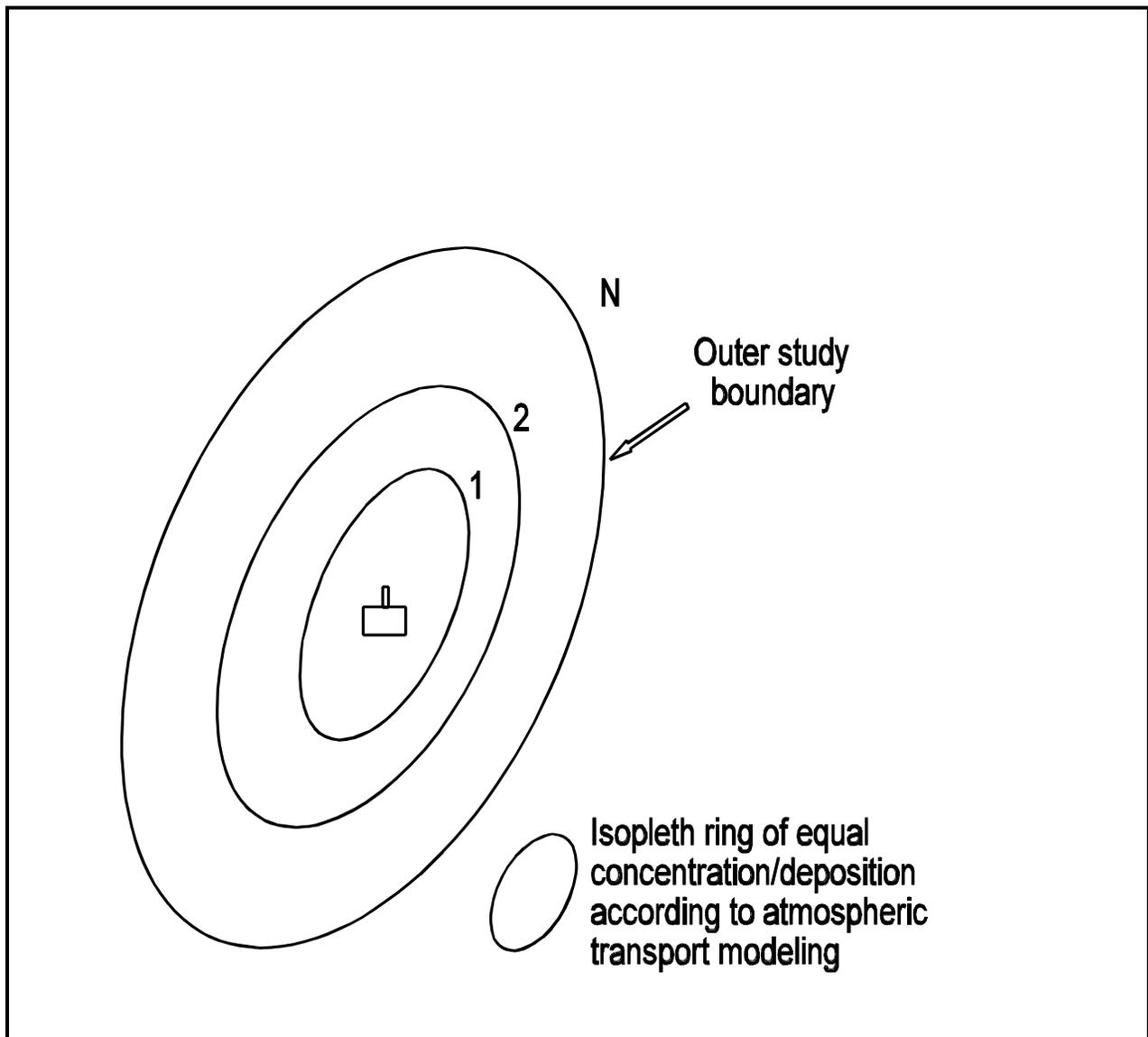


FIGURE 2-2
Simple Representation Outer Isopleth Ring Defining Study Area
and Isopleth Rings Within Study Area

2.3.4. Potential Pathways of Human Exposure. Combustor emissions can impact air, soil, water, and food products creating the potential for multiple pathway exposures. Figure 2-1 can serve as a guide to choosing which pathways are relevant for a particular site-specific assessment.

Plants and animals in the vicinity of a combustor may be impacted by its emissions and become part of the human food chain. The principal exposure pathways associated with combustor emissions are described below:

- ! **Food Ingestion** — Indirect exposure assessments should identify food production and processing activities (e.g., home gardens, farms, etc.) within the affected area. The assessment should evaluate exposures resulting from consumption of food produced in the area by people who live inside and outside the affected area. Consumption rate data for specific foods on a national or regional basis can be found in the Exposure Factors Handbook (U.S. EPA, 1997). Consumption rates of locally produced food by residents in the area is best estimated on the basis of site-specific surveys. Lacking such data, the Exposure Factors Handbook also contains consumption rate data on typical homegrown foods. These issues are discussed in greater detail in Chapter 6.

Soil in the vicinity of a combustor can be impacted by emissions, creating the potential for several pathways of exposure, including the following:

- ! **Soil Ingestion** — The importance of this pathway will depend on characteristics of the population of concern such as age and occupation, as well as soil characteristics. Soil ingestion rates in children and adults have been estimated from studies which measure the quantities of nonabsorbable tracer minerals in the feces. These issues are discussed in greater detail in Chapter 10.
- ! **Dermal Exposure to Soil** — The importance of this pathway depends on exposed surface area, adherence of soil to skin, frequency of exposure, and fraction of contaminants absorbed through skin. The amount of

contaminant that can be absorbed through the skin (i.e., absorption fraction) depends on the chemical properties of the contaminant, properties of the soil matrix, length of exposure before removal by washing, and dermal pharmacokinetics. If a compound cannot readily be absorbed through the skin, the daily intake of the compound may be small even if other exposure characteristics, such as adherence factor, are favorable. The other factors (exposed surface area, adherence and frequency of exposure) are determined largely by personal behavioral or cultural patterns. Exposure to dust may also be important in some circumstances (e.g., children playing on the floor inside the home). Specific values for the factors that affect dermal exposure are discussed in Chapter 4.

- !** **Inhalation of Resuspended Contaminated Dust** — Pollutants in contaminated soil can be resuspended as particulates in the air by wind erosion, agricultural tilling, or vehicular traffic on paved and unpaved roads. As a consequence to resuspension, persons may inhale the pollutant particulates. The amount of resuspended dust is dependent on the moisture content of the soil, the fraction of vegetation cover, the wind velocity, soil particle size, pollutant concentration in the soil, and size of the contaminated area. Methodologies have been developed to assess exposure to pollutants resuspended by wind erosion at landfills (U.S. EPA, 1985) and CERCLA sites (U.S. EPA, 1988). Application of these methodologies to combustor emissions suggests that dust resuspension by wind erosion will not be a significant pathway in most cases. This is further discussed in Chapter 5.

Combustor emissions can impact groundwater, surface water bodies, or collected precipitation, such as in a cistern. Since the predicted annual ground-level concentration of contaminants decreases with distance from the source, the location of the precipitation collection apparatus, the surface water body on which emitted pollutants are deposited, and the soil concentration (which affects leachate and runoff

concentration) are important determinants of the water concentration. As discussed below, human exposure to contaminants in these waters can occur through fishing, bathing/showering, swimming, and drinking.

! Groundwater Exposure Pathways — Contaminants emitted from the combustor can deposit on soils and then either move over the ground into a surface water body or infiltrate into the ground. Groundwater used as a domestic water supply can contribute to human exposure by direct consumption, dermal contact during bathing or inhalation of volatilized contaminants. Groundwater used for crop irrigation or livestock watering purposes can cause human exposure via the food chain. This pathway is discussed further in Section 7.4.

! Surface Water Exposure Pathways — Combustor emissions can enter surface waters by direct deposition into the water or by deposition onto the watershed and runoff to the water body. The location, topography, and size of the watershed can affect the concentration of contaminants in runoff. The chemical concentration in the water, surface area of the exposed skin, permeability of the skin to the chemical, and frequency and duration of exposure events are the variables that contribute to dermal exposure. Incidental swallowing of water during recreational activities may also contribute to exposure.

The manner in which the water is used will determine possible exposure routes. Use of the surface water body for recreation or as a drinking water source will make dermal contact and ingestion possible exposure pathways.

Another issue related to surface water is the consumption of fish. Commercial and/or recreational fishing with subsequent use of the fish and shellfish as a food source make the food web an important route of exposure for communities with a surface water body in the vicinity of a combustion source. Chapter 7 further discusses evaluation of exposure

from water ingestion. Factors that affect human exposure by ingestion of fish from a contaminated water body include sediment and water contaminant concentration, types and amounts of locally caught fish/shellfish consumed, and the bioaccumulation factor for these groups. The types of fish consumed will affect exposure because different types of fish and shellfish take up contaminants at varying rates. For example, fatty fish will tend to accumulate organic contaminants more readily than lean fish. The populations most likely to be affected are recreational and subsistence freshwater anglers. The types and amounts of fish consumed by these subpopulations are discussed in Chapter 8. If the surface water body is used for recreational purposes such as swimming and boating, dermal absorption of contaminated water becomes another possible route.

- ! **Pathways of Exposure to Collected Precipitation** — In several regions of the U.S., rain and/or snowfall are collected and stored as a source of drinking water. Individuals in these areas may be exposed to pollutants deposited on the surface area from which water is collected. The input variables for this exposure pathway include total annual deposition (both wet and dry), annual precipitation, and the daily amount of water consumed. Section 7.3. further discusses this exposure pathway.

A nursing mother exposed to contaminants by any of the pathways described above over her lifetime can pass the contaminants on to her infant children through breast milk.

- ! **Human Breast Milk Pathway** — This may be an important route of exposure for lipophilic and nonlipophilic chemicals that may be emitted from combustors. Models to estimate the daily exposure of a breast-feeding infant are presented in Chapter 9.

2.3.5. Factors Related to Human Exposures. Several exposure factors must be considered when defining the exposed individuals or subpopulations within the study

population. Human variability and personal preferences play a major role in determining actual risk.

As mentioned earlier, this section provides information on identifying potentially exposed populations, estimating potential chemical doses, and identification of potential exposure pathways. Unfortunately, it is beyond the purview of this document to provide a thorough review of the available literature in the area of enumerating individuals and their dietary preference, cultural practices, geographic setting and location which may contribute to increase susceptibility to environmental contaminants. In addition this document does not provide statistical data on human characteristics and behaviors used in estimating exposures. This type of information will be available in other U.S. EPA documents, such as the *Exposure Factors Handbook (U.S. EPA, 1997)*.

Human factors related to exposure are as follows: demographics, residential setting, recreational activities, cultural practices, lifestyle and habits, occupation, and dietary consumption.

2.3.5.1. Demographics Factors — Demographic factors include the age, race, gender, and ethnicity of the population in a particular area. In this section, the demographic factors that are common among all individuals will be discussed such as age and body weight. Specific information pertaining to gender, race and ethnicity can be obtained from the Census Bureau.

- ! Age.** The age of the individual influences exposure to the emitted pollutants since pathways, duration and quantities of exposure may vary with age. The daily activities of the individual, amounts of food and water consumed, types of food consumed, exposed skin surface area and body weight differ for children and adults. Health-based criteria are also different for children and adults. Therefore, for some exposure pathways such as soil ingestion, children may have a greater exposure and be at greater risk than adults. Human life span for risk assessment purposes is generally calculated to be 70 years.

The duration of childhood may vary somewhat in the different exposure pathways, depending on age-relatedness of the key scenario assumptions and the constraints of the available data. For example, increased soil ingestion among children is generally considered to be associated with young children; older children are thought to be more similar to adults. The current data available are limited to studies of children under 7 years of age and do not permit further subdivision of this group.

In some exposure scenarios, individuals may be exposed only during childhood or adulthood. In other cases, exposure may overlap these periods, such as in the case where a child grows into adulthood and remains in the same geographical area. Chapter 10 discusses methods for combining estimates of childhood and adult exposure to obtain an estimate of lifetime exposure.

- ! **Body Weight.** The daily intake for each pathway is defined as the dose rate on a body-weight basis. Ingestion exposures on a body-weight basis are substantially higher for infants and toddlers than for teenagers or adults. Certain behaviors, such as mouthing of dirty objects or direct ingestion of soil, which could also contribute to exposure, are also much more prevalent in children than adults. Therefore, infants and toddlers may be at greater risk when exposure is by food or soil ingestion. The effects, however, may have a long latency period, in some instances approaching the human life span. In these cases it may be reasonable to estimate daily intake using the adult values of body-weight. In cases where effects have a shorter latency (<10 years) and where children are known to be at special risk, it is appropriate to use a body weight for children under 7. For chemicals that are classified as carcinogens, adult body weight is usually assumed to derive unit risk estimates for air or water. If

exposure is lifelong, values of body weight are usually chosen so as to be representative of adults. In this document, 70 kg is used as the body weight for hypothetical adults. For children, the choice of body weight for each pathway is made to coincide with the definition of childhood employed and the available data, so that the daily intake (mg/kg-day) is accurately determined. The form of the input data and body weight value used for determination of daily intake (DI) are delineated in the chapter for each pathway. The Exposure Factors Handbook provides specific values for different age groups.

2.3.5.2. Residential Factor —

- ! Length of Time Individual Spends at Location.** A person may possibly have a lifetime exposure to emissions from a combustion source; however, data on population mobility suggest that many Americans do not remain in the same area for their assumed 70-year lifetime (U.S. EPA, 1997). Therefore, a shorter period of time may also be considered to estimate shorter duration exposure to combustor emissions.

Data collected by the U.S. Bureau of the Census (1993) show that the mobility rate in 1991-1992 was 17% of the total population (i.e., 17% of the U.S. population moved to a different residence during the year). This high mobility rate suggests that people are not likely to remain in the same residence for their assumed 70-year lifetime. In fact, it was estimated from these data that the median residence time for all householders (owners and renters) is 9 years and that the upper 90th percentile residence time is 33 years (U.S. EPA, 1995a). Based on analysis of census data from 1985 and 1987, Israeli and Nelson (1992) estimated average residence time to be only 4.6 years. These researchers also presented results showing that average residence

time was higher in rural areas (7.8 years) than urban areas (4.2 years), and highest for farm families (17.3 years).

Change of residence may not necessarily indicate change in exposure status, however. The U.S. Bureau of the Census (1993) data show that local moves (those within the same county) accounted for 62% of all moves in 1991-1992. It could be inferred from this information that the majority of people who move remain in the vicinity of the combustion source. However, the likelihood that these short distance moves will influence exposure based on factors such as atmospheric transport of pollutants can not be predicted accurately.

Local census data may be used to determine appropriate values for the duration of exposure of the local population and population subgroups of concern. Otherwise, the national data can be used to derive estimates. The risk assessor may want to take into account the expected life of the facility or duration of the burn (in the case of a mobile incinerator) when estimating this parameter. However, the assessor should consider that indirect exposures may continue after emissions stop due to accumulation of contaminants in soil, sediments, and other media.

In addition to the number of years at a particular location or residence, the amount of time spent at that location each day directly affects exposure. For example, children that attend day care or adults that work in a different location for part of the day may be exposed to higher or lower contaminant levels. This issue is discussed further under the relevant pathways in Chapters 4 through 9 and 10.

- ! **Location of the Individual Relative to the Source.** The ground-level concentration and deposition rate of pollutants emitted from the combustion source are affected by air dispersion of pollutants. Numerous factors such as source characteristics (e.g., stack height),

topography (terrain-flat or complex), meteorological data (e.g., wind speed and direction) and distance from the source determine the air dispersion and resultant deposition of the emitted pollutants. The annual ground-level concentration of emitted pollutants decreases and the population size increases with distance from the source (U.S. EPA, 1990). Maximal ground-level concentrations are usually measured at distances in very close proximity to the source, although local meteorological conditions and source characteristics play a role. In generalizing this information to other combustors, the location of the individual relative to the combustor becomes an important determinant of exposure. Generally, individuals located closer to the source could be expected to have higher direct exposure to emitted pollutants than those at further distances from the source. In most cases, location will refer to the residence of the individual. A range of exposures for individuals representing the general public could be estimated by choosing several distances from the combustor.

2.3.5.3. Other Exposure Related Factors — In addition to demographic and residential factors, other exposure related occurrences must be considered which are as follows:

- ! **Recreational Activities:** Activities such as sport fishing, hunting, outdoor exercise, and sports may cause increased exposure to environmental pollutants. Also certain personal hobbies may increase exposure to contaminated media (e.g., home gardening).
- ! **Cultural Practices:** Identification of certain cultural practices such as subsistence hunting or fishing can significantly influence exposure. The risk assessor should be aware of cultural rituals involve consuming soils for either spiritual or medicinal purposes.
- ! **Occupational:** Although this methodology focuses on population/individual exposures in the general study area, it may be

prudent to evaluate if an individual included in the study population is also a member of the work force at the combustor facility. This type of scenario could yield a “high-end” exposed individual.

- ! **Lifestyle and Habits:** Smoking, alcohol and drug abuse may not be directly related to combustion emission; however, personal habits can add to the susceptibility of the individual to environmental pollutants.

2.4. DEFINING HUMAN EXPOSURE

This section will be divided into three parts: 1) a discussion of the different descriptors of exposure, 2) identifying study populations, and 3) identifying subpopulations or individuals who could be highly susceptible to facility emissions.

2.4.1. Approaches used to Describe Exposure/Risk Descriptors. The risk assessment can be designed as a screening or as an in-depth assessment tool depending on the needs of the risk manager. Initially, for many risk assessments, a screening framework is typically designed and employed; a “maximally exposed individual(s)” or reasonable maximally exposed individual is defined. This individual ideally represents the 99th+ percentile of the distribution of exposure to the population for all pollutants, pathways, and exposure routes. If this individual is deemed to not be at risk, an additional assessment may not be needed. If certain pollutants, pathways, or routes are predicted to contribute insignificantly to exposure, they may be eliminated from further consideration. The remaining pollutants, pathways, and routes can then be assessed in more detail.

2.4.1.1. Descriptors of Exposure and Risk — An exposure assessment may be used to provide several different descriptors of risk. Individual risks can be presented in two ways:

- ! Point estimates - Exposure scenarios can be constructed to represent specific subpopulations that utilize the resources of a potentially affected area around the combustion source. Ideally, point estimates should be made to cover a range of scenarios representing both central tendencies and high end estimates (generally above the 90th percentile) for the

population (or subpopulation) affected by the combustor (U.S. EPA, 1992b and 1995b).

- ! Distributions - Where sufficient data are available, a complete distribution of individual exposures/risks should be developed. Typically this involves the use of probabilistic techniques such as Monte Carlo methods.

Population risks should also be expressed in several ways:

- ! For nonthreshold-acting pollutants such as many carcinogens, risks may be presented as the potential number of cancer cases in the affected population (either yearly or over a longer period, such as the projected life of the combustor).
- ! For threshold-acting pollutants such as noncarcinogens, long-term population risk can be presented as the number of persons whose exposure exceeds a specific dose level or the RfD, or number of persons whose exposure might exceed an acute effect threshold (if known).

For both carcinogens and noncarcinogens, specific subgroups of the population should be highlighted, either because they are of interest (e.g., children), or because of potentially high exposure/risk (e.g., subsistence farmers), or because they represent a sensitive subpopulation.

2.4.2. Study Population. Individuals who live within the study area will form the basic segment of the population to be evaluated, and should be evaluated for all appropriate and relevant pathways. These individuals include, but are not limited to:

- ! persons living, working, or otherwise spending significant amounts of time within the "study area boundary" defined through dispersion/deposition modeling;
- " persons potentially exposed to contaminated media such as air, soil, and/or water -- near the emission source;
- ! persons potentially exposed to foodstuffs contaminated by the combustor emissions.

Certain individuals who live outside the study area boundary should be included as well. For example, individuals who work, attend school, or otherwise spend significant amounts of time within the study area boundary, even though they do not live within the boundary, should also be evaluated and included in the studied population.

The population must be defined in such a way that it is clear whether any given individual is "in" or "out" of the population being considered. Geographical boundaries and activity related criteria can serve a useful purpose here. If the population is defined as "all those who live or work within [some specific] boundaries," these are relatively straightforward criteria that can be used to define the size of the population being evaluated.

Another factor that varies with distance from the combustion facility is the size of the population. The cumulative population increases as distance from the combustion facility increases; increasing radial distances from the source encompass more of the population. The total population in the study area then represents all persons who could be exposed to the emissions, excluding those persons that temporarily travel into the area (e.g., for work). After defining the study population, the next step in this process is to define the exposed individuals.

2.4.3. Defining the Exposed Individual(s) and Developing Exposure Estimates.

The goal of this step is to assign an exposure to the individuals within the study population. This is done by considering media concentrations and activities. By the combination of concentration and activities, individual exposure estimates can be made. Therefore, the assessor should attempt to reduce the scope of this effort in terms of chemicals and pathways. One way to do this is to make bounding type assessments using maximum exposure parameter values applied at points of maximum concentrations or depositions. If these bounding assessments demonstrate exposure below a concern level, then the associated chemicals and pathways can be safely eliminated from further study.

The risk assessor can identify the types of activities (e.g., vegetable gardening, dairy farming, schooling, recreational angling, etc.) and numbers of people within a study area by using land-use maps, aerial photographs, local surveys, "patch" population information from the Human Exposure Model (HEM), and other sources. Because each activity is associated with certain pathways of exposure, the risk assessor can use this information to identify which media levels to calculate for each area (e.g., soil and vegetation in one block, and surface water and fish in another). Media levels of concern can then be calculated from the air modeling data, using the methodology presented in this document.

Based on the land-use activities identified, the risk assessor can construct exposure scenarios for various subgroups of the study population (e.g., city resident, suburban resident with garden, non-resident sport angler, subsistence farmer, etc). Each scenario includes exposure by one or more pathways. In order to construct the scenario, the assessor must characterize the physical and temporal parameters for each pathway (e.g., soil ingestion rate, exposure duration, etc). The level of detail used in characterizing behavior is dictated by the amount of data which is available or could be collected. Theoretically, each person in the study area could be surveyed and behavior identified, but this is clearly impractical in most situations due to the size of the population and available resources. However, even a limited (statistically based) local survey can be quite informative and is highly recommended. Some options, in order of increasing detail on how to approach this problem include:

- ! Select the exposure parameter values that represent best judgement of central tendency estimates for current conditions of the groups identified.

- ! Divide each group into a low-, medium- or high-exposure concentration and select the exposure parameter values for each. The number of people in each subgroup should also be identified.

- ! Determine statistical distributions for the exposure parameter values in each group.

Data available regarding activity parameters for receptors in each exposure pathway are discussed in the accompanying "Parameter Guidance Document" and in subsequent parts of this document.

Each of the scenarios employed by the risk assessor should be representative of some portion of the population at the site. Local and national survey data and population information from the HEM may be used to estimate the size of the subpopulation represented by each of the scenarios employed. The process of assigning risk estimates can be achieved by using isopleths of constant concentration/deposition, and differentiating among activities (e.g., starting with one isopleth and grouping the individuals by activity, such as farmers, residents with home gardens, residents without home gardens, non-resident workers, etc.).

U.S. EPA (1993) suggests the following list of steps in assigning risk estimates. These are based on the assumption of constant concentration/deposition isopleths. If emission rates and resulting concentration/deposition isopleths are likely to be changing over time, then these steps can be applied to time periods during which the emissions are relatively constant and summed to get the total exposure.

1. First, using the methodology presented in this document, compute contaminant levels in media of concern (e.g., air, water, soil, groundwater, beef, fruit/vegetables, milk) for each ring. This information can be conveniently summarized on a table such as Table 2-1, or kept in a spreadsheet. The model inputs should be based on local information as much as possible. Considerable uncertainty is likely to be associated with these estimates. See Chapter 10 for further information on how to assess this uncertainty.
2. Next, overlay isopleths onto aerial photographs, population maps, land use maps, etc. to identify the types of activities and numbers of people in each ring. Several PC-based models are available for generating population density maps based on census data. These include the Human Exposure Model (HEM) from the EPA's Office of Air Quality Planning and Standards

and the Geographic Exposure Modeling System (GEMS) from the EPA's Office of Prevention, Pesticides and Toxic Substances. Geographic Information Systems (GIS) could be used to identify land-use, complex terrain, and population centers. Some of these systems use old census, data and it would be more accurate to use the TIGER files from the most recent census. Satellite photographs may provide the most recent information. Local surveys may also help locate farms and home gardeners.

| TABLE 2-1 Example Table for Media Levels | | | | | |
|---|--------|--------|--------|--------|--------|
| | Ring 1 | Ring 2 | Ring 3 | Ring 4 | Ring 5 |
| Air ($\mu\text{g}/\text{m}^3$) | | | | | |
| Soil ($\mu\text{g}/\text{g}$) | | | | | |
| Surface water (mg/L) | | | | | |
| Beef (mg/kg) | | | | | |
| Milk (mg/L) | | | | | |
| Fish (mg/kg) | | | | | |
| Vegetables (mg/kg) | | | | | |
| Others | | | | | |

- For each isopleth ring, estimate the number of farmers, residents with home gardens, other residents, and other groups defined in the study population (such as intermittently exposed non-resident workers). Also, for each ring locate schools, fishing areas and other areas where unusual exposure may occur. In addition, estimate the number of school children (school location), and the number of people in any other special interest group like subsistence fishermen, developments for retired people, etc. This information could also be kept in a spreadsheet.
- For each isopleth ring and population group, determine which exposure pathways apply. Characterize exposure parameters for each pathway, e.g., ingestion rate, exposure duration, etc. This information can be summarized in a table such as Table 2-2, or stored in a spreadsheet. The

level of detail used in characterizing behavior is dictated by the amount of data which is available or could be collected. Theoretically, each person in the ring could be surveyed and behavior identified, but this is clearly impractical in most situations due to the size of the population and resources available. However, even a limited (statistically based) local survey can be quite informative and is highly recommended. Some options in order of increasing detail are offered below for ways to approach this problem:

- a. Select the parameter values that represent best judgement of central values for current conditions of the groups identified above.
 - b. Divide each group into a low-, medium- or high-exposure level and select the parameter values for each. The number of people in each subgroup should also be identified.
 - c. Estimate statistical distributions for the parameter values in each group.
5. The next step is to compute exposures and compile results. Once exposure scenarios have been fully described and media levels have been calculated, exposure and risks for the various scenarios can be calculated. The results can be displayed in a variety of ways. Cumulative distributions (exposure or risk vs number of people) are useful for identifying central and high-end exposure levels. A frequency distribution showing the number of people exposed at various exposure or risk levels is a particularly effective way to communicate the results of the analysis. These distributions can be based on the entire study population or individual special interest groups such as farmers, gardeners, school children, etc. A variety of options are available for creating these

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| TABLE 2-2 Example Exposure Parameters for an Isopleth Ring Within the Study Area | | | | |
|---|-----------|-----------------|---------|-----------------|
| | Gardeners | Other Residents | Farmers | School Children |
| Population size | | | | |
| Residence time (yr) | | | | |
| Soil ingestion: RATE (mg/d) FREQ (d/yr) | | | | |
| Inhalation: RATE (m ³ /d) FREQ (hr/d) | | | | |
| Water ingestion: RATE (L/d) FREQ (d/yr) | | | | |
| Beef Ingestion: RATE (g/d) FREQ (d/yr) percent local | | | | |
| Milk Ingestion: RATE (g/d) FREQ (d/yr) percent local | | | | |
| Fish Ingestion: RATE (g/d) FREQ (d/yr) percent local | | | | |
| Vegetable ingestion: RATE (g/d) FREQ (d/yr) percent local | | | | |

distributions. If exposure parameters can be expressed as distributions, then a Monte Carlo simulation is currently considered as the best approach. This approach would involve using a frequency histogram of number of people in each ring (based on information generated in Steps 2 and 3 presented above) to select a location and associated media concentrations for each iteration. Further guidance on these issues and other aspects about how to conduct Monte Carlo analysis is provided in Chapter 10 of this document. For example, if it is not feasible to conduct a Monte Carlo analysis, a series of point estimates can be used to approximate the distribution. As discussed in Step 4, local surveys could be used to characterize consumption rates of local grown foods, frequency and duration. For example, if the surveys support generation of a low, medium and high consumption rate for farmers and the isopleth construction generates 5 rings, then 15 point estimates of exposure could be made and plotted vs number of farmers. This yields an approximation of the distribution. Since three consumption rates do not represent the full range of variability, upper percentiles will be underestimated and lower percentiles will be overestimated to some degree. Judgment will need to be decide if this uncertainty is acceptable.

6. In addition to presenting the distributions of exposure, the assessor should highlight individual exposure/risk estimates for several locations (i.e., maximum deposition, place where most people are exposed, schools, etc.) and subpopulations of interest (i.e., subsistence farmers, recreational and subsistence anglers, nursing infants, ethnic groups or any other population segment with unusually high exposures). For more specific guidance on recommended exposure scenarios, the user should refer to U. S. EPA (1998). These scenarios could be characterized using a central or range of exposure values combined with an estimate of the number of people in the group.

This effort should first focus on characterizing behavior describing exposure that occurs at a person's residence. A second step is to consider exposure that occurs outside the residence. Certain activities may involve exposure from a ring different than the residence. For example, a child may attend school in a different ring or an adult may eat food grown in a different ring or fish in a different ring. In later refinements, evaluation of how these parameter values and group sizes might change in the future may be desired, especially if the area has seasonal residents.

The above discussion focuses on developing distributions of individual risk. It is also possible to calculate overall risk to the exposed population. Issues associated with characterization of population risk are discussed in Chapter 10.

Area blocks for which the calculated risk for the chosen scenario exceeds a specified level of concern will be identified. The outer boundary of the larger area composed of all area blocks with risks in excess of the concern level will identify an approximate risk isopleth corresponding to the specified level of concern for the chosen scenario (Figure 2-3).

The assessor can directly compare the approximate risk isopleth to population corresponding exactly with the "patch" reporting units in the latter. The assessor can constrain the size of the study area by eliminating areas with little or no relevant use by humans. These concentration/deposition isopleth drawings can be printed on transparencies and overlaid on a scaled land use map to provide the risk assessor with another tool to help define the study area.

It should be noted that a risk isopleth derived in the manner described above is an approximation; this is because concentration/deposition levels (and consequently, the risk estimate) at a polar grid junction point are assumed to be representative of the

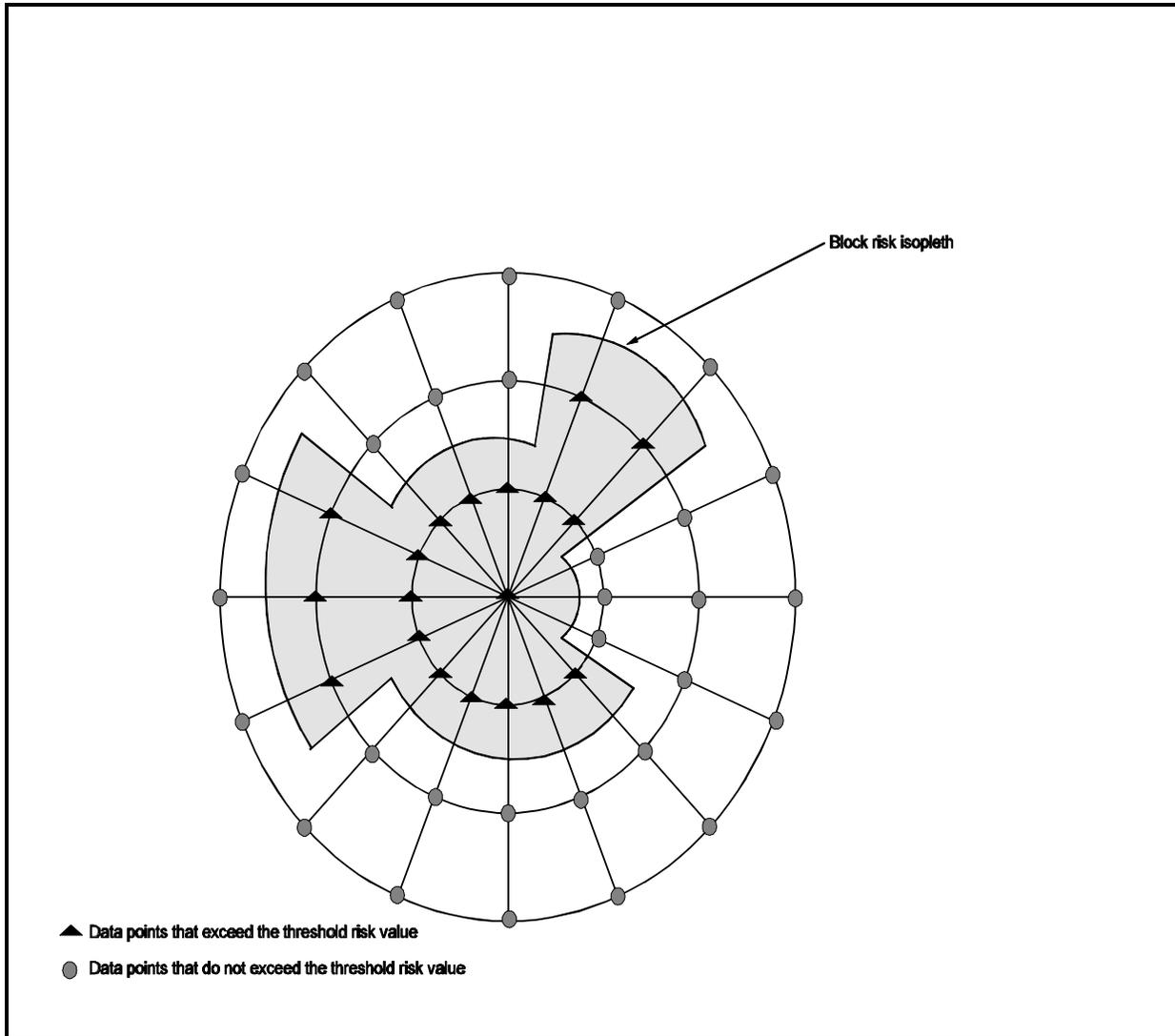


FIGURE 2-3
Approximate Risk Isopleth Derived from Area Blocks

entire area block surrounding it. As shown in Figure 2-4, the true risk isopleth (if it could be identified) probably would not correspond exactly to the block isopleth, and could potentially encompass areas not included within the block risk isopleth. There are several ways to correct this problem. One solution would be to use a specific level of concern for the site based on information from the U.S. EPA Office of Air Quality Planning and Standards' Human Exposure Model (HEM). An alternative would be to model the true level of concern, and add one row of blocks around the perimeter of the critical area as a buffer zone. Another solution would be to acknowledge that the isopleth is approximate and allow the risk assessor to exercise professional judgment regarding whether to include border regions in the critical study area based on land use and the population within these areas. In case of a question about whether to include some specific border area or not, the assessor can re-run the air model, placing a tight grid around the area in question. The ensuing block risk isopleth would have a corresponding increased resolution. It is possible that the study area definition methodology described above will produce a study area that reaches the 50 km radius in one or more locations. In this case, it would be desirable to extend the air modeling radius beyond 50 km. However, doing so would require the application of long-range atmospheric transport models, the use of which would add considerably to the uncertainties inherent in the methodology. Therefore, until models of long-range atmospheric transport are sufficiently developed, it would be reasonable to make 50 km the outer border for the study area.

Successful application of this method depends on the judgment of the risk assessor. Choice of an appropriate exposure scenario to define the study area is especially important. If risks along the outer boundary are estimated to be above the concern level during the subsequent detailed analysis (considering all chemicals and pathways), the study area will need to be expanded.

2.4.4. Commodity Shed Approach. Another approach for examining exposure to combustor emissions examines the distribution of commodities produced locally which

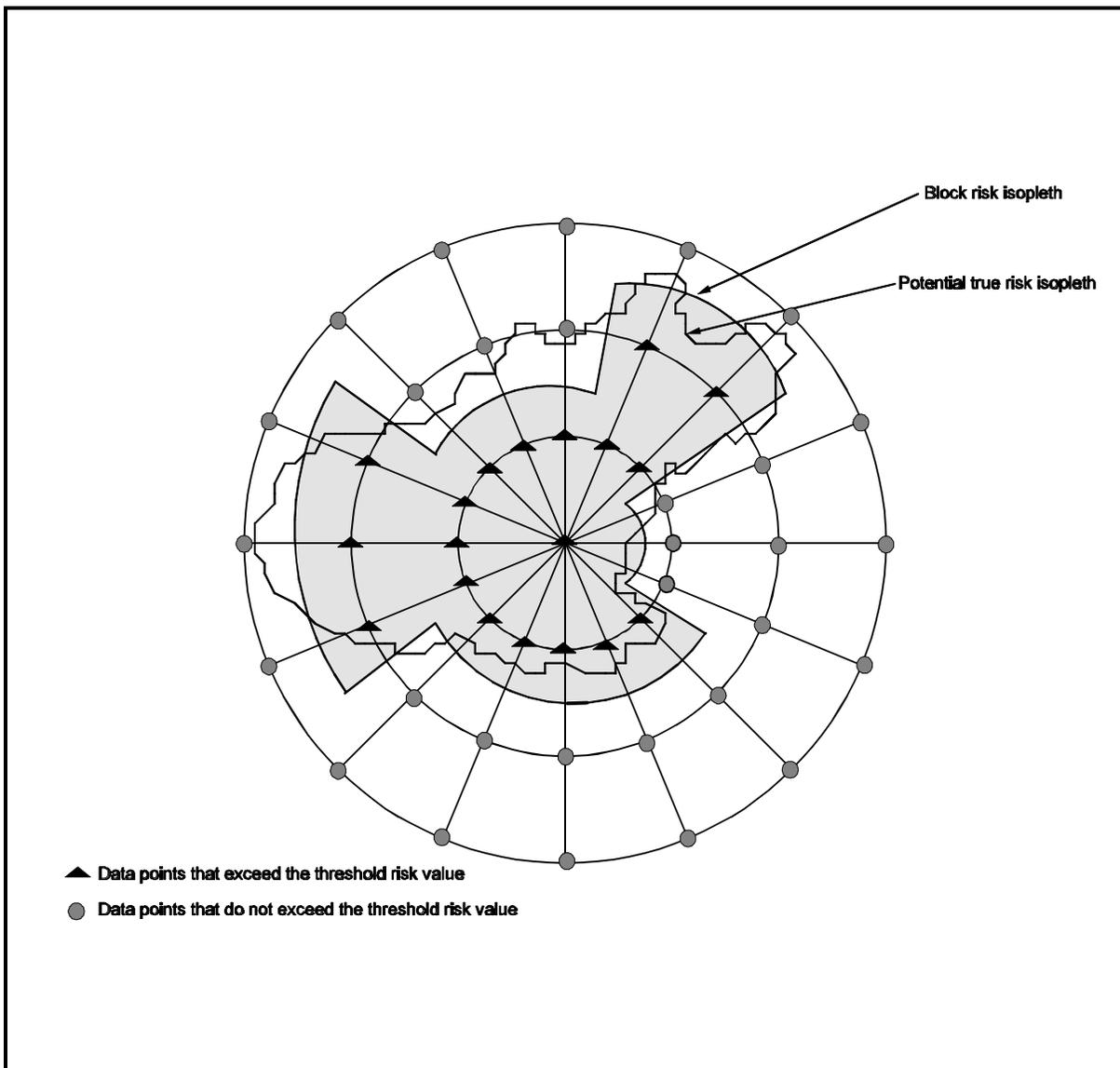


FIGURE 2-4
Comparison of Approximate Risk Isopleth Derived from
Area Blocks to a Potential True Risk Isopleth

are predicted to exhibit increased pollutant concentrations. This is known as the “commodity shed” approach, which is a population based assessment. The method can be utilized for any medium to which a significant fraction of the population is exposed, but is most applicable to foods. It can also be utilized in conjunction with the isopleth approach. The isopleth approach could be used to estimate exposure for specific subgroups and this approach for the general population.

The first step of this approach requires an analysis of the land uses within 50 km of the source. Again, the 50 km distance selection is for the ISC3 Model. The land uses of concern may include commercial farms or large water bodies. Subpopulations who reside in the area and do not exhibit a normal pattern of dietary diversity should be identified. These subpopulations may derive a large fraction of their nutritional requirements from either a single commodity (e.g., fish consumption may fulfill a daily protein or a daily energy requirement) or from a group of commodities collected from a small geographical area (e.g., a large fraction of subsistence farmers’ daily intake may be derived from a single location). These subpopulations should be assessed on a site-specific basis in relation to the combustor. Estimates of the sizes of these subpopulations and the fraction of the entire population they comprise should be included in the risk characterization. As stated previously in this chapter, annual average air concentrations and deposition rates should be utilized for the farm fields or the watershed.

Exposure for the rest of the population that does not derive its food in these manners could be assessed through the commodity shed approach. If one of the goals of the assessment is to predict population exposure and risk, then the initial analysis of the site (at the beginning of the assessment), should include a determination of the areas where foods are produced and an estimate of the average annual production rates for each area. When modeling, determine the average concentration of pollutant in the foods produced at each area. The sites could include farms which produce plants or meats for the population or lakes which are fished for recreational or commercial purposes.

Use the following procedure to estimate population exposure within the modeled region:

1. Identify each site (i) in the area around the combustor which produces a specific food item for public consumption. These sites could include commercial farms or water bodies large enough to be fished recreationally or commercially. Consider imported commodity (from outside the modeled region) as a separate site.
2. Predict the contaminant concentration for each commodity (k) produced at each site i ($C_{k,i}$). Include an estimate of the contaminant concentration in the imported commodity.
3. Determine the quantity of each commodity at each site ($Q_{k,i}$) that is produced for public consumption (e.g., 2000 Kg of corn and 200 Kg of cucumbers from a farm). Include an estimate of the amount of imported commodity.
4. Construct a discrete distribution of contaminant concentration for each commodity (C_k) assuming that the probability of consumption of commodity produced at any given site is proportional to the amount produced at that site $\{Pr[C_k=(C_{k,i})] = (Q_{k,i}) / \sum(Q_{k,i})\}$. If only the mean population exposure is desired, the production-weighted mean contaminant concentration for each commodity can be calculated as in Equation 2-1.

$$C_k = \frac{\sum(C_{k,i} \times Q_{k,i})}{\sum Q_{k,i}} \quad (2-1)$$

where:

C_k = production-weighted mean contaminant concentration for commodity k (mg/Kg)

$C_{k,i}$ = contaminant concentration for commodity k at site i (mg/Kg)

$Q_{k,i}$ = production quantity of commodity k at site i (Kg)

5. Determine the distribution of the population consumption rates (CR) from consumption survey data. Local or regional consumption data are best but national studies are acceptable. Commodity consumption rates are often given as g/day in the literature. In these cases, the consumption rates must be converted to an intake on a per body weight basis. This may be accomplished by assuming a specific body weight for the entire population (e.g., 70 Kg). Alternatively, some consumption rate data bases may contain enough information to estimate a relationship between consumption rate and body weight. This relationship may be factored into the analysis. Some consumption analyses may measure the body weight of respondents directly; these data are the most appropriate for this approach.
6. Calculate the estimated mean contaminant intake for the local human population by substituting the average values for consumption rates and contaminant concentrations in Equation 2-2 or perform a Monte Carlo analysis as described in Chapter 10 to obtain a population distribution of contaminant intake.

$$DI = \sum(CR_k \times C_k) \quad (2-2)$$

where:

- DI = human daily intake of the contaminant (mg/kg-day)
- CR_k = the daily consumption rate of the k^{th} commodity as a fraction of body weight (Kg commodity/Kg Bw per day)
- C_k = the predicted pollutant concentration for the k^{th} commodity source (mg contaminant/Kg commodity)

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AIR DISPERSION AND DEPOSITION MODELING OF POLLUTANT STACK EMISSIONS

3.1. INTRODUCTION

Estimation of health risks associated with exposure to air releases of contaminants from stationary industrial and combustion sources requires estimates of the atmospheric concentrations and annual wet and dry deposition rates of the emitted contaminants in the areas around these facilities. When atmospheric concentrations and deposition rates cannot be measured in the vicinity of operating sources, U.S. EPA customarily uses air dispersion/deposition models to estimate the atmospheric transport, the surface deposition flux, and the ambient air concentrations of specific compounds attributable to smokestack emissions from an industrial combustion source. Air dispersion models are mathematical constructs that approximate the physical and chemical processes occurring in the atmosphere that directly influence the dispersion of gaseous and particulate emissions from the stack of a combustion source. These models are computer programs encompassing a series of partial differential and algebraic equations that calculate the dispersion and deposition of the emissions. Concentration and deposition estimates of the contaminants discharged from the stack are computed at specified distances from the source. These quantities are used to estimate the magnitude of potential exposures to receptors, and to estimate the potential health risks in populations living and working in the vicinity of the stationary combustion source.

The Guideline on Air Quality Models (U.S. EPA, 1997) has recommended the use of numerous air dispersion and deposition models that may be applied to the regulatory analysis of source stack emissions. The guideline is intended for use by EPA Regional Offices in judging the adequacy of modeling analyses performed by EPA, State and local agencies and by industry. A primary purpose of the guidelines is to promote consistency in the application of air quality models, and to identify those

techniques and data bases EPA considers acceptable. This chapter recommends the application of the Industrial Source Complex 3 (ISC3) model for analysis of potential exposures to combustor emissions. ISC3 is listed as a recommended model in Appendix A to the Air Modeling Guidelines. The reader is reminded that air quality models are continuing to be changed in response to regulatory requirements and the expanded requirements for models to cover even more complex problems. Therefore this current recommendation for the use of ISC3 may be changed as the state-of-the art in model development changes.

The 1990 Methodology for Assessing Health Risks Associated With Indirect Exposure to Combustor Emissions (U.S. EPA, 1990) and Addendum to Methodology for Assessing Health Risks Associated With Indirect Exposure to Combustor Emissions (U.S. EPA, 1993) discussed the need for modeling techniques that predict the effects of contaminant dispersion and deposition in the presence of complex terrain (i.e., receptor location above the source of contamination).

The purpose of this chapter is to provide general guidance on the use of the ISC3 model in the context of the overall exposure assessment of emissions released from the stacks of stationary combustion processes. Accordingly, the chapter is subdivided by topic area, which are :

- (a) Selection of toxic air pollutants that are commonly measured in stack emissions from the incineration and combustion of anthropogenic waste materials;
- (b) Estimation of the stack emission rate of the toxic air pollutants for air modeling purposes;
- (c) Increases in emissions during equipment malfunctions, start-up and shutdown;
- (d) Air dispersion modeling of the stack gas emissions including descriptions the ISC3 model applications and associated wet and dry deposition algorithms;

(e) Procedures for applying the ISC3 model using vapor phase and particulate phase partitioning of the emitted pollutants, and a specific particle size distribution of particulate matter; and

(f) Method for estimating exposure through inhalation of dispersed pollutants.

3.2. SELECTING TOXIC AIR POLLUTANTS

The first step in the analysis of multiple pathways of exposure is the identification and selection of contaminants that may be emitted to the air during the combustion process. The selection process should focus on chemicals that are potentially toxic, and that have a definite propensity for bioaccumulating or bioconcentrating in the human and ecological food chains. As the initial step in the selection process, a select list of compounds that have been detected in combustor emissions is shown in Tables 3-1, 3-2, and 3-3. These tables list potentially toxic organic and inorganic contaminants that should be considered when assessing risks associated with direct and indirect exposures to the combustor emissions. This list includes chemicals identified as most frequently detected and measured in stack emissions from incinerators, boilers and industrial furnaces combusting hazardous waste, sewage sludge, municipal solid waste, biomass, automobile tires, and medical and hospital waste (Dempsey and Oppelt, 1993; CARB, 1990a,b, 1991; CAPCOA, 1991; U.S. EPA, 1986, 1988). In addition the constituents listed have toxicity values available on IRIS. To the extent possible, chemical speciation of the various forms of these compounds should be identified. Using these tables as a starting point, the assessor can narrow the number of compounds of concern for a particular combustor using the following three steps, identified in Sections 3.2.1., 3.2.2. and 3.2.3.

3.2.1. Consider the Feed Material Being Combusted. The selection of the chemicals for site-specific analysis will depend largely on the waste materials that will routinely be accepted and incinerated at the combustion facility. If chlorine is present in the feed, then it is imperative that chlorinated dioxins and dibenzofurans be evaluated in the exposure assessment. Even if chlorine is not specifically identified in

the waste feed, it is recommended that this class of compounds be addressed in the assessment.

| TABLE 3-1 | |
|--|---------------------------|
| Initial List of Dioxin-Like Compounds Identified in Emissions from the Incineration and Combustion of Anthropogenic Wastes | |
| Chlorinated Dibenzop-dioxins (CDDs) | Chlorinated Dibenzofurans |
| 2,3,7,8-TCDD | 2,3,7,8-TCDF |
| 1,2,3,7,8-PentaCDD | 1,2,3,7,8-PentaCDF |
| 1,2,3,4,7,8-HexaCDD | 2,3,4,7,8-PentaCDF |
| 1,2,3,6,7,8-HexaCDD | 1,2,3,4,7,8-HexaCDF |
| 1,2,3,7,8,9-HexaCDD | 1,2,3,6,7,8-HexaCDF |
| 1,2,3,4,6,7,8-HeptaCDD | 1,2,3,7,8,9-HexaCDF |
| 1,2,3,6,7,8,9-OctaCDD | 2,3,4,6,7,8-HexaCDF |
| Other TetraCDDs | 1,2,3,4,6,7,8-HeptaCDF |
| Other PentaCDDs | 1,2,3,4,7,8,9-HeptaCDF |
| Other HexaCDDs | 1,2,3,4,6,7,8,9-OctaCDF |
| Other HeptaCDDs | Other TCDFs |
| | Other PentaCDFs |
| | Other HexaCDFs |
| | Other HeptaCDFs |

TABLE 3-2

Initial List of Organic Compounds Identified in Emissions from the Incineration and Combustion of Anthropogenic Wastes

| Organic Compounds | RfD ^a | RfC ^b | Carc ^c | Reference |
|-----------------------------|------------------|------------------|-------------------|----------------------|
| Acrylonitrile | IRIS | IRIS | B1, IRIS | U.S. EPA, 1989, 1998 |
| Anthracene | None | None | D, IRIS | U.S. EPA, 1989, 1998 |
| Azobenzene | IRIS | IRIS | B2, IRIS | U.S. EPA, 1989, 1998 |
| Benzaldehyde | IRIS | None | None | U.S. EPA, 1989, 1998 |
| Benzene | None | None | A, IRIS | U.S. EPA, 1989, 1998 |
| Benz(a)anthracene | None | None | B2, IRIS | U.S. EPA, 1998 |
| Benzo(a)pyrene | None | None | B2, IRIS | U.S. EPA, 1998 |
| Benzo(b)fluoranthene | None | None | B2, IRIS | U.S. EPA, 1998 |
| Benzo(e)pyrene | None | None | C, IRIS | U.S. EPA, 1998 |
| Benzo(g,h,i)perylene | None | None | D, IRIS | U.S. EPA, 1998 |
| Benzo(j)fluoranthene | None | None | B2, IRIS | U.S. EPA, 1998 |
| Benzo(k)fluoranthene | None | None | B2, IRIS | U.S. EPA, 1998 |
| Benzyl chloride | None | None | B2, IRIS | U.S. EPA, 1989, 1998 |
| 1,1-Biphenyl | IRIS | None | D, IRIS | U.S. EPA, 1989, 1998 |
| Bis(2-chloroethoxy) methane | None | None | D, IRIS | U.S. EPA, 1998 |
| Bis(2-chloroethyl) ether | None | None | B2, IRIS | U.S. EPA, 1998 |
| Bis(2-ethylhexyl) phthalate | None | None | * | U.S. EPA, 1989 |
| Bis(chloromethyl) ether | None | None | A, IRIS | U.S. EPA, 1989, 1998 |
| Bromochloromethane | None | None | D, IRIS | U.S. EPA, 1998 |
| Bromodichloromethane | IRIS | None | B2, IRIS | U.S. EPA, 1998 |
| Bromomethane | IRIS | IRIS | D, IRIS | U.S. EPA, 1989, 1998 |
| 1,3-Butadiene | None | None | B2, IRIS | U.S. EPA, 1998 |

TABLE 3-2 (cont.)

| Organic Compounds | RfD ^a | RfC ^b | Carc ^c | Reference |
|-----------------------------|------------------|------------------|-------------------|----------------------|
| Butyl benzyl phthalate | IRIS | None | C, IRIS | U.S. EPA, 1989, 1998 |
| Captan | IRIS | None | B2, IRIS | U.S. EPA, 1998 |
| Carbon disulfide | IRIS | IRIS | None | U.S. EPA, 1998 |
| Carbon tetrachloride | IRIS | None | B2, IRIS | U.S. EPA, 1989, 1998 |
| Chlorobenzene | IRIS | None | D, IRIS | U.S. EPA, 1998 |
| Chlorocyclopentadiene | None | None | D, IRIS | U.S. EPA, 1998 |
| Chloroform | IRIS | None | B2, IRIS | U.S. EPA, 1989, 1998 |
| Chloromethane | None | None | None | U.S. EPA, 1998 |
| Chrysene | None | None | B2, IRIS | U.S. EPA, 1998 |
| Cumene | IRIS | None | None | U.S. EPA, 1989, 1998 |
| Di(2-ethylhexyl)phthalate | IRIS | None | B2, IRIS | U.S. EPA, 1998 |
| Dibenzofuran | None | None | D, IRIS | U.S. EPA, 1989, 1998 |
| Dibenzo(a,e)fluoranthene | None | None | B2, IRIS | U.S. EPA, 1998 |
| Dibenzo(a,h)anthracene | None | None | B2, IRIS | U.S. EPA, 1998 |
| 1,2-Dibromo-3-chloropropane | None | IRIS | B2, IRIS | U.S. EPA, 1998 |
| 1,2-Dichlorobenzene | IRIS | None | D, IRIS | U.S. EPA, 1989, 1998 |
| 1,3-Dichlorobenzene | None | None | D, IRIS | U.S. EPA, 1989, 1998 |
| 1,4-Dichlorobenzene | None | IRIS | None | U.S. EPA, 1989, 1998 |
| 1,1-Dichloroethane | None | None | C, IRIS | U.S. EPA, 1989, 1998 |
| 1,2-Dichloroethane | None | None | B2, IRIS | U.S. EPA, 1998 |
| 1,1-Dichloroethylene | IRIS | None | C, IRIS | U.S. EPA, 1989, 1998 |
| Dichloromethane | IRIS | None | B2, IRIS | U.S. EPA, 1998 |
| 2,4-Dichlorophenol | IRIS | None | None | U.S. EPA, 1989, 1998 |

TABLE 3-2 (cont.)

| Organic Compounds | RfD ^a | RfC ^b | Carc ^c | Reference |
|----------------------------|------------------|------------------|-------------------|----------------------|
| Dimethyl phthalate | None | None | D, IRIS | U.S. EPA, 1998 |
| 1,4-Dioxane | None | None | B2, IRIS | U.S. EPA, 1998 |
| Ethyl benzene | IRIS | IRIS | D, IRIS | U.S. EPA, 1989, 1998 |
| Fluoranthene | IRIS | None | D, IRIS | U.S. EPA, 1998 |
| Formaldehyde | IRIS | None | B1, IRIS | U.S. EPA, 1998 |
| Hexachlorobenzene | IRIS | None | B2, IRIS | U.S. EPA, 1989, 1998 |
| Hexachlorobutadiene | IRIS | None | C, IRIS | U.S. EPA, 1989, 1998 |
| Hexachloroethane | IRIS | None | C, IRIS | U.S. EPA, 1989, 1998 |
| Mercuric chloride | IRIS | None | C, IRIS | U.S. EPA, 1998 |
| Mercury, elemental | None | IRIS | D, IRIS | U.S. EPA, 1998 |
| Methylene bromide | + | - | - | U.S. EPA, 1989* |
| Methyl ethyl ketone | IRIS | IRIS | D, IRIS | U.S. EPA, 1989, 1998 |
| Naphthalene | None | None | D, IRIS | U.S. EPA, 1989, 1998 |
| Pentachlorobenzene | IRIS | None | D, IRIS | U.S. EPA, 1989, 1998 |
| Pentachlorophenol | IRIS | None | B2, IRIS | U.S. EPA, 1989, 1998 |
| Phenol | IRIS | None | D, IRIS | U.S. EPA, 1989, 1998 |
| Polychlorinated biphenyls | None | None | B2, IRIS | U.S. EPA, 1998 |
| Polycyclic organic matter | None | None | B1, IRIS | U.S. EPA, 1998 |
| Pyrene | IRIS | None | D, IRIS | U.S. EPA, 1989, 1998 |
| Quinones | | | | |
| Styrene | IRIS | IRIS | None | U.S. EPA, 1989, 1998 |
| 1,2,4,5-Tetrachlorobenzene | IRIS | None | None | U.S. EPA, 1989, 1998 |

TABLE 3-2 (cont.)

| Organic Compounds | RfD ^a | RfC ^b | Carc ^c | Reference |
|---------------------------|------------------|------------------|-------------------|----------------------|
| 1,1,1,2-Tetrachloroethane | IRIS | None | C, IRIS | U.S. EPA, 1998 |
| 1,1,2,2-Tetrachloroethane | None | None | C, IRIS | U.S. EPA, 1998 |
| Tetrachloroethylene | IRIS | None | B2, IRIS | U.S. EPA, 1989, 1998 |
| Dibutyl phthalate | IRIS | None | D, IRIS | U.S. EPA, 1998 |
| Toluene | IRIS | IRIS | D, IRIS | U.S. EPA, 1989, 1998 |
| 1,2,4-Trichlorobenzene | IRIS | IRIS | D, IRIS | U.S. EPA, 1989, 1998 |
| 1,1,1-Trichloroethane | None | None | D, IRIS | U.S. EPA, 1989, 1998 |
| 1,1,2-Trichloroethane | IRIS | None | C, IRIS | U.S. EPA, 1989, 1998 |
| Trichloroethylene | None | None | IRIS | U.S. EPA, 1998 |
| 2,4,5-Trichlorophenol | IRIS | None | None | U.S. EPA, 1989, 1998 |
| 2,4,6-Trichlorophenol | None | None | B2, IRIS | U.S. EPA, 1989, 1998 |
| Vinyl chloride | None | None | A, IRIS | U.S. EPA, 1989, 1998 |
| m-Xylene | None | None | None | U.S. EPA, 1989, 1998 |
| o-Xylene | None | None | None | U.S. EPA, 1989, 1998 |
| p-Xylene | None | None | None | U.S. EPA, 1989, 1998 |
| Xylenes | IRIS | None | D, IRIS | U.S. EPA, 1989, 1998 |

^aRfD is the reference dose-defined as an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

^bRfC is the reference concentration-defined as an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

^cGroup A carcinogen: Human carcinogen (sufficient evidence of carcinogenicity in humans). Group B carcinogen: Probable human carcinogen (B1 -limited evidence of carcinogenicity in humans; B2 -sufficient evidence of carcinogenicity in animals with

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inadequate or lack of evidence in humans). Group C carcinogen: Possible human carcinogen (limited evidence of carcinogenicity in animals and inadequate or lack of human data). Group D carcinogen: Not classifiable as to human carcinogenicity (inadequate or no evidence).

| Inorganic Contaminants | RfD ^a | RfC ^b | Carc ^c | Reference |
|------------------------|------------------|--------------------------|-------------------|----------------------|
| Antimony | IRIS | IRIS (AsO ₃) | — | U.S. EPA, 1989, 1998 |
| Arsenic, inorganic | IRIS | — | IRIS; A | U.S. EPA, 1989, 1998 |
| Barium | IRIS | — | — | U.S. EPA, 1989, 1998 |
| Cadmium | IRIS | — | IRIS; B1 | U.S. EPA, 1989, 1998 |
| Chromium (III) | IRIS | — | — | U.S. EPA, 1989, 1998 |
| Chromium (VI) | — | — | IRIS; A | U.S. EPA, 1998 |
| Lead + compounds | — | — | IRIS; B2 | U.S. EPA, 1998 |
| Manganese | IRIS | IRIS | IRIS; D | U.S. EPA, 1998 |
| Mercuric chloride | IRIS | — | IRIS | |
| Mercury, elemental | | IRIS | IRIS; D | U.S. EPA, 1989, 1998 |
| Nickel, soluble salts | IRIS | — | — | U.S. EPA, 1989, 1998 |
| Selenium + compounds | IRIS | — | IRIS; D | U.S. EPA, 1989, 1998 |
| Silver | IRIS | — | IRIS; D | U.S. EPA, 1998 |
| Zinc + compounds | IRIS | — | IRIS; D | U.S. EPA, 1989, 1998 |

^aRfD is the reference dose—defined as an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

^bRfC is the reference concentration—defined as an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

^cGroup A carcinogen: Human carcinogen (sufficient evidence of carcinogenicity in humans); Group B carcinogen: Probable human carcinogen (B1 -limited evidence of carcinogenicity in humans; B2 -sufficient evidence of carcinogenicity in animals with inadequate or lack of evidence in humans); Group C carcinogen: Possible human carcinogen (limited evidence of carcinogenicity in animals and inadequate or lack of human data); Group D carcinogen: Not classifiable as to human carcinogenicity (inadequate or no evidence); I = Carcinogenic by the inhalation route.

It may be that only an extremely small concentration of chlorine in the waste is sufficient to participate in the formation of CDDs/CDFs. In addition, combustion air may contain precursor compounds and halides that may cause dioxins to be thermally formed. Therefore, it is generally suggested that assessments of waste incineration sources include dioxin-like compounds in the analysis of emissions. Products of incomplete combustion (PICs) will form in the stack gas emissions as a consequence of the incomplete destruction of all organic species leaving the combustion chamber. Therefore, the polycyclic aromatic hydrocarbons (PAHs), i.e. benzo(a)pyrene, will need to be routinely considered. Finally, to the extent a combustion facility accepts and incinerates metal-bearing materials and wastes, the heavy metals having significant toxicologic or bioaccumulative properties e.g., arsenic, cadmium, chromium, lead, mercury and nickel, will need to be addressed in the exposure analysis.

3.2.2. Consider the Availability of Appropriate Toxicological Information. Risk assessments cannot be completed for compounds that lack verified dose-response relationships for specific health endpoints. Accordingly, such compounds can be eliminated from consideration in the exposure assessment. Although they may need to be considered only in a qualitative manner, the potential risks posed by emissions of these compounds do need to be considered in the risk characterization. Tables 3-2 and 3-3 contain information that can assist in a toxicological evaluation, including availability of reference doses (RfD), reference concentrations (RfC), and the current carcinogenicity assessment that appears on U.S. EPA's IRIS database. The risk assessor should review the latest version of IRIS to confirm if new chemicals have been added, if additional RfDs or RfCs have been verified, and if the carcinogenicity assessment has been updated.

3.2.3. Narrow the List with a Quantitative Ranking Scheme. After following the first two steps, the list in Tables 3-1 through 3-3 may be substantially narrowed. However, it may not be necessary to conduct full assessments on the remaining chemicals. Say, for example, a credible ranking scheme could be developed that would rank a list of 50

chemicals (and there are more than 90 chemicals listed in Tables 3-1 through 3-3) from most to least concern. If the detailed site-specific assessment on the 20 chemicals of most concern indicated that chemicals 15 through 20 resulted in negligible indirect health risk, then there would be credible grounds to conclude that chemicals 21 through 50 do not require further indirect assessment. Likewise, if the assessment indicated a health risk of potential consequence for chemicals 15 through 20, then evaluation of more chemicals on the list of 50 would be required.

The Risk Assessment Guidance for Superfund (RAGS; U.S. EPA, 1989) suggests a simple linear ranking scheme for focusing on the “most significant” chemicals. This scheme multiplies a quantitative toxicity value (e.g., slope factor) by a quantitative concentration of the contaminant in the exposure medium (e.g., soil). For combustor emissions, the “concentration” term should be replaced with the emission rate of the chemical. Procedures to estimate emission rates are presented in Section 3.3. below. A third factor that should be considered is the potential for the chemical to bioaccumulate. Factors indicating bioaccumulation potential include persistence in the environment (more persistence translates to more bioaccumulation) and partitioning tendencies (more partitioning onto soils and sediments translates to more bioaccumulation). A surrogate factor that can be used for bioaccumulation potential is the logarithm of the octanol-water partition coefficient, denoted as $\log K_{ow}$. The higher the value of the $\log K_{ow}$ the greater the possibility for partitioning onto soils and sediments. Longer persistence is correlated to tighter sorption to soils/sediments, which is why the $\log K_{ow}$ can capture both persistence and partitioning tendencies appropriately.

3.3. ESTIMATING THE STACK EMISSION RATE OF THE TOXIC AIR POLLUTANTS

For a Gaussian plume model, such as ISC3, the predicted ground-level concentrations are directly proportional to the rate at which pollutants are emitted from a source in units of mass per unit time. The emission rate is a variable source characteristic. This rate may vary over time because of changing conditions (e.g.,

increases in volatile emissions with increases in temperature or a malfunction within the stack processes). This section will focus on emission rates from stacks, both intentional and accidental, as presented in the Addendum to Methodology for Assessing Health Risks Associated With Indirect Exposure to Combustor Emissions (U.S. EPA, 1993).

For the purposes of chemical selection as described above, and for air modeling and exposure assessment, the release rate of pollutants from the combustor stack is expressed in metric units of mass of the pollutant emitted per unit time (e.g., grams/s). The release rate used in indirect exposure assessments should generally be reflective of the expected average emissions from the facility over the long term (e.g., over the engineered life of the combustion facility). However, if acute inhalation exposures are of concern, the release rate should be reflective of maximum short-term emissions (e.g., as a result of equipment malfunction, startup and shutdown, or possible accidental releases). Additionally, given the typically short duration of these events, a wide range of meteorologic conditions (e.g., inversions) should be modeled to encompass a range of potential impacts. Although mass emission rates can be estimated in any number of ways, the following hierarchical order of preference is recommended.

3.3.1. Operational Facilities. For facilities that are built and operational, it is preferred that direct stack measurements be used, using U.S. EPA-recommended chemical-specific (and, wherever possible, species- or congener-specific) stack sampling, analytical, quality control, and quality assurance protocols and procedures. Stack monitoring should provide information on the concentrations of the pollutants (e.g., ng/dscm), the actual velocity of stack gas release (m/s), and stack gas temperature (K). In addition, based on the characteristics and heat value of the waste feed, the temperature of combustion, and stoichiometric conditions, the volume of flue gases evolved per unit of time should be estimated (in metric units of dry standard cubic meters per minute [dscm] at 12% CO₂ or 7% O₂). To calculate a mass emission rate of the pollutant, it is necessary to multiply the estimated dry flue gas volume (m³)

per minute associated with combustion by the measured in-stack concentration of the contaminant in units of g/dscm. (It should be noted that concentrations reported on an equivalent oxygen or carbon dioxide basis or on a dry volume basis must be adjusted to the actual stack gas conditions in order to determine the actual, in-stack concentrations.) The product of this calculation (g/min) is then divided by 60 s/min to give the grams per second emission rate needed as an input into the ISC3 model. In cases where there are multiple stack tests from the same facility, care should be taken to ensure that the emissions characterization reflects a wide range of operating conditions and also accounts for any expected deterioration in facility performance that would affect the facility's emissions over its useful life. In arriving at the final estimate of emissions of the contaminant, the average value is considered representative of long-term emissions, taking into consideration the average yearly operating hours of the combustion facility.

3.3.2. Planned Facilities. For facilities that have been constructed but are not yet operational, or are in the planning stages of development, the following approach is recommended. Reports of stack tests measuring the emissions of the pollutants of interest should be collected from facilities that are most similar in technology, design, operation, capacity, auxiliary fuels used, waste feed types and composition, and air pollution controls to the facility under consideration. The stack test reports should be evaluated to determine if U.S. EPA-recommended protocols, or equivalent, that are appropriate for the specific pollutants being measured, were used for stack sampling and analysis. When data from test results for a number of facilities are combined, care should be taken to convert concentrations and stack gas parameters to a common basis (and consistent units of measurement) appropriate for the facility under consideration, considering process feed rates and other facility-specific operating conditions. For purposes of exposure assessment and risk characterization, ranges and average values should be developed in order to address uncertainties inherent in the emissions estimates. However, the average emission rate of the contaminant is the

value used to represent long-term and expected emissions from the combustor under study.

3.3.3. Planned Facility With No Comparable Existing Facility. If no data exist relevant to a specific facility, then the Office of Air Quality Planning and Standards' AP-42, *Compilation of Air Pollution Emission Factors* (U.S. EPA, 1985) can be used. Care should be taken to select emission factors that were developed for technologies that best match the facility under consideration. The basic limitation of these data is the fact that emission factors are not usually reflective of specific emission control equipment. Also, information is available for only a limited number of pollutants.

Specifically, the AP-42 document provides guidance on emission factors for municipal waste combustors, sewage sludge incinerators, and medical waste incinerators. At this time, emissions from hazardous waste incinerators are not addressed in AP-42. Emission factors presented in AP-42 are designed for estimating emissions from a large number of sources over a wide area. The use of AP-42 emission factors to estimate emissions from any one facility should be done with great care. Whenever possible, emissions measured from the facility in question should be used in preference to the emission factor. In the absence of site-specific emission test data, emissions measured at an identical or similar facility combusting the same or similar material should be used. AP-42 emission factors should be the last alternative because they are averages of values determined at one or more individual facilities. The individual values that are used to develop the average may vary considerably (for example, the extreme values used for the emission factor for mercury from municipal mass burn combustors vary by more than a factor of 5 from the value presented in AP-42). Emission factors for the following compounds will be available for the following types of incineration systems:

- ! Municipal waste combustors: arsenic, cadmium, chromium, mercury, nickel, lead, total tetra through octa chlorinated dibenzo-p-dioxin and furans.

- ! Sewage sludge incinerators: antimony, arsenic, cobalt, beryllium, cadmium, chromium, lead, manganese, mercury, nickel, selenium, various chlorinated dibenzo-p-dioxin and furans.

- ! Medical waste incinerators: antimony, arsenic, beryllium, cadmium, chromium, manganese, mercury, nickel, chlorobenzene, chlorophenol, total tetra through octa chlorinated dibenzo-p-dioxin and furans, total PCB.

In the absence of suitable AP-42 emission factors, clearly documented engineering evaluations may be used. Documentation should include copies of emission test reports used to derive the emission estimates, any assumptions made, and the rationale for the conclusions that are drawn.

3.4. INCREASES IN EMISSIONS DURING EQUIPMENT MALFUNCTIONS; STARTUP, AND SHUTDOWN

One of the more difficult aspects in deriving pollutant emission rates from incineration sources is accounting for temporary increases in emissions that may occur as a result of startup and shutdown in operations, malfunctions or perturbations in the combustion process, or changes in the removal efficiency of the air pollution control equipment. In deriving a quantitative measure of the magnitude and duration of increased emissions associated with these events, it is recommended that a procedure similar to the one used to derive estimates of routine emissions be applied. In this context the following sources of information, in order of preference, should be reviewed:

- ! The modeler should review stack emission testing and engineering reports on the performance and operations of combustion technologies, furnace designs, and air pollution control devices that are most similar in every respect to the facility under review. Often the emissions testing is accompanied by records that may give a gross indication of whether the system is functioning according to design specifications. Most facilities routinely monitor carbon monoxide (CO) in the stack to provide a general indication of combustion efficiency. Carbon monoxide inversely correlates with combustion efficiency, and a sudden increase in concentration could imply that an upset in the quality of the burn may have occurred. The engineering analysis in the test report may summarize these data, and qualitatively discuss upset conditions and the

length of time they were maintained. Most facilities also routinely monitor furnace temperature. Furnace temperature is directly related to combustion efficiency and gives a qualitative measure of whether incineration of the wastes is occurring according to the design of the combustion chamber. Temperatures outside the prescribed envelope of routine operations may signal a temporary malfunction or upset in the quality of the burn. This may be due to the delivery of a highly combustible and/or wet material into the combustion chamber. During these conditions, temporary excursions in emissions of pollutants from the stack may occur, and this may have been recorded in the engineering test report.

- ! A second area of information regarding temporary increases in emissions during equipment malfunctions is tests designed to determine the removal efficiency of the air pollution control devices (APCD). More specifically, some facilities may have been required by state air pollution control agencies to provide information on the longer-term performance of the APCD. In most cases such tests involve determining the variability in the efficiency of removal of particulate matter from the combustion gases, and/or the removal of acid gases such as sulfur dioxide and hydrogen chloride. In some rare instances the engineering evaluation may have been undertaken to determine the extent mercury was being reduced, or to what extent dioxins were controlled with the APCD. These engineering analyses may be public documents, and it may be possible to obtain copies from the appropriate state agency or the EPA regional office. In any case, these data may be helpful in establishing a quantitative basis for estimating the magnitude, duration, and frequency of occurrence of higher-than-expected emissions.

In the event these sources of information do not provide a quantitative (e.g., numerical) basis for estimating the magnitude and duration of increase of the pollutant during upset conditions, then the procedure required by the State of California Air Resources Board (CARB, 1990) can be applied. In this procedure, defaults for estimating emissions representative of emergency operating conditions and poor operating conditions at the facility are provided, as follows:

- ! Emergency operating conditions. Estimation of stack emissions of the contaminants representative of emergency operating conditions should be based on uncontrolled emissions over a 1-hour period. For example, if dioxin is assumed to be controlled by the APCD at a rate of 99% relative to uncontrolled concentration, then under the emergency operating

conditions scenario the stack concentration would be assumed to be 100 times higher during a 1-hour period. The CARB has defined this emergency condition as a sudden upset in which the air pollution control device (APCD) is bypassed to a waste stack, and uncontrolled emissions occur until the facility is completely shutdown. These operating conditions include such events as a turbine trip, blown boiler tubes, failure in the APCD, feed system failure, fire, etc. However if the source could demonstrate that the APCD would never be bypassed during an emergency event, then use of uncontrolled emissions would not realistically reflect the potential emissions from the facility. CARB gives no guidance on an alternative approach, but does indicate that the evaluation of potential health impacts resulting from acute exposures should represent a range of operating conditions. These should reflect poor operation of the equipment and total equipment failure. For these operating conditions the increase in emissions resulting from reduced control efficiency should be estimated and the duration of the event should be noted.

- ! Poor operating conditions. To represent stack emissions during operating conditions that are less than normal, CARB recommends, as a default, multiplying the average emissions (found from the source test database) by 10. This factor is incorporated into the annual emission rate of organic and metal emissions. CARB further recommends using a default value for the fraction of the time a facility operates under poor conditions on an annual basis. For organic contaminants, it is assumed that the facility operates normally 80% of the time and operates poorly for the other 20%. For metal emission estimates, CARB recommends the default assumption that the facility operates normally 95% of the time and under poor conditions for the other 5% of the time during the year.

The appropriate regulatory authority may give consideration to exempting a source from an analysis of potentially increased emissions during upset conditions. However, it is recommended that such an exemption be based on a careful review of present and past performance of the subject combustor. The 'burden-of-proof' should rest with the applicant of an air permit to demonstrate, with factual information, that there exists a low likelihood that upsets and process malfunctions will occur at the facility. If the combustor is a planned facility, then it is recommended that the applicant provide technical supporting information that has been derived from a study of a facility most similar in design, size and operation as the subject facility.

3.5. AIR DISPERSION/DEPOSITION MODELING OF THE STACK GAS EMISSIONS

It has been customary for EPA to use air dispersion and surface deposition models to estimate the atmospheric transport, deposition flux, and ambient air concentrations of specific pollutants attributable to smokestack emissions from an industrial combustion source. Air dispersion models are mathematical constructs that approximate the physical and chemical processes occurring in the atmosphere that directly influence the dispersion of gaseous and particulate emissions from smokestacks of stationary combustion sources. These models are computer programs encompassing a series of partial differential and algebraic equations to calculate the dispersion and deposition of the emissions. Concentration and deposition isopleths of the toxic air contaminants discharged from the stack are computed at specified distances from the smokestack. These quantities are used to estimate the magnitude of potential exposures to the human receptor.

Numerous dispersion/deposition models have been developed. This document focuses on the Industrial Source Complex (ISC3) dispersion model recently developed by EPA to provide modeling outputs useful in the analysis of wet/dry deposition and ambient air concentrations of stack emitted contaminants in all terrain settings (U.S. EPA, 1995a,b). The ISC3 was developed as a general replacement to the COMPDEP model first described in U.S. EPA (1990b). Modeling enhancements of ISC3 included more refined small-particle dry and wet deposition algorithm than used by the COMPDEP model. The ISC3 was used to generate the results for the hypothetical incinerator of this assessment. However, the use of ISC3 in this assessment is not intended to imply that ISC3 is the only acceptable model.

Section 3.5.1. below presents an overview of the dispersion and deposition algorithms in the ISC3 model. Section 3.5.2. discusses dry deposition fluxes, including pertinent assumptions made in the application of the ISC3 model. Section 3.5.3. discusses particle size distributions for emitted particles. Wet deposition flux is reviewed in Section 3.5.4. Estimating the phase distribution of semivolatile organic

contaminants is reviewed in Section 3.5.5. Section 3.5.6. highlights the current recommendations for the regulatory use of ISC3. The guidance indicates that the ISC3 model should be run with two simultaneous modes of operation: one providing estimates of particulate concentrations in air and wet/dry particle deposition flux; the other providing for the estimation of vapor-phase concentrations of dioxin-like compounds in ambient air.

3.5.1. Basic Physical Principles Used to Estimate Atmospheric Dispersion and Deposition of Stack Emissions. Air dispersion/deposition models mathematically simulate the basic physical processes in the atmosphere to estimate the ground-level air concentrations and deposition flux of contaminants known to be released from the stacks/vents of stationary combustion sources. These processes include advection, turbulent diffusion, and removal of atmospheric particles. Advection describes the physical movement of the air contaminants by the horizontal movement of wind. Turbulent diffusion is the “spreading” of the emissions plume with distance from the stack through multidirectional fluctuations in air movement. Removal refers to mechanisms that remove emissions from the atmosphere. This can be caused by the force of gravity exerted on the particle mass, Brownian movement of aerosol particles, and scavenging of particles. Scavenging is the removal of particles or vapors by precipitation.

ISC3 contains modifications of the Industrial Source Complex model (short-term version) and COMPLEX I to incorporate algorithms to estimate dispersion and resulting ambient air concentrations and wet and dry deposition flux. COMPLEX I is a second-level screening model applicable to stationary combustion sources located in complex and rolling topography (U.S. EPA, 1986). The ISC3 model was developed by EPA to provide estimates of air concentrations and deposition rates of the stack emissions of contaminants from industrial sources located in varied terrain (e.g., from simple to complex terrain). Simple and complex terrain are defined as topography that is either below or above the effective stack height of the source (Turner, 1986). To account for pollutant deposition, the concentration algorithms in COMPLEX 1 were replaced with

those from the Multiple Point Source Algorithm with Terrain Adjustments Including Deposition and Sedimentation (MPTER-DS) model (Rao and Sutterfield, 1982). The MPTER-DS algorithms incorporate the gradient transfer theory described by Rao and Sutterfield (1982) and are extensions of the traditional Gaussian plume algorithms. The dispersion algorithms contained in the Industrial Source Complex, short-term version (ISCST), have been incorporated in ISC3 to analyze ground-level receptors located below the height of the emission plume (U.S. EPA, 1986). For a steady-state Gaussian plume, the hourly concentrations at downwind distance x (meters) and crosswind distance y (meters) are given by:

$$X = \frac{QKVD}{2\pi\mu_s\sigma_y\sigma_z} \exp\left[-0.5\left(\frac{y}{\sigma_y}\right)^2\right] \quad (3-1)$$

where:

- X = ambient air concentration of contaminant, $\mu\text{g}/\text{m}^3$
- Q = contaminant emissions rate, g/s
- K = units conversion factor
- V = vertical term - accounts for vertical distribution of the Gaussian plume, dimensionless
- D = plume depletion term relating removal by physical or chemical processes, dimensionless
- σ_y, σ_z = standard deviation of lateral and vertical concentration distribution, m
- μ_s = mean wind speed at release height, m/s
- y = crosswind distance from source to receptor, m

ISC3 uses the generalized Briggs (1975, 1979) equation to estimate plume-rise and downwind dispersion as a function of wind speed and atmospheric stability. A wind-

profile exponent law is used to adjust the observed mean wind speed from the measurement height to the emission height for the plume rise and pollutant concentration calculations. The Pasquill-Gifford curves are used to calculate lateral and vertical plume spread (U.S. EPA, 1986). These curves are based on Pasquill's definitions of atmospheric stability classes, e.g., extremely unstable, moderately unstable, slightly unstable, neutral, slightly stable, and moderately stable, that correspond to various intensities of solar radiation and wind speeds (Seinfeld, 1986). Equations that approximately fit the Pasquill-Gifford curves (Turner, 1970) are used to calculate σ_y and σ_z (in meters) for the rural mode. The equations used to calculate σ_y are of the form:

$$\sigma_y = 465.11628(x)\tan(\text{TH}) \tag{3-2}$$

where:

$$\text{TH} = 0.017453293[c - d \ln(x)] \tag{3-3}$$

In Equations 3-2 and 3-3 the downwind distance x is in kilometers, and the coefficients c and d are listed in Table 3-4. The equation used to calculate σ_z is of the form:

$$\sigma_z = ax^b \tag{3-4}$$

where the downwind distance x is in kilometers and σ_z is in meters.

Tables 3-4 and 3-5 show the equations used to determine σ_y and σ_z for the urban option. These expressions were determined by Briggs as reported by Gifford (1976) and represent a best fit to urban vertical diffusion data reported by McElroy and Pooler (1968). While the Briggs functions are assumed to be valid for downwind distances less than 100 m, the user is cautioned that predicted concentrations at

receptors less than 100 m from a source may be suspect. The incorporation of these two basic models into ISC3 permits analysis of a source located in all types of terrain.

| TABLE 3-4 Parameters Used to Calculate Pasquill-Gifford σ_y | | |
|---|---|---------|
| Pasquill Stability Category | $\sigma_y = 465.11628 (x)\tan(\text{TH})$ $\text{TH} = 0.017453293 [c - d \ln(x)]$ | |
| | c | d |
| A | 24.167 | 2.5334 |
| B | 18.333 | 1.8096 |
| C | 12.5 | 1.0857 |
| D | 8.333 | 0.72382 |
| E | 6.25 | 0.54287 |
| F | 4.1667 | 0.36191 |

3.5.2. Estimation of Dry Surface Deposition Flux. The dry deposition of particle-bound contaminants is a physical atmospheric removal process that is simulated by the ISC3 model. Dry deposition refers to the transfer of airborne particulate matter to the Earth's surface (including water, soil, and vegetation) whereby it is removed from the atmosphere. The deposition of vapor-phase organic contaminants (e.g., gaseous deposition) is not currently considered in the ISC3 model. The general processes controlling the transfer of particulate from some height above the surface through the surface layer down to the immediate vicinity of the surface are the forces of gravity and turbulent diffusion, followed by diffusion through the laminar sub-layer (defined as a thickness of 10^{-1} to 10^{-2} cm) to the surface (Seinfeld, 1986). The term "deposition flux" is mass concentration of a contaminant sorbed to atmospheric particulates that is delivered to the surface per unit of time by the physical forces of gravity, atmospheric

turbulence, and diffusion (Kapahi, 1991). Deposition flux is represented mathematically by F_d . Note that the parameter F_d in equation 3-5 is synonymous with D_{yd} in equation

| TABLE 3-5 | | | |
|--|---------------|--|-----------|
| Parameters Used to Calculate Pasquill-Gifford σ_z | | | |
| Pasquill Stability Category | x (km) | $\sigma_z(\text{meters}) = ax^b$ (x in km) | |
| | | a | b |
| A ^a | <0.10 | 122.800 | 0.94470 |
| | 0.10 - 0.15 | 158.080 | 1.05420 |
| | 0.16 - 0.20 | 170.220 | 1.09320 |
| | 0.21 - 0.25 | 179.520 | 1.12620 |
| | 0.26 - 0.30 | 217.410 | 1.26440 |
| | 0.31 - 0.40 | 258.890 | 1.40940 |
| | 0.41 - 0.50 | 346.750 | 1.72830 |
| | 0.51 - 3.11 | 453.850 | 2.11660 |
| | >3.11 | <u>b/</u> | <u>b/</u> |
| B ^a | <0.20 | 90.673 | 0.93198 |
| | 0.21 - 0.40 | 98.483 | 0.98332 |
| | >0.40 | 109.300 | 1.09710 |
| C ^a | All | 61.141 | 0.91465 |
| D | <0.30 | 34.459 | 0.86974 |
| | 0.31 - 1.00 | 32.093 | 0.81066 |
| | 1.01 - 3.00 | 32.093 | 0.64403 |
| | 3.01 - 10.00 | 33.504 | 0.60486 |
| | 10.01 - 30.00 | 36.650 | 0.56589 |
| | >30.00 | 44.053 | 0.51179 |

| | | | |
|---|---------------|--------|---------|
| E | <0.10 | 24.260 | 0.83660 |
| | 0.10 - 0.30 | 23.331 | 0.81956 |
| | 0.31 - 1.00 | 21.628 | 0.75660 |
| | 1.01 - 2.00 | 21.628 | 0.63077 |
| | 2.01 - 4.00 | 22.534 | 0.57154 |
| | 4.01 - 10.00 | 24.703 | 0.50527 |
| | 10.01 - 20.00 | 26.970 | 0.46713 |
| | 20.01 - 40.00 | 35.420 | 0.37615 |
| | >40.00 | 47.618 | 0.29592 |

4-2 used in calculating deposition rates. The annual dry deposition flux, F_d , is defined as the product of the ambient air concentration of the chemical contaminant, C_{pa} , sorbed to atmospheric particles times a deposition velocity (ms^{-1}) of the contaminated particles, and adjusted per year as in Equation 3-5.

$$F_d = 0.31536 V_d C_{pa} \quad (3-5)$$

where:

| | | |
|----------|---|---|
| F_d | = | dry deposition flux of contaminants sorbed to particles, $\text{g/m}^2\text{-yr}$ |
| 0.31536 | = | unit conversion factor $[3.1536\text{E}+07 \text{ seconds/year}]/[100 \text{ cm/m}] [10^6 \mu\text{g/g}]$ |
| V_d | = | dry deposition velocity, m/sec |
| C_{pa} | = | particle-bound concentration of contaminant on settling particles, $\mu\text{g/m}^3$ |

In general, Chamberlain and Chadwick (1953) first defined the deposition velocity, V_d , as the quotient of the deposition flux, F_d , divided by the airborne concentration, C_{pa} :

$$V_d = - \frac{F_d}{C_{pa}} \quad (3-6)$$

The value for F_d in Equation 3-6 has a minus sign because the downward flux is negative, whereas the deposition velocity is positive (Sehmel, 1980). By this relationship, Chamberlain and Chadwick (1953) first introduced the concept of plume depletion, i.e., as the emission plume is dispersed with downwind distance from the stack, the deposition flux decreases with distance from the source.

The basic dynamics of the physics of modeling dry deposition have not changed significantly since Sehmel's (1980) comprehensive scientific review. The factors that most influence the predicted deposition flux can be divided as meteorological influences or the influences of the properties of the pollutant under analysis. Meteorological influences include the friction velocity, represented as μ_o , and the aerodynamic surface roughness, represented as z_o . These terms are used to describe the wind speed profile above the Earth's surface. In most cases, the analyst uses a graphical procedure to determine values for μ_o and z_o . If the logarithm of wind speed is plotted for near neutral atmospheric stability as a function of height from the surface, then the values for the constant z_o are fitted to a straight line on a semi-logarithmic scale. This can be described mathematically by Equation 3-7. In most cases, the friction velocity is a percentage of the wind speed.

$$\mu = \left(\frac{\mu^*}{\lambda}\right) \ln \left(\frac{z + z_o}{z_o}\right) \tag{3-7}$$

where:

- μ = measured wind speed, cm/s
- μ^* = the friction velocity, cm/s
- z = the measured height above the surface, cm
- z_o = surface roughness length, cm
- λ = von Karman's constant, approx. = 0.4

As a general rule, particles greater than 30 micrometers (μm) in diameter will be removed from the atmosphere primarily by the force of gravity, whereas particles less than 30 μm will be removed primarily by atmospheric turbulence. The deposition flux for the smaller particles is influenced by many factors, including the distribution of particles by diameter and density, the atmospheric turbulence, the friction of the ground

surface, and the height of the stack release of emissions. Deposition flux is also affected by the partitioning properties of the pollutant. These properties will determine how much of the pollutant is sorbed to the particle and how much is in the vapor phase. A detailed list of the many factors that can affect dry deposition is shown in Table 3-6.

The ISC3 estimates dry deposition flux on the basis of empirical associations developed by Sehmel (1980) and Sehmel and Hodgson (1978) relating the deposition flux to the deposition velocity of particles. The downward motion represented by deposition velocity is controlled by the gravitational settling velocity, atmospheric resistance, surface resistance, and the atmospheric surface friction layer. This model assumes that a fraction of the particulate comes into contact with the ground surface by the combined processes of gravitational settling, atmospheric turbulence, and Brownian diffusion. The ISC3 model contains enhancements to calculate dry deposition flux using a dry deposition model developed by Pleim et al. (1984). The Pleim et al. (1984) algorithms represent Sehmel's (1980) empirical relationships for transfer resistances as a function of particle size, density, surface roughness, and friction velocity. In the Pleim et al. (1984) model, integrated resistances to mass transfer are computed within two layers. In the first layer, which extends from 1 cm to 1m above the surface, atmospheric turbulence dominates mass transfer. This is a fully turbulent region where vertical fluxes are nearly constant, and is referred to as the aerodynamic resistance. In the second layer, which lies within 1 cm of the surface, the resistance to mass transfer is derived from particle deposition measurements that were taken in a wind tunnel over various surfaces using monodispersed particles (Sehmel, 1980; Sehmel and Hodgson, 1978). The general approach used by ISC3 in the resistance methods for estimating the dry deposition velocity of particles is given by Equation 3-8:

$$v_d = \frac{1}{r_a + r_d + I_a I_d I_s} + Vg \quad (3-8)$$

where:

V_d = dry deposition velocity, cm/sec

V_g = gravitational settling velocity, cm/sec

| TABLE 3-6 | | | |
|---|--|---|--|
| Factors That Influence the Dry Deposition Removal Rate in the Atmosphere* | | | |
| Micro-meteorological Variables | Characteristics of Particles | Characteristics of Gases | Surface Variables |
| Aerodynamic roughness Mass transfer of Particles Gases Heat transfer Momentum transfer Atmospheric stability Diffusion Friction velocity Inversion layer Pollutant concentration Relative humidity Seasonal variation Solar radiation Surface heating Temperature Terrain effects Turbulence Wind velocity Zero plane displacement effect | Agglomeration Diameter Diffusion effects Brownian Eddy Electrostatic effects Attraction Repulsion Gravity settling Hygroscopicity Impaction Interception Momentum Physical properties Resuspension Solubility Thermophoresis | Chemical activity Diffusion effects Brownian Eddy Partial pressure in equilibrium with the surface Solubility | Accommodation Exudates Trichomes Pubescence Wax Biotic surface Canopy growth Dormant Expanding Senescent canopy structure Areal density Bark Bole Leaves Porosity Soils Stem Type Electrostatic properties Penetration of canopy |

*Source: Adapted from Sehmel (1980)

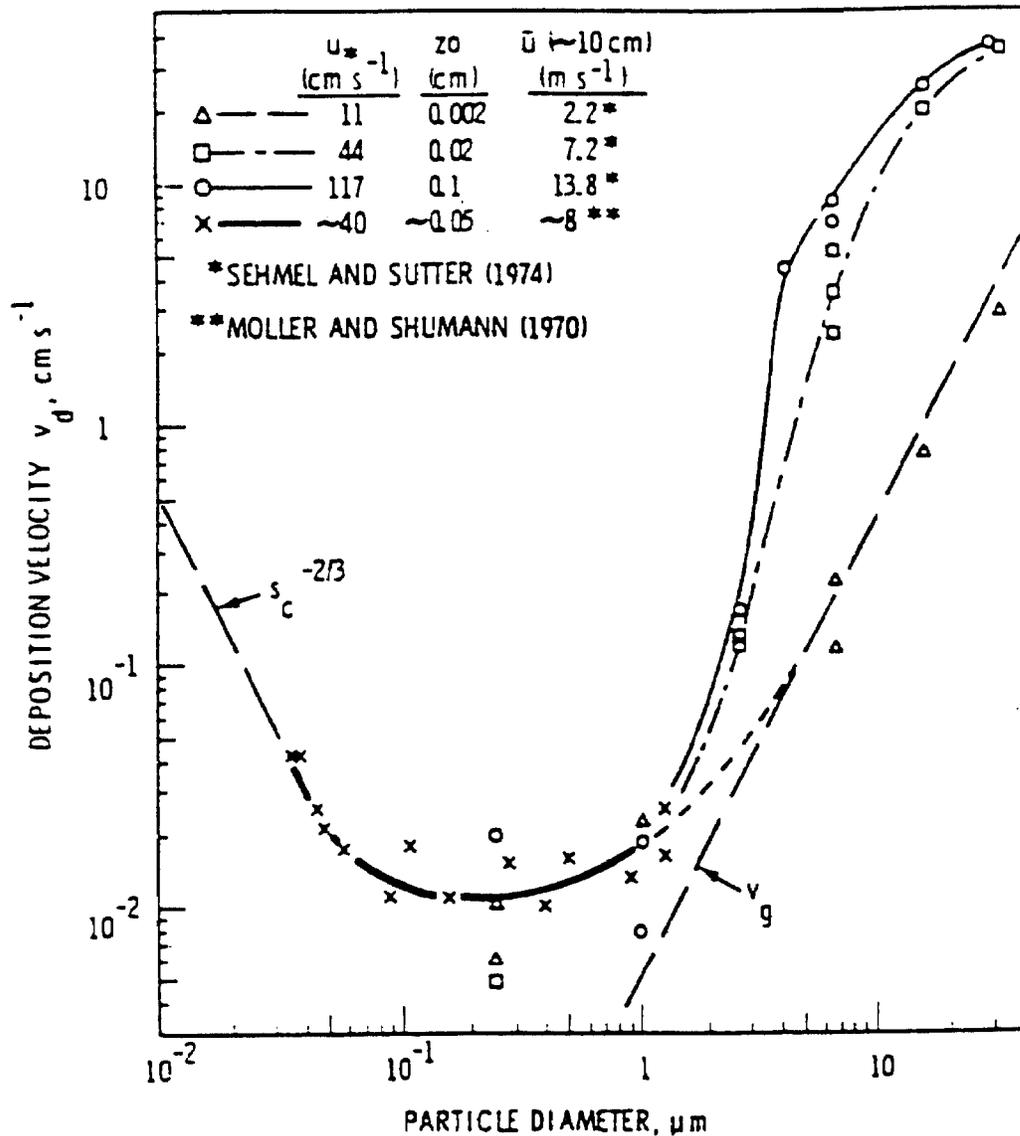
r_a = aerodynamic resistance, sec/cm

r_d = deposition layer resistance, sec/cm

Despite what is currently known about the physical and chemical processes that influence the final deposition flux of particles released from a stationary combustion source, a more thorough understanding of the influence of particle size on deposition velocity is needed. In Sehmel's (1980) review of settling velocities corresponding to particle diameter it was noted that the range of values spanned several orders of magnitude. This complicates efforts to make generalizations of V_d by particle diameter for air modeling purposes. Although dry particle deposition velocities have been estimated from both field studies and laboratory experiments, derived velocities are limited and highly uncertain. This is due largely to the complex and variable array of factors that can influence the rate of deposition (as summarized in Table 3-6). Thus Slinn et al. (1978) has noted the experimentally observed differences in V_d as shown in Figure 3-1.

There are generally two modes in the general definitions of particle size fractions of stack emitted particles: the coarse mode and the fine mode. The coarse mode is defined as the distribution of particles with diameters mostly greater than the minimum in the particle mass distribution, which generally occurs between 1 and 3 μm (U.S. EPA, 1996b; Whitby, 1978). These particles are usually mechanically generated. The fine mode is the distribution of particles with diameters mostly smaller than the minimum in the particle mass distribution, which generally occurs between 1 μm and 3 μm . These particles are usually formed from gases. Over the years the definition proposed by Whitby (1978) has been relaxed, and currently there is no standard definition in the scientific literature (U.S. EPA, 1996b). A more commonly applied definition of the mode distributions is the one used by Sehmel (1980). Sehmel (1980) defines the fine particle mode as consisting of particles <2.5 micrometers (μm) in diameter, and those >2.5 μm are "coarse particles." Sehmel (1980) offers the most current review of dry deposition

Figure 3-1 Observed deposition velocities as a function of particle size for 1.5 g/cm density particles.



Source: Slinn et al. (1978) as adapted from Sehmel and Sutter (1974) and Moller and Shumann (1970)

settling velocities for a variety of depositing materials having a broad range of particle diameters. This summary appears in Table 3-7.

| TABLE 3-7 | | | |
|---|------------------------|--------------------|----------------------------|
| Summary of Dry Deposition Velocities for Particles* | | | |
| Depositing Material | Particle Diameter (μm) | Deposition Surface | Deposition Velocity (cm/s) |
| Particles | 0.03-30 | Grassland | 10 ⁻³ -40 |
| Pollen | 20 32-35 90-100 | Grassland | 4.5 9.9 20 |
| Natural aerosol | 1-10 | Grass shard | 0.8 |
| Pb auto exhaust | | | |

*Source: Sehmel (1980)

3.5.3. The Particle Size Distribution in the Stack Emissions and Estimation of

Contaminant Particle-Bound Emission Rate. A distribution of particle size and the diameter of the particulate stack emissions must be known before the ISC3 program can predict deposition flux of the contaminant. The diameters of small particles comprising particulate matter in stack emissions are usually measured in units of one millionth of a meter (micrometer, commonly called micron, abbreviated by μm).

However, few studies have been conducted that describe the distribution of particulate matter entrained in the emissions from various combustion technologies broken down and fractionated by particle diameter. The characterization of particulate matter by particle diameter will differ from one combustion process to another, and is greatly dependent on such factors as (1) the efficiency of various air pollution control devices in removing particles over a broad range of diameters from the gas stream, (2) the

composition of the feed/fuel, (3) the design of the combustion chamber, (4) the amount of air used to sustain combustion, and (5) the temperature of combustion. Table 3-8 gives an example of a particle diameter distribution as measured at a stack of an incinerator and, when data are lacking, the assessor may resort to this as a default particle size distribution. Also, generalized particle size distributions for specific combustor types and air pollution control systems may be found in Appendix B-1 and B-2 to the *Compilation of Air Pollution Emission Factors* (U.S. EPA, 1995c). These generic distributions have been developed from about 200 stationary source emissions.

| Particle Diameter (am) ^a | Particle Radius (am) | Surface Area/ Volume | Fraction of Total Weight | Proportion Available Surface Area | Fraction of Total Surface Area |
|-------------------------------------|----------------------|----------------------|--------------------------|-----------------------------------|--------------------------------|
| >15.0 | 7.50 | 0.400 | 0.128 | 0.0512 | 0.0149 |
| 12.5 | 6.25 | 0.480 | 0.105 | 0.0504 | 0.0146 |
| 8.1 | 4.05 | 0.741 | 0.104 | 0.0771 | 0.0224 |
| 5.5 | 2.75 | 1.091 | 0.073 | 0.0796 | 0.0231 |
| 3.6 | 1.80 | 1.667 | 0.103 | 0.1717 | 0.0499 |
| 2.0 | 1.00 | 3.000 | 0.105 | 0.3150 | 0.0915 |
| 1.1 | 0.55 | 5.455 | 0.082 | 0.4473 | 0.1290 |
| 0.7 | 0.40 | 7.500 | 0.076 | 0.5700 | 0.1656 |
| <0.7 | 0.40 | 7.500 | 0.224 | 1.6800 | 0.4880 |

Total surface area: $3.4423 \mu\text{m}^2$.

Geometric mean diameter in a distribution. Distribution from U.S. EPA (1980).

Although the ISC3 model can simulate up to 10 particle size categories, the use of generalized distributions warrants using only three particle size categories. For example, the three sizes categories below were generalized from the data in Table 3-8:

- ! Category 1: $\leq 2 \mu\text{m}$
- ! Category 2: > 2 to $\leq 10 \mu\text{m}$
- ! Category 3: $> 10 \mu\text{m}$

After selecting the particle size distribution, it is necessary to calculate the emission rate of the particulate-bound contaminant by particle size category. This may be accomplished in one of two ways: 1) by a surface area weighting approach, and 2) by a mass weighting approach.

3.5.3.1. Surface area weighting approach — The surface area weighting approach assumes that the contaminant adsorbs to the surface of the particles during emissions from the stack. First it is necessary to calculate the proportion of surface area (available for adsorption of the contaminant) for a given particle diameter. With the assumption of an aerodynamic shape to the particle, surface area available to adsorption is determined as the ratio of the surface area to volume in proportion to the ratio of the surface area to weight for a particle with a given radius. Multiplying this proportionality by the weight fraction of particles of a specific diameter (μm) in a particle size distribution gives a value that approximates the amount of surface area available for chemical adsorption. The surface area to volume ratio can be described as follows:

- (a) Assume aerodynamic spherical particles.
- (b) Specific surface area of a spherical particle with radius r :
$$S = 4 \pi r^2$$
- (c) Volume of spherical particle with radius r :
$$V = 4/3 \pi r^3$$
- (d) The ratio of surface area to volume is:
$$S/V = 4 \pi r^2 / (4/3 \pi r^3)$$
$$S/V = 3/r$$

Dividing the surface area for each particle category by the total available surface area for all particles gives an estimation of the fraction of total area on any size particle.

Multiplication of the emission rate of the dioxin-like congener by the fraction of available surface area will estimate the emission rate of the pollutant per particle size.

The fraction of total surface area was computed for the three particle size categories.

The fractions of total surface areas for the ranges of particle diameters are summed with each particle size category to represent a single fraction of total surface area for the given particle size category. For example, if the three particle size categories from Table 3-8 is assumed, then fraction of total surface is calculated to be as follows:

- ! Particulate size category 1: fraction of total surface area = 0.875
- ! Particulate size category 2: fraction of total surface area = 0.095
- ! Particulate size category 3: fraction of total surface area = 0.030

The interpretation of this result is that 87.5% of the emission rate of the contaminant adsorbed to particles is associated with particles ≤ 2 μm in diameter, 9.5% of the emission rate is associated particles size of >2 to ≤ 10 μm , and only 3% of the emission rate is associated with particles >10 μm . To assist in deposition modeling of the particle-bound emissions from a combustor, it is recommended that the particle size distribution be further simplified by assuming a median particle diameter to represent each broad particle size category, as follows:

- ! Particulate category 1 = 1 μm particle diameter
- ! Particulate category 2 = 6.78 μm particle diameter
- ! Particulate category 3 = 20 μm particle diameter

3.5.3.2. Mass weighting approach — The mass weighting approach assumes that the emission rate of the contaminant that is particle bound is proportional to the mass distribution of particles emitted from the stack. This assumes that the contaminant enriches the particles as the particles are formed withing the combustion

system. Under the column heading "Fraction of the Total Weight" to Table 3-8 shows an example of the type of information that is needed to compute the particle bound emission rate of the contaminant by the mass weighting approach. To establish the fraction by mass by particle size requires the measurement of the particle size distribution of total mass emissions of particulate matter from the stack of a particular combustor. This is accomplished with a measurement device attached to the stack such as a cascade impactor. These devices collect and trap particles within segmented compartments that allow for only specific particle diameters to be trapped and retained (U.S. EPA, 1996b). If these specific measurements are not available for the source of interest, then secondary sources of information must be used to estimate the fractional distribution of particles by weight. It is recommended that the distribution in Table 3-8 be used as a default, or the the AP-42 guidance for specific distributions from specific combustors be used (U.S. EPA, 1995c).

In general, the effects on ambient concentrations of gravitational settling and dry deposition can be neglected for gaseous pollutants and small particulates (less than about 0.1 μm in diameter). The vertical term (V) without deposition effects is then given by:

$$\begin{aligned}
 V = & \exp \left[-0.5 \left(\frac{z_r - h_e}{\sigma_z} \right)^2 \right] + \exp \left[-0.5 \left(\frac{z_r + h_e}{\sigma_z} \right)^2 \right] \\
 & + \sum_{i=1}^{\infty} \left\{ \exp \left[-0.5 \left(\frac{H_1}{\sigma_z} \right)^2 \right] + \exp \left[-0.5 \left(\frac{H_2}{\sigma_z} \right)^2 \right] \right. \\
 & \left. + \exp \left[-0.5 \left(\frac{H_3}{\sigma_z} \right)^2 \right] + \exp \left[-0.5 \left(\frac{H_4}{\sigma_z} \right)^2 \right] \right\}
 \end{aligned}
 \tag{3-9}$$

where:

$$h_e = h_s + \Delta h$$

$$\begin{aligned} H_1 &= z_r - (2iz_i - h_e) \\ H_2 &= z_r + (2iz_i - h_e) \\ H_3 &= z_r - (2iz_i + h_e) \\ H_4 &= z_r + (2iz_i + h_e) \\ z_r &= \text{receptor height above ground (flagpole) (m)} \\ z_i &= \text{mixing height (m)} \end{aligned}$$

The infinite series term in Equation 3-9 accounts for the effects of the restriction on vertical plume growth at the top of the mixing layer. The method of image sources accounts for multiple reflections of the plume from the ground surface and at the top of the mixed layer. It should be noted that if the effective stack height, h_e , exceeds the mixing height, z_i , the plume is assumed to fully penetrate the elevated inversion and the ground-level concentration is set equal to zero.

Equation 3-9 assumes that the mixing height in rural and urban areas is known for all stability categories. As explained below, the meteorological preprocessor program uses mixing heights derived from twice-daily mixing heights calculated using the Holzworth (1972) procedures. The ISC models currently assume unlimited vertical mixing under stable conditions, and therefore delete the infinite series term in Equation 3-9 for the E and F stability categories.

The vertical term defined in Equation 3-9 changes the form of the vertical concentration distribution from Gaussian to rectangular (i.e., a uniform concentration within the surface mixing layer) at long downwind distances. Consequently, in order to reduce computational time without a loss of accuracy, Equation 3-9 is changed to the form:

$$V = \frac{\sqrt{2\pi}\sigma_z}{z_i} \tag{3-10}$$

at downwind distances where the σ_z/z_i ratio is ≥ 1.6 (U.S. EPA, 1995b).

3.5.4. Estimation of Wet Deposition Flux. Wet deposition occurs by precipitation (rain, hail, snow) physically washing out the chemically contaminated particulate and vapors from the atmosphere. Vapor scavenging is not yet well understood and is not addressed in the ISC3 model. The remainder of this discussion refers only to the wet deposition of particles.

Wet deposition flux depends primarily on the fraction of the time precipitation occurs and the fraction of material removed by precipitation per unit of time by particle size. Based on these relationships, scavenging coefficients were developed by Jindal and Heinold (1991) for varying types and intensities of precipitation relative to different particle diameters by incorporating the observations of Radke et al. (1980) in a study of scavenging of aerosol particles by precipitation. The principal assumptions made in computing wet deposition flux are: (1) the intensity of precipitation is constant over the entire path between the source and the receptor; (2) the precipitation originates at a level above the top of the emission plume so that the precipitation passes vertically through the entire plume and (3) the flux is computed on the basis of the hour precipitation occurs, as determined by hourly precipitation measurements compiled by the National Weather Service. The remaining fraction is subject only to dry deposition processes. Thus, no dry deposition occurs during hours of steady precipitation, and dry deposition occurs between the periods of precipitation.

Wet deposition flux is estimated by ISC3 using a scavenging ratio approach in which the flux of contaminant to the surface (F_w) is the product of the scavenging ratio times the contaminant concentration, as in the following equation.

$$F_w = 3.1536 \Lambda \chi \tag{3-11}$$

where:

F_w = wet deposition flux, g/m²-year

Λ = scavenging ratio, sec⁻¹

3.1536 = unit conversion factor [3.1536E+07 sec/year]/[10⁻⁶ µg/g]
X = contaminant air concentration value calculated from
Gaussian plume equation, µg/m³

The scavenging ratio (Λ) is calculated as the product of the scavenging coefficient and precipitation rate (Scire et al., 1990), as follows:

$$\Lambda = \lambda * R \quad (3-12)$$

where:

Λ = scavenging ratio, s⁻¹
 λ = scavenging coefficient, (s/mm/h)⁻¹
R = precipitation rate, mm/h

The scavenging coefficient depends on the size distribution for particles and the nature or form of precipitation, i.e., liquid or frozen.

Across the plume, the total flux to the surface must be approximately equal to the mass lost from the plume. ISC3 contains a plume wet deposition depletion equation as follows:

$$Q(x) = Q_0 e^{-\Lambda x/u} = Q_0 e^{-\Lambda t} \quad (3-13)$$

where:

Q(x) = wet plume depletion factor, dimensionless
 Λ = precipitation scavenging ratio, s⁻¹
t = x/u = plume travel time, s

The relationship between the scavenging coefficient, Λ , and the particle size and precipitation intensity was derived from the review of wet deposition studies of aerosol particles by Jindal and Heinold (1991), and is shown in Figure 3-2. Table 3-9 displays the scavenging coefficients assigned to the generalized particle size categories and

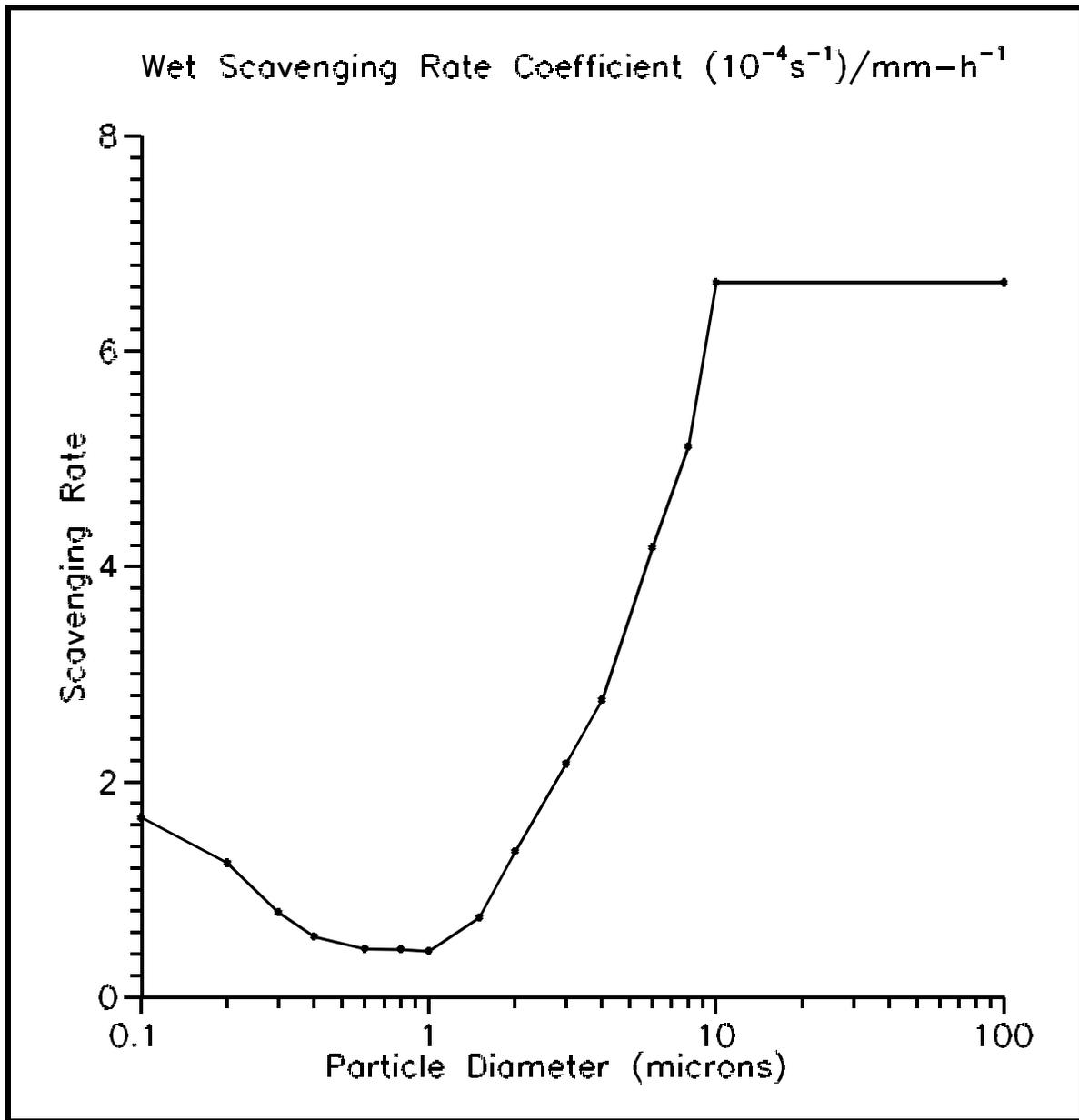


FIGURE 3-2

Wet Scavenging Rate Coefficient as a Function of Particle Size

Source: Jindal and Heinold, 1991

| TABLE 3-9 | | | |
|---|-----------------------|-----------------------|-----------------------|
| Unit Wet Deposition Scavenging Coefficients Per Particle Diameter Category (micrometers) Used In the Example ISC3 Analysis, Expressed as 1/(s/mm/r) | | | |
| Form of Precipitation | | | |
| | 1 | 6.78 | 20 |
| Liquid (rain) | 0.43×10^{-4} | 0.46×10^{-3} | 0.66×10^{-3} |
| Frozen (snow) | 0.14×10^{-4} | 0.16×10^{-3} | 0.22×10^{-3} |

forms of precipitation (liquid rainfall, frozen) used as a default for computing estimates of wet deposition in the application of the ISC3.

3.5.5. Estimation of the Phase Distribution of Semivolatile Organic Emissions. At the point of stack emission and during the atmospheric transport, partitioning of the contaminants occurs between two physical phases: vapor and particle. A vapor-to-particle ratio (V/P) needs to be established for each pollutant of interest. The V/P ratio represents the ratio of the concentration of the pollutant in the vapor phase to the concentration of that pollutant in the particulate phase, usually expressed in terms of percentage with V plus P adding to 100%, e.g., 60% vapor and 40% particle-bound. A relationship first proposed by Junge (1977) in Equation 3-14, and later reviewed and critically evaluated by Pankow (1987) is the most widely used model for estimating the adsorption of semivolatile compounds (e.g., SOCs) to atmospheric aerosol particles:

$$\phi = \frac{c \Theta}{p^{\circ}_L + c \Theta} \tag{3-14}$$

where:

- ϕ = fraction of compound adsorbed to aerosol particles
- p°_L = saturation liquid-phase vapor pressure of pure compound at ambient temperature, Pa
- Θ = particle surface area per unit volume of air, $\text{cm}^2 \text{ aerosol}/\text{cm}^3 \text{ air}$
- c = constant related to difference between heat of desorption from particle surface, Q_d , and heat of vaporization of the compound, Q_v . The value of c is often estimated at 17.2 Pa/cm

Pankow (1987) argued that different values of $Q_d - Q_v$ (and therefore c) may be appropriate for different classes of compounds.

Although Junge (1977) did not specify the physical state of the sorbing compound in Equation 3-14, field and laboratory studies of the particle/gas distribution of PAHs and organochlorine compounds indicate that the process is better described by using the vapor pressure of the subcooled liquid rather than the solid-phase vapor pressure (p°_s) (Bidleman et al., 1986; Cotham and Bidleman, 1992; Foreman and Bidleman, 1987). In Equation 3-15, the two vapor pressures are related by:

$$\ln \frac{p^{\circ}_L}{p^{\circ}_s} = \frac{\Delta S_f (T_m - T)}{RT} \quad (3-15)$$

where:

- p°_L = liquid subcooled vapor pressure of pure compound, Pa
- p°_s = crystalline solid-phase vapor pressure of pure compound, Pa
- ΔS_f = entropy of fusion, J/mol/K
- T_m = melting point of the compound, K
- T = ambient temperature, K
- R = ideal gas constant, 8.314 J/mol/K

Values of ΔS_i have been summarized for PCDD/Fs (Rordorf 1989) and other semivolatile compounds (Hinckley et al., 1990). In the absence of an experimental value, an average $\Delta S_i/R = 6.79$ is often used (Hinckley et al., 1990), and is used in this assessment. Liquid-phase vapor pressures have also been estimated for PCBs, PAHs, PCDD/Fs, and organochlorine pesticides by capillary gas chromatography (Falconer and Bidleman, 1994; Eitzer and Hites, 1988; Eitzer and Hites, 1989; Hinckley et al., 1990; Yamasaki et al., 1984). The hypothesis that p_L^o controls sorption to aerosols is especially significant for PCDD/Fs, as many of these compounds have high melting points and thus large differences between p_L^o and p_S^o .

Estimates of θ are given by Bidleman (1988), based on a study by Whitby (1978) of the size distribution of accumulation-mode aerosols. Whitby also estimated the average total volume of particles per unit volume of air ($V_T = \text{cm}^3 \text{ aerosol}/\text{cm}^3 \text{ air}$). Values of θ and V_T are given in Table 3-10. From V_T and an assumed particle density of $1.4 \text{ g}/\text{cm}^3$, the average TSP concentrations in urban and average background air are 98 and $42 \mu\text{g}/\text{m}^3$. These can be compared to average monitored TSP concentrations of 79 and $30 \mu\text{g}/\text{m}^3$ in 46 U.S. cities and 20 rural locations in 1975 (Shah et al., 1986). Similar calculations using values of θ yield estimates of the aerosol specific surface area (A_{tsp}) of $11 \text{ m}^2/\text{g}$ in urban air and $3.6 \text{ m}^2/\text{g}$ in average background air (Bidleman, 1988). Measurements of A_{tsp} from particles collected on glass fiber filters were 1.9-3.1 m^2/g in Pittsburgh (Corn et al., 1971) and 2.3-8.7 m^2/g in Portland, OR (Sheffield and Pankow, 1994).

The latter authors noted that particles tended to agglomerate to a greater extent on teflon membrane filters than on glass fiber filters, and that experimentally determined specific surface areas were higher on the glass fiber filters. This suggests that values of A_{tsp} measured on filtered particles may be biased on the low side, although more data are needed in this regard.

| TABLE 3-10 | | | |
|---|---|--|--------------------------|
| Values of θ , V_T , and TSP in Different Air Regimes | | | |
| Airshed type | θ cm ² aerosol/cm ³ air | V_T cm ³ aerosol/cm ³ air | TSP μg/m ³ |
| Clean continental background | 4.2*10 ⁻⁷ | 6.5*10 ⁻¹² | 9 |
| Average background | 1.5*10 ⁻⁶ | 3.0*10 ⁻¹¹ | 42 |
| Background plus local sources | 3.5*10 ⁻⁶ | 4.3*10 ⁻¹¹ | 60 |
| Urban | 1.1*10 ⁻⁵ | 7.0*10 ⁻¹¹ | 98 |

Sources: Bidleman (1988) and Whitby (1978)

The particulate fraction can also be expressed by Equation 3-16:

$$\phi = \frac{C_p (TSP)}{C_g + C_p (TSP)} \quad (3-16)$$

where:

- ϕ = fraction of compound adsorbed to aerosol particles
- C_p = concentration of semivolatile compounds associated with aerosols, ng/μg particles
- C_g = gas-phase concentration, ng/m³
- TSP = total suspended particle concentration, μg/m³

Equation 3-16 is a general relationship that applies to any experimental or model estimate of C_g and C_p . Combining Equations 3-14 and 3-16 yields:

$$\text{Log } \frac{C_p}{C_g} = \text{Log } K_p = \text{Log } \frac{c \theta}{TSP} - \text{Log } p^{\circ}_L \quad (3-17)$$

Here and in other work (Falconer et al., 1995; Kamens et al., 1995; Hart and Pankow, 1994; Pankow and Bidleman, 1992) C_p/C_g is referred to as the particle/gas partition coefficient, K_p ($\text{m}^3/\mu\text{g}$). Its inverse, $C_g/C_p = 1/K_p$, has also been used for these correlations (Cotham and Bidleman, 1992). According to Equation 3-17, the expected slope of $\log K_p$ vs. $\log p^{\circ}_L$ is -1 and the intercept is related to the specific surface area of the aerosol A_{tsp} (m^2/g) = $10^8\theta/TSP$. Plots of $\log K_p$ vs. $\log p^{\circ}_L$ for partitioning data obtained with filtration air samplers are usually well correlated and follow the general relationship as expressed in Equation 3-18:

$$\text{Log } K_p = m \text{Log } p^{\circ}_L + b \quad (3-18)$$

It is often the case that $m \neq -1$ because of kinetic limitations and/or sampling artifacts. In these situations the intercept b is partially dependent on the slope and cannot be used to estimate θ (Pankow and Bidleman, 1992).

3.5.6. Recommendations for Regulatory Use. ISC3 is considered appropriate for the following applications:

- ! Industrial source complexes;
- ! Rural or urban areas;
- ! Flat or rolling terrain;
- ! Transport distances less than 50 km;
- ! 1-hour to annual averaging times; and
- ! Continuous toxic air emissions.

ISC3 contains a regulatory default feature that controls the selection of modeling options. When this feature is selected, ISC3 will implement the following regulatory options:

- ! Use stack-tip downwash (except for Schulman-Scire downwash);
- ! Use buoyancy-induced dispersion (except for Schulman-Scire downwash);
- ! Do not use gradual plume rise (except for building downwash);
- ! Use calm processing routines;
- ! Use upper-bound concentration estimates for sources influenced by building downwash from super-squat buildings;
- ! Use default wind profile exponents; and
- ! Use default vertical potential temperature gradients.

3.5.7. Dispersion Parameters. The ISCST3 model uses the steady-state Gaussian plume equation for a continuous elevated source. For each source and each hour, the origin of the source's coordinate system is placed at the ground surface at the base of the stack. The x axis is positive in the downwind direction, the y axis is crosswind (normal) to the x axis, and the z axis extends vertically. The fixed receptor locations are converted to each source's coordinate system for each hourly concentration calculation. The hourly concentrations calculated for each source at each receptor are summed to obtain the total concentration produced at each receptor by the combined source emissions.

3.5.8. Treatment of Terrain. Before modeling, the physical geography within 50 km of the combustor location needs to be systematically examined. This examination should include surrounding terrain elevation and the dimensions of structures that may impact dispersion of the plume. Sources of these data may include detailed maps (such as those provided by the U.S. Geologic Survey), aerial photographs, other survey information, and architectural plans of nearby buildings.

ISCST3 incorporates the COMPLEX1 screening model dispersion algorithms for complex terrain, i.e., where the terrain elevation is above the top of the source's lowest stack. Terrain below the top of the stack is termed simple terrain. The user has the option of specifying only simple terrain (i.e., ISCST) calculations, only complex terrain (i.e., COMPLEX1) calculations, or of using both simple and complex terrain algorithms. In the latter case, the model will select the higher estimate of the simple and complex terrain calculations on an hour-by-hour, source-by-source and receptor-by-receptor basis for receptors in intermediate terrain, i.e., terrain between the lowest stack tip and the base of the stack.

If no terrain is specified, the default is simple terrain. If the user wishes to model receptors on elevated terrain, then the TERRHGTS keyword must be included on the CO pathway. This keyword, which is described in more detail in Section 3.2.3. of the ISC3 User's Manual, accepts one of two possible secondary keywords, either FLAT or ELEV. ISCLT3 does not include any complex terrain algorithms.

The user can input elevated receptor heights in order to model the effects of terrain above (or below) stack base, and may also specify receptor elevations above ground level to model flagpole receptors. For simple terrain calculations, any terrain heights input above the release height for a particular source are "chopped off" at the release height for that source's calculations.

In the ISC short-term model, intermediate terrain is defined as terrain that exceeds the height of the release but is below the plume centerline height. The plume centerline height that defines whether a given receptor is on intermediate terrain is the distance-dependent plume height calculated for the complex terrain algorithm, before the terrain adjustment (Section 1.5.6.2. of the User's Manual) is applied. If the plume height is equal to or exceeds the terrain height, then that receptor is defined as complex terrain for that hour and that source, and the concentration is based on the complex terrain screening algorithm only. If the terrain height is below the plume height but exceeds the physical release height, then that receptor is defined as intermediate terrain for that hour and source. For intermediate terrain receptors, concentrations

from both the simple terrain algorithm and the complex terrain algorithm are obtained and the higher of the two concentrations is used for that hour and that source. If the terrain height is less than or equal to the physical release height, then that receptor is defined as simple terrain, and the concentration is based on the simple terrain algorithm only. For deposition calculations, the intermediate terrain analysis is first applied to the concentrations at a given receptor, and the algorithm (simple or complex) that gives the highest concentration at that receptor is used to calculate the deposition value. Figure 3-3 illustrates the typical behavior of combustor emission plumes in elevated terrain.

3.5.9. Stack-Tip Downwash. Stack tip downwash generally occurs with poorly constructed stacks or when the ratio of the stack exit velocity to wind speed is small. An algorithm developed by Briggs (Hanna et al., 1982) is recommended for this situation and is found in the point source preferred models. In order to consider stack-tip downwash, modification of the physical stack height is performed following Briggs (1975). The modified physical stack height h_s' is found from:

$$h_s' = h_s + 2d_s \left[\frac{v_s}{u_s} - 1.5 \right] \quad \text{for } v_s < 1.5u_s$$

or

$$h_s' = h_s \quad \text{for } v_s \geq 1.5u_s \quad (3-19)$$

where h_s is physical stack height (m), v_s is stack gas exit velocity (m/s), and d_s is inside stack top diameter (m). This h_s' is used throughout the remainder of the plume height computation. If stack tip downwash is not considered, $h_s' = h_s$.

3.5.10. Transitional/Final Rise. The plume rise methods of Briggs (1975) and Hanna et al. (1982) are incorporated in the preferred models and are recommended for use in all modeling applications. No provisions are made in these models for fumigation,

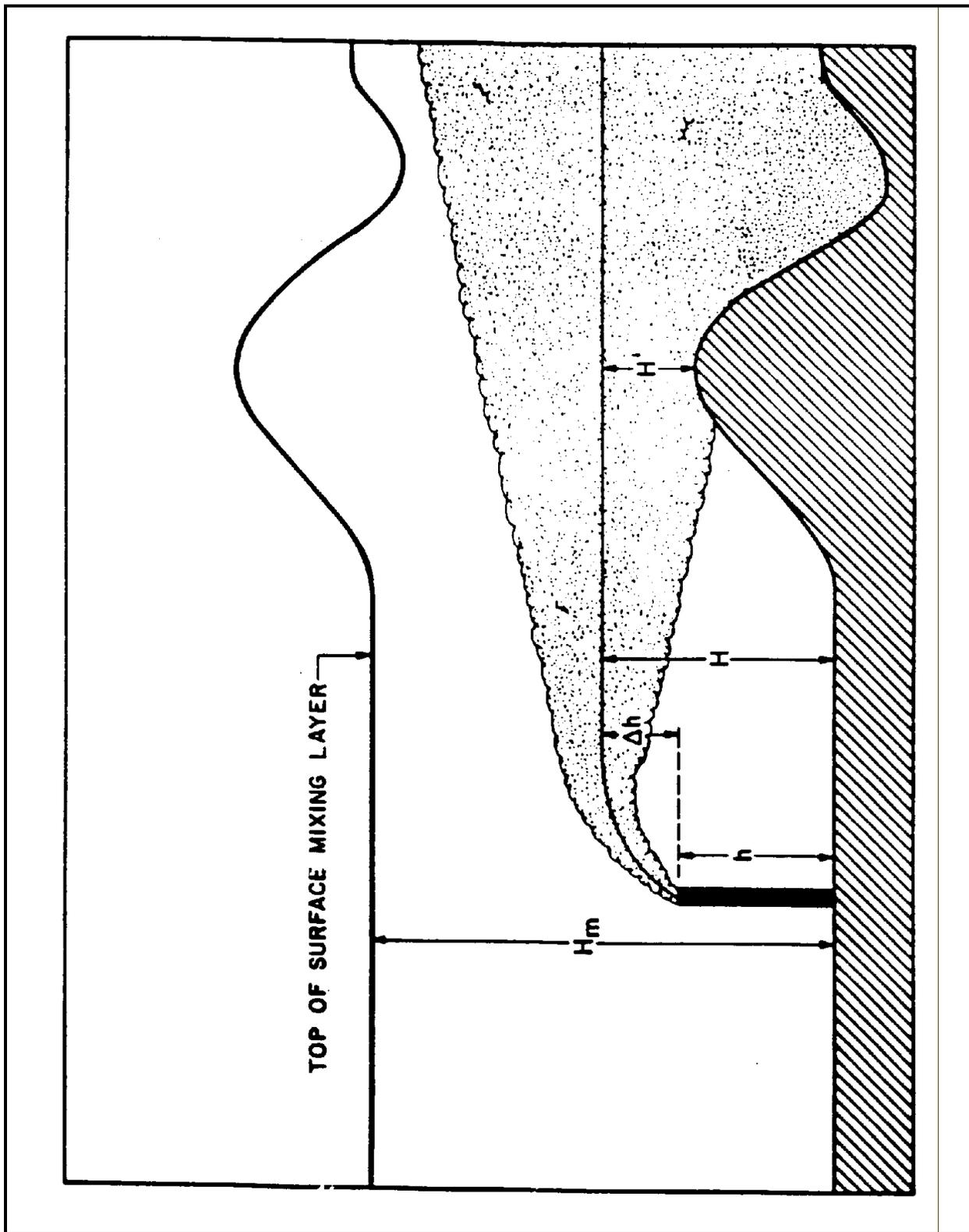


FIGURE 3-3. Illustration of Plume Behavior in Elevated Terrain Assumed by the ISC3 Model.

multistack plume rise enhancement, or the handling of such special plumes as flares; these problems should be considered on a case-by-case basis.

Because there is insufficient information to identify and quantify dispersion during the transitional plume rise period, gradual plume rise is not generally recommended for use. There are two exceptions: in complex terrain screening procedures to determine close-in impacts, or when calculating the effects of building wakes. The building wake algorithm in the ISC model incorporates and automatically (i.e., internally) exercises the gradual plume rise calculations. If the building wake is calculated to affect the plume for any hour, gradual plume rise is also used in downwind dispersion calculations to the distance of final plume rise, after which final plume rise is used. In general, the wind speed used in determining plume rise is defined as the wind speed at stack top.

3.5.11. Buoyancy Induced Dispersion. Buoyancy-induced dispersion (BID), as identified by Pasquill, is included in the preferred models and should be used where buoyant sources, e.g., those involving fuel combustion, are involved. For most plume rise situations, the value of the Briggs buoyancy flux parameter, F_b (m^4/s^3), is needed. The following equation is equivalent to Equation 12, (Briggs, 1975):

$$F_b = g v_s d_s^2 \left(\frac{\Delta T}{4 T_s} \right) \quad (3-20)$$

where:

$$\begin{aligned} \Delta T &= T_s - T_a \\ T_s &= \text{stack gas temperature (K)} \\ T_a &= \text{ambient air temperature (K)} \end{aligned}$$

For determining plume rise due to the momentum of the plume, the momentum flux parameter, F_m (m^4/s^2), is calculated based on Equation 3-21:

$$F_m = v_s^2 d_s^2 \frac{T_a}{4T_s} \quad (3-21)$$

3.5.12. Calms Processing. ISC uses CALMPRO (U.S. EPA, 1984), a post-processor computer program coded to follow U.S. EPA recommendations. This program disregards hourly concentrations calculated under calm conditions (<1 m/s wind speed). Critical concentrations for 3-, 8- and 24-hour averages are calculated by dividing the sum of the hourly concentration for the period by the number of valid hours. If the total number of valid hours is less than 18 for 24-hour averages, less than 6 for 8-hour averages or less than 3 for 3-hour averages, the total concentration is divided by 18 for the 24-hour average, 6 for the 8-hour average, and 3 for the 3-hour average. For annual averages, the sum of all valid hourly concentrations is divided by the number of non-calm hours during the year.

3.5.13. Building Wake Effects. The procedures used by the ISC models to account for the effects of the aerodynamic wakes and eddies produced by plant buildings and structures on plume dispersion originally followed the suggestions of Huber and Snyder (1976). The data used by Huber and Snyder reflect only a specific stability, building shape, and building orientation with respect to the mean wind direction. To account for this, ISC models also provide for the revised treatment of building wake effects for certain sources, which use modified plume rise algorithms following the suggestions of Schulman and Hanna (1986). When the stack height is less than the building height plus half the lesser of the building height or width, the methods of Schulman and Scire are followed. Otherwise, the methods of Huber and Snyder are followed. In the ISC models, direction-specific building dimensions may be used with either the Huber-Snyder or Schulman-Scire downwash algorithms.

3.6. MODEL PARAMETER REQUIREMENTS

ISC3 requires four different kinds of inputs: control, source, meteorological, and receptor. Most input requirements are identical for both the short-term and long-term

models. In some cases the short-term model requires additional inputs, and this is noted in the text.

3.6.1. Control Inputs. Control inputs are required to specify which options the model is going to use to evaluate the specific case. Dispersion options, averaging time options, pollutant type, exponential decay options, terrain options, and elevated receptor options all require specification. The regulatory default option is also a control input, and when it is selected the model uses all of the standard regulatory defaults.

3.6.1.1. Land Use for Dispersion Coefficients — The selection of either rural or urban dispersion coefficients in a specific application should follow one of the procedures briefly described below. These include a land-use classification procedure or a population-based procedure to determine whether the character of an area is primarily urban or rural.

Of the two methods, the land-use procedure is considered more definitive. Population density should be used with caution and should not be applied to highly industrialized areas where the population density may be low and thus a rural classification would be indicated, but the area is sufficiently built up so that the urban land-use criteria would be satisfied. In this case, the classification should already be “urban” and urban dispersion parameters should be used.

The land-use method of Auer (1978) is described in the Guideline on Air Quality Models (U.S. EPA, 1997). This method can be used to specify appropriate dispersion coefficients for use with ISCST3. Land use is categorized as “rural” or “urban.” Areas typically defined as rural include residences and estates with grass lawns and trees, metropolitan parks and golf courses, agricultural areas, undeveloped land, and water surfaces. If an area has less than 35% vegetative cover or can be described as predominantly industrial/ commercial or dense single or multifamily homes, then for air modeling purposes it is considered urban. Although geographic information systems and other land-use databases may be used, visual inspection of the area around the combustor is also acceptable.

The determination of the rural or urban classification (i.e., the Auer method) involves the following five steps:

Step 1 Locate the facility on a 7.5 minute topographical relief map. Site map. Draw a circumference with a radius of 3 km around the center the stack.

Step 2 Determine from the surface features and land uses identified on the map whether the area within the radius is rural or urban. This is according to Aurer's definitions that less than 35% of vegetative cover is urban and greater than 35% vegetative cover is rural.

Step 3 Classify smaller areas within the 3 km radius as either rural or urban based on Auer's definition of rural/urban based on vegetative cover of the surface area. For this exercise, a grided overlay may be used within the radius, for example, a square grid 100 m by 100 m. Each grid square should be identified as either rural or urban.

Step 4 Count the number of squares that have been identified as rural. If more than 50% of the total squares are rural, the area is rural, and if less than 50% of the total number of squares are rural, then the area is urban.

Step 5 If the area within the 3 km radius of the stack(s) has been determined to be urban, then further subclassification of urban land use types can be made using the definitions in Table 3-11.

| Type Code | Use and Structures | Vegetative Cover |
|-----------|---------------------------------------|------------------|
| 11 | Heavy industrial | <5% |
| 12 | Light/moderate industrial | <5% |
| C1 | Commercial | <15% |
| R2 | Dense single/multi-family residential | <30% |
| R3 | Multi-family, two-story residential | <35% |

*Source: U.S. EPA, 1997

3.6.1.2. Terrain — There are three general classifications of terrain: simple, intermediate, and complex. Simple terrain is an area in which terrain features are all lower in elevation than the top of the source(s). Terrain between release height and plume height is intermediate terrain. Complex terrain is an environment wherein the receptor elevation is above the release height of the source.

Placement of receptors requires very careful attention when complex terrain is modeled. Often the highest concentrations are predicted to occur under very stable conditions, when the plume is near, or impinges on, the terrain. The plume under such conditions may be quite narrow in the vertical, so that even relatively small changes in a receptor's location may substantially affect the predicted concentration (U.S. EPA, 1996a). Receptors within about a kilometer of the source may be even more sensitive to location. Thus, a dense array of receptors may be required in some cases. In order to avoid excessively large computer runs due to such a large array of receptors, it is often desirable to model the area twice. The first model run would use a moderate number of receptors carefully located over the area of interest. The second run would use a more dense array of receptors in areas showing potential for high concentrations, as indicated by the results of the first run.

The ISC complex terrain algorithm makes the following assumptions about plume behavior in complex terrain (U.S. EPA, 1995b):

- ! The plume axis remains at the plume stabilization height above mean sea level as it passes over complex terrain for stable conditions (categories E and F), and uses a “half-height” correction factor for unstable and neutral conditions (categories A-D).

- ! The plume centerline height is never less than 10 m above the ground level in complex terrain.

- ! The mixing height is terrain following, i.e, the mixing height above ground at the receptor location is assumed to be the same as the height above ground at the source location.

- ! The lateral (crosswind) distribution of concentrations is uniform across a 22.5-degree sector.

- ! The attenuation correction factor has a value of unity for receptors located at or below the elevation of the plume centerline in free air prior to encountering terrain effects, and decreases linearly with increasing height of the receptor above plume level to a value of zero for receptors located at least 400 m above the undisturbed plume centerline height.

3.6.2. Source Inputs. ISC3 requires the completion of two different cards with source input data. The first, the location card, requires a source identification, the source type (point, area, volume, or open pit), and the Cartesian coordinates of the source. The second card specifies the release source parameters and is dependent on the source type that was selected in the location card. Each source type requires certain parameters to define the source. For example, if a point source is selected as the source type, the required inputs are emission rate, release height, exit temperature, exit velocity, and stack diameter.

In addition to these required cards, several other parameters about the source can be specified. The models allow specification of parameters for building downwash, variable emission rates, and settling-removal-deposition. The short-term model also allows parameter specification for precipitation scavenging and wet deposition.

Sources with multiple smokestacks require additional analysis. If the critical stack parameters such as exit gas velocity, stack height, and emitted pollutant concentrations are the same for each stack, the results of the ISC3 modeling for the emissions from an individual stack can be modified to account for the other stacks. If a source has multiple stacks, each with different stack parameter values and pollutant emission rates, then each stack should be modeled separately with ISCST3. The results of the individual stacks can then be added at each receptor to estimate the total predicted concentrations and deposition from the source.

3.6.3. Meteorological Inputs. The short-term ISC3 model requires hourly meteorological data as one of its basic inputs. The program has several options to

specify the file format. Parameters required include hourly stability class, wind direction, wind speed, temperature, and mixing height. The long-term model uses a standard stability array meteorological data file in place of the sequential hourly meteorological data file. From this file stability wind rose, average afternoon mixing height, average morning mixing height, and average air temperature are required.

Meteorological data should be selected on the basis of spatial and climatological (temporal) representativeness as well as the ability of the individual parameters selected to characterize the transport and dispersion conditions in the area of concern. The representativeness of the data is dependent on (1) the proximity of the meteorological monitoring site to the area under consideration, (2) the complexity of the topography, (3) the exposure of the meteorological monitoring site, and (4) the period of time during which data are collected. The spatial representativeness of the data can be adversely affected by large distances between the source and receptors of interest and the complex topographic characteristics of the area. Temporal representativeness is a function of the year-to-year variations in weather conditions.

Five years of representative meteorological data should be used when estimating concentrations with an air quality model. Consecutive years from the most recent, readily available 5-year period are preferred. The meteorological data may be data collected either on-site or at the nearest National Weather Service (NWS) station. If the source is large, e.g., a 500 MW power plant, the use of 5 years of NWS meteorological data or at least 1 year of site-specific data is required. Local universities, Federal Aviation Administration (FAA), military stations, industry and pollution control agencies may also be sources of such data.

Meteorological data and building dimension data to be used by ISCST3 must be in the proper format for this model to run. Manipulation of these large data files is typically accomplished through preprocessing programs. Two programs are commonly used: PCRAMMET and BPIP. PCRAMMET (Personal Computer Version of the Meteorological Preprocessor for the old RAM program) prepares meteorological data for use with the ISCST3 model by organizing the data so that it can be input to the

model. See the PCRAMMET User's Guide (U.S. EPA, 1995b). The Building Profile Input Program (BPIP) calculates the maximum crosswind widths of buildings, which the air model uses to predict effects on dispersion. This is typically termed building downwash or wake effects (U.S. EPA, 1995b).

3.6.3.1. Wind Direction and Speed — Wind carries pollutants to receptors around the source. The direction and speed of the wind determines where pollutants will be transported, as well as the concentration being transported. Wind direction and speed vary with time and are often given in the form of a wind rose as shown in Figure 3-4. The type of wind direction and speed information (e.g., hourly vs. average) required depends of the level of accuracy needed in the results.

3.6.3.2. Stability — In general, higher turbulence results in lower air concentrations occurring over a greater distance. The amount of turbulence is quantified in terms of the atmospheric stability. A stable atmosphere suppresses vertical motions and increases air concentration. Atmospheric turbulence is difficult and expensive to measure, and it is usually estimated from other, more easily measurable quantities. In particular, the stability of the atmosphere is typically characterized by the atmosphere's vertical temperature profile or lapse rate.

For an isolated parcel of air in which no heat is transferred in or out (adiabatic), one can show using the first law of thermodynamics and the hydrostatic equation that there is a 1°C decrease for every 100-m increase in altitude, and a 1°C increase for every 100-m decrease. This is called the adiabatic lapse rate.

In most cases, the actual environmental lapse rate is not the same as the adiabatic lapse rate because it is both heated and cooled. The three broad classes of stability and their associated lapse rates are summarized in Table 3-12.

It should be noted that any time the temperature increases with altitude, the atmospheric condition is termed an inversion. Under these conditions, vertical motion is minor and pollutant concentrations may be more dense.

The most widely used scheme of atmospheric stability classification was developed by Pasquill (1961) and modified by Gifford (1976). In this scheme, there are six stability classes, denoted with the letters A through F. In general, classes A through

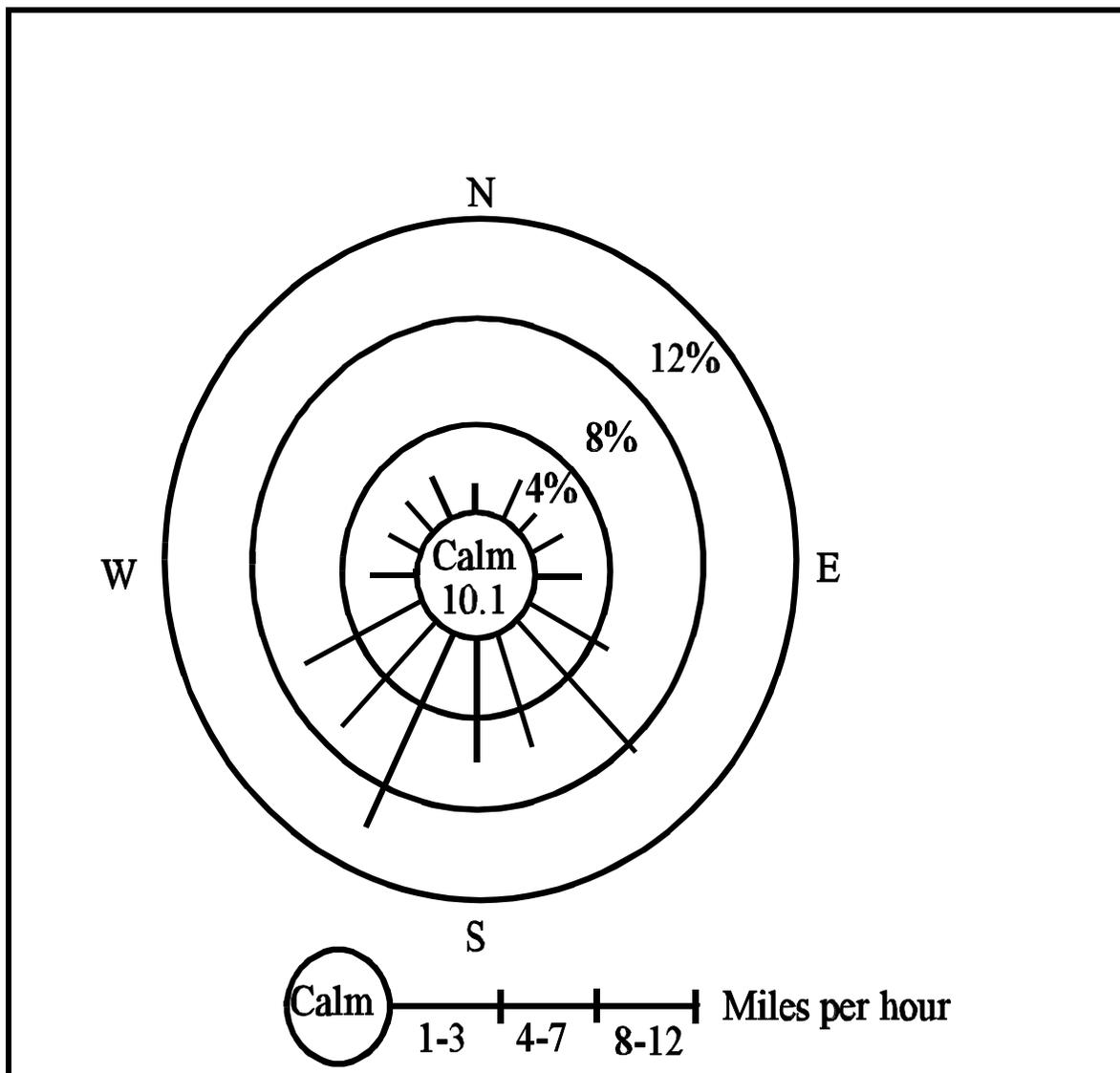


FIGURE 3-4

Hypothetical Wind Rose

C indicate unstable conditions, D is roughly neutral, and classes E and F represent stable conditions. The meteorological conditions that are used to

determine the stability class are shown in Table 3-13.

From this table, it can be seen that extremely unstable conditions (class A) occur during the day, with light winds and moderate to strong solar radiation. Conversely, extremely stable conditions can occur only at night with clear skies and light winds.

Other stability classification schemes exist. For example, Smith (1951) proposed a classification scheme that is based on wind direction, and Cramer (1957) advocated a method based on observed wind fluctuations at a height of 10 m (often referred to as the Brookhaven National Laboratory, or BNL, stability classes). In addition, Irwin (1979) proposed a method of allowing for a continuum of stability, as opposed to a discrete approach such as the Pasquill method. Use of the Pasquill letter classes is common because of their ease of use, and because they have produced satisfactory results.

3.6.3.3. Atmospheric Temperature — The greater the difference between the atmospheric temperature and the stack gas temperature, the higher the plume rise.

The atmospheric temperature input depends upon the model used and the situation the model is to represent. For example, certain models require the input of hourly temperature. Others require the input of an average temperature. This temperature is used to model contaminant movement over the lifetime of the source and should therefore represent the average temperature over this lifetime.

3.6.3.4. Mixing Height — Mixing height is the depth through which atmospheric pollutants are typically mixed by dispersion processes. It is affected by the surface characteristics around the source as well as by meteorological parameters. The greater the mixing height, the larger the volume of atmosphere available to dilute the pollutant concentration. It should be noted that if the effective stack height exceeds the mixing height the plume is assumed to fully penetrate the elevated inversion and the ground-level concentration is set equal to zero.

| TABLE 3-12 | | |
|---|-------------------------------|--------------------|
| Classes of Atmospheric Stability and Associated Vertical Temperature Distribution | | |
| Environmental Lapse Rate | General Result | Class of Stability |
| Increases with height, or decreases less rapidly than adiabatic lapse rate | Vertical motions inhibited | Stable |
| Nearly identical with adiabatic rate | No significant buoyant forces | Neutral |
| Decreases with height faster than adiabatic lapse rate | Vertical motions enhanced | Unstable |

| TABLE 3-13 | | | | | |
|---|--------------------------------------|----------|--------|----------------------|--------------|
| Meteorological Conditions Defining Pasquill Turbulence Types ^a | | | | | |
| Surface wind speed (m/sec) | Daytime Solar Radiation ^b | | | Nighttime Conditions | |
| | Strong | Moderate | Slight | Mostly Overcast | Mostly Clear |
| <2 | A | A-B | B | | |
| 2-3 | A-B | B | C | E | F |
| 3-4 | B | B-C | C | D | E |
| 4-6 | C | C-D | D | D | D |
| >6 | C | D | D | D | D |

^aSource: Gifford, 1976

^bA, extremely unstable; B, moderately unstable; C, slightly unstable; D, neutral (applicable to heavy overcast day or night); E, slightly stable; F, moderately stable; (for A-B take average of values for A and B, etc.)

3.6.4. Receptor Inputs. Receptor coordinates are required for each receptor, and these may be input in either a Cartesian or polar format. In addition to the coordinates, the receptor can have a height specified if there is elevated terrain or if the receptor is modeled as a flagpole receptor.

3.6.4.1. Receptor Locations — Receptors are located at some fixed distance from the source. Locations may be sectors within a grid surrounding the source or at some specified location from the source in a given direction. If complex terrain is involved, receptors may be at a given distance above stack height as well.

Typical receptor locations are:

- ! The boundary of the installation
- ! The closest actual dwelling downwind of the source
- ! Areas of agricultural development
- ! Sensitive locations such as schools, playgrounds, and hospitals
- ! Watershed area and water body surface area
- ! Wildlife refuges and nature preserves

In addition, estimates of the concentration and deposition rates and the resulting concentrations in other media and biota at the location of maximum concentration should be included.

3.6.4.2. Surface Roughness Height — The surface roughness height (also referred to as the roughness length) is the height above the ground (meters) at which the wind speed theoretically goes to zero. Urban and rural land uses as well as types of vegetation covering the surface will cause the momentum of the wind to change as a result of friction. This loss of wind speed induced by the friction along the features on the surface primarily effects the deposition velocity of settling atmospheric particles. On the basis of the surface roughness height, the ISC3 model allows a particle to impact the terrain at a point near the surface of the terrain. The difference (typically in meters) between the point of particle impact and the surface of the terrain is defined as

the surface roughness height. It marks the point of departure of the particle from the ambient air patterns to the “captured” area of deposition.

Surface roughness height is determined by individual components of the landscape and may vary with the season of the year. Default surface roughness heights are presented in Table 3-14.

| Land Use Type | Spring | Summer | Autumn | Winter |
|-------------------|--------|--------|--------|--------|
| Water surface | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| Deciduous forest | 1.00 | 1.30 | 0.80 | 0.50 |
| Coniferous forest | 1.30 | 1.30 | 1.30 | 1.30 |
| Swamp | 0.20 | 0.20 | 0.20 | 0.05 |
| Cultivated land | 0.03 | 0.20 | 0.05 | 0.01 |
| Grassland | 0.05 | 0.10 | 0.01 | 0.001 |
| Urban | 1.00 | 1.00 | 1.00 | 1.00 |
| Desert shrub land | 0.30 | 0.30 | 0.30 | 0.15 |

*Source: Sheih et al., 1979

Typically, professional judgment is combined with aerial survey or physical site inspection to determine land use and the corresponding surface roughness. For some sites an average or “composite” surface roughness is utilized, based on a combination of two or more land use types present in the modeling domain.

3.7. OUTPUT

Printed output options include:

- ! Program control parameters, source data, and receptor data;
- ! Tables of hourly meteorological data for each specified day;
- ! "N"-day average concentration or total deposition calculated at each receptor for any desired source combinations;
- ! Concentration or deposition values calculated for any desired source combinations at all receptors for any specified day or time period within the day; and
- ! Tables of highest and second highest concentration or deposition values calculated at each receptor for each specified time period during a(n) "N"-day period for any desired source combinations, and tables of the maximum 50 concentration or deposition values calculated for any desired source combinations for each specified time period.

Model outputs include both pollutant concentration and wet and dry atmospheric deposition over a given receptor area. These include:

- ! Highest 1-, 3-, and 24-hour average concentrations at each receptor,
- ! Deposition values calculated for any desired source combinations at all receptors for any specified day or time period within the day, and
- ! Limited individual source contribution list

3.8. ISC3 MODEL APPLICATIONS

In short-term ISC3 model, the user may select any or all of the output types, e.g., air concentration, wet deposition, dry deposition, and combined wet and dry deposition, to be generated in a single model run. Instructions for this appear in the User's Guide for ISC3 (U.S. EPA, 1995a). To facilitate the modeling exercise, the modeler should assume a "unit emissions release rate" of the contaminant from the stack, e.g., 1 gram contaminant per second (1 g/s). Results from these unit runs can easily be transformed to final outputs given assumptions on contaminant emissions in vapor and particle forms. Two assumptions are required. One assumption is the total emission

rate of the compound, in units of mass/time (g/s), and the second is the vapor/particle partitioning of this total emission. The two modes are:

Mode 1. To estimate vapor-phase concentration of the contaminant in ambient air. The first mode assumes that the emissions of the contaminant of interest are gaseous, e.g., with the wet/dry deposition switches turned to the “off” position. This is to isolate the ambient air concentration of the contaminant in vapor phase from the calculation of wet and dry particle deposition flux. This inactivates a plume depletion equation that subtracts out losses in ambient air concentration due to particle deposition. What remains is the Gaussian dispersion algorithm to calculate ambient air concentrations.

With the “unitized” emission rate, one can reconstruct the actual predicted ambient air concentration ($\mu\text{g}/\text{m}^3$) of vapors by multiplying the “actual” vapor-phase emission rate (g/s) by the “unitized” modeling result. For example, let the actual stack gas emission rate of total (vapor plus particle components) contaminant be 1×10^{-5} g/s, and the V/P ratio (expected under ambient conditions) be 60%V/40%P. Then the “actual” emission rate of the vapor-phase portion of the contaminant is calculated to be 6×10^{-6} g/s (1×10^{-5} g/s * 0.6). If the “unitized” ambient air concentration at the ground-level receptor is estimated by the ISC3 model to be 1×10^{-8} $\mu\text{g}/\text{m}^3$ (i.e., this concentration is predicted with a unit emission rate of 1 g/s), then the “actual” predicted air concentration at that receptor can be estimated as:

$$(6 \times 10^{-6} \text{ g/s} \div 1 \text{ g/s}) * 1 \times 10^{-8} \mu\text{g}/\text{m}^3 = 6 \times 10^{-14} \mu\text{g}/\text{m}^3 \quad (3-22)$$

Mode 2. To estimate wet and dry particle deposition flux, and the ambient air concentration of the contaminant that is particle-bound. ISC3 should be run with the wet/dry particle deposition switches turned to the “on” position, and using a “unit emission rate” of 1 g/s. This second run is considered a simulation of particle-

bound contaminant only. Outputs of this run include unitized deposition rate and unitized ambient air concentrations of particles.

Like the vapor-phase run, the “actual” deposition flux ($\text{g}/\text{m}^2/\text{yr}$) and “actual” particle-phase airborne concentrations can then be determined by multiplying the “actual” emission rate (g/s) of the particle-bound portion of the total contaminant emissions by the “unitized” modeling result at the ground receptor. For example, let the “actual” emission rate of the particle-bound portion of the contaminant be $4 \times 10^{-6} \text{ g}/\text{s}$, and the “unitized” dry deposition flux at the ground receptor be $1 \times 10^{-5} \text{ g}/\text{m}^2\text{-yr}$. Then the “actual” predicted dry deposition flux is $4 \times 10^{-11} \text{ g}/\text{m}^2$ ($4 \times 10^{-6} \text{ g}/\text{s} \div 1 \text{ g}/\text{s} * 1 \times 10^{-5} \text{ g}/\text{m}^2/\text{yr}$). Using this same procedure, this second run provides the airborne concentration of contaminants bound to particles ($\mu\text{g}/\text{m}^3$).

There are two meteorological preprocessors used by the ISC3 model program to access local conditions necessary to compute model concentrations in both modes of operation: PCRAMMET (Catalano et al., 1987) and MPRM (Irwin and Paumier, 1990). These files contain hourly data for the wind speed, wind direction, stability class, mixing height, ambient air temperature, precipitation, and surface friction velocity.

Inhalation exposures are estimated as the sum of vapor- and particle-phase concentrations. Air-to-plant transfers require the vapor-phase concentrations for vapor transfers and the particle-phase depositions. The air-to-soil algorithm requires particle-phase depositions.

3.8.1. Calculation of Amount Deposited. For some assessments involving carcinogens and for estimation of mass balance, estimates of the total amount of an emitted pollutant deposited within a 50-km radius may be needed. The total amount of a pollutant deposited within a given annular region surrounding a facility is calculated as the average of two methods, the difference between the two methods being the interpolation scheme used to estimate deposition at unmodeled locations. For a given number of radii r_1, \dots, r_N , exactly M receptors are placed at equal angles at each radius. In this example, the values used were $N=30$ (radii of 0.2, 0.5, 0.75, 1.00, 1.25, 1.50,

1.75, 2.00, 2.25, 2.50, 2.75, 3.00, 3.25, 3.50, 3.75, 4, 4.25, 4.5, 4.75, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, and 50 km) and $M=16$, for a total of 480 receptors.

Let $f(r_i, \theta_j)$ denote the predicted deposition rate (total, dry or wet) at the radius r_i and angle $\theta_j (=2\pi j/M)$. The amount deposited over the annular region defined by the radii r_1 and r_{30} is given by

$$\text{Amount deposited between } r_1 \text{ and } r_2 \text{ km} = \int_{r_1}^{r_2} \int_0^{2\pi} f(r, \theta) r dr d\theta$$

(3-23)

This integral is approximated in two methods.

With one method, the value predicted at a given radius r_i and angle θ_j is assumed representative of the wedge-shaped region defined by $r_i < r < r_{i+1}$, $\theta_j - 2\pi/M < \theta < \theta_j + 2\pi/M$. With this method, the values predicted at the largest radius considered are not used in the calculation. The approximation to the integral is then

$$\begin{aligned} \sum_{i=1}^{29} \sum_{j=1}^{16} \int_{r_i}^{r_{i+1}} \int_{\theta_j - \pi/16}^{\theta_j + \pi/16} f(r, \theta) r dr d\theta &\approx \sum_{i=1}^{29} \sum_{j=1}^{16} f(r_i, \theta_j) \int_{r_i}^{r_{i+1}} \int_{\theta_j - \pi/16}^{\theta_j + \pi/16} r dr d\theta \\ &= \pi/8 \sum_{i=1}^{29} \sum_{j=1}^{16} f(r_i, \theta_j) \left(\frac{r_{i+1}^2 - r_i^2}{2} \right) \\ &= \pi/16 \sum_{i=1}^{29} \sum_{j=1}^{16} f(r_i, \theta_j) (r_{i+1}^2 - r_i^2) \end{aligned}$$

(3-24)

With the other method, the value predicted at a given radius r_i and angle θ_j is assumed representative of the wedge-shaped region defined by $r_{i-1} < r < r_i$, $\theta_j - 2\pi/M < \theta < \theta_j + 2\pi/M$. With this method, the values predicted at the smallest radius considered are not used in the calculation. In particular,

$$\begin{aligned}
\sum_{i=1}^{29} \sum_{j=1}^{16} \int_{r_i}^{r_{i+1}} \int_{\theta_j - \pi/16}^{\theta_j + \pi/16} f(r, \theta) r dr d\theta &\approx \sum_{i=1}^{29} \sum_{j=1}^{16} f(r_{i+1}, \theta_j) \int_{r_i}^{r_{i+1}} \int_{\theta_j - \pi/16}^{\theta_j + \pi/16} r dr d\theta \\
&= \pi/8 \sum_{i=1}^{29} \sum_{j=1}^{16} f(r_{i+1}, \theta_j) \left(\frac{r_{i+1}^2 - r_i^2}{2} \right) \\
&= \pi/16 \sum_{i=1}^{29} \sum_{j=1}^{16} f(r_{i+1}, \theta_j) (r_{i+1}^2 - r_i^2)
\end{aligned}
\tag{3-25}$$

The average of these two methods is then given by

$$\text{Amount deposited between } r_1 \text{ and } r_N \approx \pi/16 \sum_{i=1}^{29} \sum_{j=1}^{16} \frac{f(r_{i+1}, \theta_j) + f(r_i, \theta_j)}{2} (r_{i+1}^2 - r_i^2)
\tag{3-26}$$

The area-averaged value is simply the total amount deposited divided by the area of the region.

It should be noted that this method is only an approximation; the grid size was chosen as a balance between computation time required to run a year's worth of data (which consists of 8,760 hours) and the accuracy of the approximation. In the analyses for a fixed hour performed in the sensitivity analyses, a much finer grid is used.

3.9. FUGITIVE DUST/EMISSIONS

Fugitive dust usually refers to the dust put into the atmosphere by the wind blowing over plowed fields, dirt roads, or desert or sandy areas with little or no vegetation. Reentrained dust is that which is put into the air by reason of vehicles driving over dirt roads (or dirty roads) and dusty areas. Such sources can be characterized as line, area, or volume sources. Emission rates may be based on site-specific data or values from the general literature.

Fugitive emissions are usually defined as emissions that come from an industrial source complex. They include the emissions resulting from the industrial process that are not captured and vented through a stack, but may be released from various locations within the complex. Where such fugitive emissions can be properly specified, the ISC model, with consideration of gravitational settling and dry deposition, is the recommended model. In some unique cases a model developed specifically for the situation may be needed. Because of the difficult nature of characterizing and modeling fugitive dust and fugitive emissions, it is recommended that the proposed procedure be cleared by the appropriate Regional Office for each specific situation before the modeling exercise is begun. (Please see Chapter 5.)

3.10. MODELING INHALATION EXPOSURE

Exposure scenarios have several functions in risk assessment: they are a means to quantify exposure and dose; they are a way to develop descriptors; and they are a tool for evaluating remediation options (ORNL, 1996). The procedure for estimation of inhalation exposure and dose and characterizing the risk is presented in the following sections.

3.10.1. Estimating Exposure and Dose from Contaminant Concentrations in the Air. Exposure results from the contact of an organism with environmental media (air, water, food, soil) containing the contaminant. Exposure, as measured by the intensity and duration of contact at the external boundary of the organism, can be represented by a time-dependent profile of the environmental concentration at the point of contact. The area under the curve of the profile is the magnitude of the exposure in concentration-time units. The biologically significant measure of exposure, the intake or dose, is the amount of the contaminant that crosses the external boundary of the organism. Substances cross the external boundaries of an organism primarily through inhalation, ingestion, or absorption through the skin. A brief summary of the concepts of direct exposure and dose, as described in the U.S. EPA (1992) Exposure Assessment Guidelines is presented in the following sections.

3.10.2. Inhalation Doses. For the inhalation pathway, the assumption is made that the substance is homogeneously distributed through the environmental medium (e.g., air, water) and that the intake of the chemical into the body is proportional to the intake of the medium. Therefore, the dose is the integration of the chemical intake rate (i.e., the exposure concentration times the intake rate of the medium) over time. In cases where the actual contact or exposure time is short and intermittent, such as in the ingestion of food or drinking water, the intake rate can be expressed in terms of the frequency of events times the intake per event, and the total dose can be expressed as the sum of the doses received during each event. If the assumption is made that the exposure concentration and the intake of the medium are nearly constant during each event, the resulting dose can be expressed as:

$$DI = \bar{C} \cdot \bar{IR} \cdot ED \quad (3-27)$$

where:

| | | |
|------------|---|--|
| DI | = | dose (mg) |
| ED | = | exposure duration or frequency (days) |
| \bar{C} | = | concentration (mg/m ³ of air) |
| \bar{IR} | = | intake rate (m ³ of air) |

Doses are usually expressed in terms of the rate of intake of the substance per unit time (e.g., mg/day) per unit body weight (e.g., mg/kg body weight/day). Therefore, for the above equation, the average daily dose (ADD) is:

$$ADD = \frac{\bar{C} \cdot \bar{IR} \cdot ED}{BW \cdot AT} \quad (3-28)$$

where:

- ADD = average daily dose [(mg)/(kg × day)]
BW = body weight (kg)
AT = time period over which dose is averaged (days)

The average daily dose presented above is a measure of the potential or administered dose (ADD_{adm}) at the point of contact with the exposed individual. It may or may not be equivalent to the “applied dose” (ADD_{app}) or the dose available for absorption at the tissue interface (i.e., at the surface of the respiratory or gastrointestinal tract), and it may or may not be equivalent to the “internal dose” ($ADD_{internal}$), the dose that is absorbed and is available for interaction with biological significant receptors. Theoretically, the internal dose can be estimated from the concentration of the chemical in the gastrointestinal or respiratory tract, the internal surface area, and the permeability coefficient for the specific tissue; however, this information is not usually available. Therefore, U.S. EPA recommends that it be assumed that the applied dose is equal to the administered (potential) dose (i.e., that all the chemical ingested in food or drinking water or all that is inhaled touches an absorption barrier inside a person). If this assumption is made, then the following equation can be used to estimate the internal dose:

$$DI_{internal} = \bar{C} \cdot \bar{TR} \cdot ED \cdot AF \quad (3-29)$$

where:

- AF = absorption fraction (units of mass absorbed per units of mass applied)
and the average daily internal dose ($ADD_{internal}$) becomes:

$$ADD_{internal} = \frac{\bar{C} \cdot \bar{TR} \cdot ED \cdot AF}{BW \cdot AT} \quad (3-30)$$

Rates of absorption may differ among individuals, populations, and species, resulting in different internal doses for the same administered dose. Information on absorption factors is limited. Reference toxicity values for inhalation exposures are expressed in terms of reference concentrations (RfC).

3.11. TREATMENT OF UNCERTAINTY

Increasing reliance has been placed on concentration estimates from models as the primary basis for regulatory decisions concerning source permits and emission control requirements. In many situations, such as review of a proposed source, no practical alternative exists. Therefore, there is an obvious need to know how accurate models really are and how any uncertainty in the estimates affects regulatory decisions. U.S. EPA recognizes the need for incorporating such information and has sponsored workshops (Fox, 1981; Burton, 1981) on model accuracy, the possible ways to quantify accuracy, and considerations in the incorporation of model accuracy and uncertainty in the regulatory process. The Second (U.S. EPA) Conference on Air Quality Modeling, August 1982 (U.S. EPA, 1981a) was devoted to that subject.

3.11.1. Overview of Model Uncertainty. Dispersion models estimate pollutant transport through the air to specific receptor locations. Transport is characterized by measured or known conditions that are input to the models, e.g., wind speed, mixed layer height, surface heat flux, emission characteristics, etc. However, in addition to the known conditions, there are unmeasured or unknown variations in the transport, e.g., unresolved details of the atmospheric flow such as the turbulent velocity field. These unknown conditions may vary among repetitions of the event. As a result, deviations in observed concentrations from those estimated by the model are likely to occur even though the known conditions are fixed. Even with a perfect model, there are likely to be deviations from the observed concentrations due to variations in the unknown conditions. The statistics of these concentration residuals are termed "inherent" uncertainty. Available evidence suggests that this source of uncertainty

alone may be responsible for a typical range of variation in concentrations of as much as 50% (Hanna, 1982).

Moreover, because neither models nor databases are perfect, there is reducible uncertainty associated with the model and its input conditions. Reducible uncertainties are caused by three factors:

- ! Uncertainties in the input values of the known conditions—source characteristics, meteorological data, and receptor parameters;
- ! Errors in the measured concentrations used to compute the concentration residuals; and
- ! Inadequate model physics and formulation.

The “reducible” uncertainties can be minimized through better (more accurate and more representative) measurements and better model physics.

To use the terminology correctly, reference to model accuracy should be limited to the portion of reducible uncertainty that deals with the physics and the formulation of the model. The accuracy of the model is normally determined by an evaluation procedure that involves the comparison of model concentration estimates with measured air quality data (Bowne, 1981). The statement of accuracy is based on statistical tests or performance measures such as bias, noise, correlation, etc. (Fox, 1981). However, information that allows a distinction among contributions of the various elements of inherent and reducible uncertainty is only now beginning to emerge. As a result, most discussions of the accuracy of models make no quantitative distinction between limitations of the model and limitations of the database or of knowledge concerning atmospheric variability. Note that statements on model accuracy and uncertainty may imply the need for improvements in model performance that even the “perfect” model could not satisfy.

3.11.2. Studies of Model Accuracy. A number of studies (Bowne and Londergan, 1983; Moore et al., 1982) have been conducted to examine model accuracy, particularly with respect to the reliability of short-term concentrations required for

ambient standard and increment evaluations. These studies show that models are more reliable for estimating longer time-averaged concentrations than for estimating short-term concentrations at specific locations and that the models are reasonably reliable in estimating the magnitude of highest concentrations occurring sometime, somewhere within an area.

3.11.3. Use of Uncertainty in Decision-Making. The accuracy of model estimates varies with the model used, the type of application, and site-specific characteristics. Thus, it is desirable to quantify the accuracy or uncertainty associated with concentration estimates used in decision making. Communications between modelers and decision makers must be fostered and further developed. Communications concerning concentration estimates currently exist in most cases, but communications dealing with the accuracy of models and their meaning to the decision maker are limited by the lack of a technical basis for quantifying and directly including uncertainty in decisions. Although procedures for quantifying and interpreting uncertainty are beginning to evolve (Burton, 1981; U.S. EPA, 1981b; Fox, 1983) much study is still required.

In all applications of models, an effort is encouraged to identify the reliability of the model estimates for that particular area and to determine the magnitude and sources of error associated with the use of the model. The analyst is responsible for recognizing and quantifying limitations in the accuracy, precision, and sensitivity of the procedure. Information that might be useful to the decision maker in recognizing the seriousness of potential air quality violations includes such model accuracy estimates as accuracy of peak predictions, bias, noise, correlation, frequency distribution, spatial extent of high concentration, etc. Both space/time pairing of estimates and measurements and unpaired comparisons are recommended. Emphasis should be on the highest concentrations and the averaging times of the standards or increments of concern. Where possible, confidence intervals about the statistical values should be provided. However, although such information can be provided by the modeler to the decision maker, it is unclear how this information should be used to make an air

pollution control decision. Given a range of possible outcomes, it is easiest and tends to ensure consistency if the decision maker confines his judgment to use of the “best estimate” provided by the modeler (i.e., the design concentration estimated by a model recommended in the Guideline or an alternative model of known accuracy). This is an indication of the practical limitations imposed by current abilities of the technical community.

3.12. REFERENCES

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SOIL CONCENTRATION AND EXPOSURE PATHWAYS

4.1. INTRODUCTION

Contaminants emitted from combustors either deposit onto land surfaces in the vicinity of the facility or travel and deposit downwind from the facility. Atmospheric pollutants contact the soil layer through processes of wet (i.e., precipitation) or dry (i.e., gravitational force) deposition. Following deposition, contaminants may be incorporated into the upper layers of soil where crops or other vegetation are grown. This chapter focuses on estimating the cumulative concentration of a given contaminant in the soil following deposition from a combustor. The concentrations will be used to estimate the risk to humans who may have dermal contact with contaminated soil, ingest soil or household dust directly, or consume vegetation and animals that have been exposed to contaminated soil.

Contaminant levels in soil are the result of both wet and dry particle deposition onto soil, vapor diffusion into soil, and the loss of contaminants from soil through leaching, abiotic and biotic degradation, volatilization, soil erosion, and surface water runoff. Figure 4-1 illustrates the factors required to determine the cumulative soil concentration. Soil conditions such as pH, soil structure and characteristics, organic matter content, and water content affect the distribution and mobility of contaminants after deposition onto soil. Loss of contaminants from soil is modeled using rates that depend on site-specific data about the physical and chemical characteristics of the soil. Note that the cumulative soil concentration (C_s) represents the concentration increment due to accumulation of contaminant deposited onto soil from the combustor. The cumulative soil concentration does not represent the total concentration, because it does not take into account background concentrations of the contaminant that may already be present, whether natural or from other pollution sources.

4.2. OVERVIEW OF SOIL CONCENTRATION CALCULATIONS

The cumulative soil concentration of a pollutant is derived from the deposition

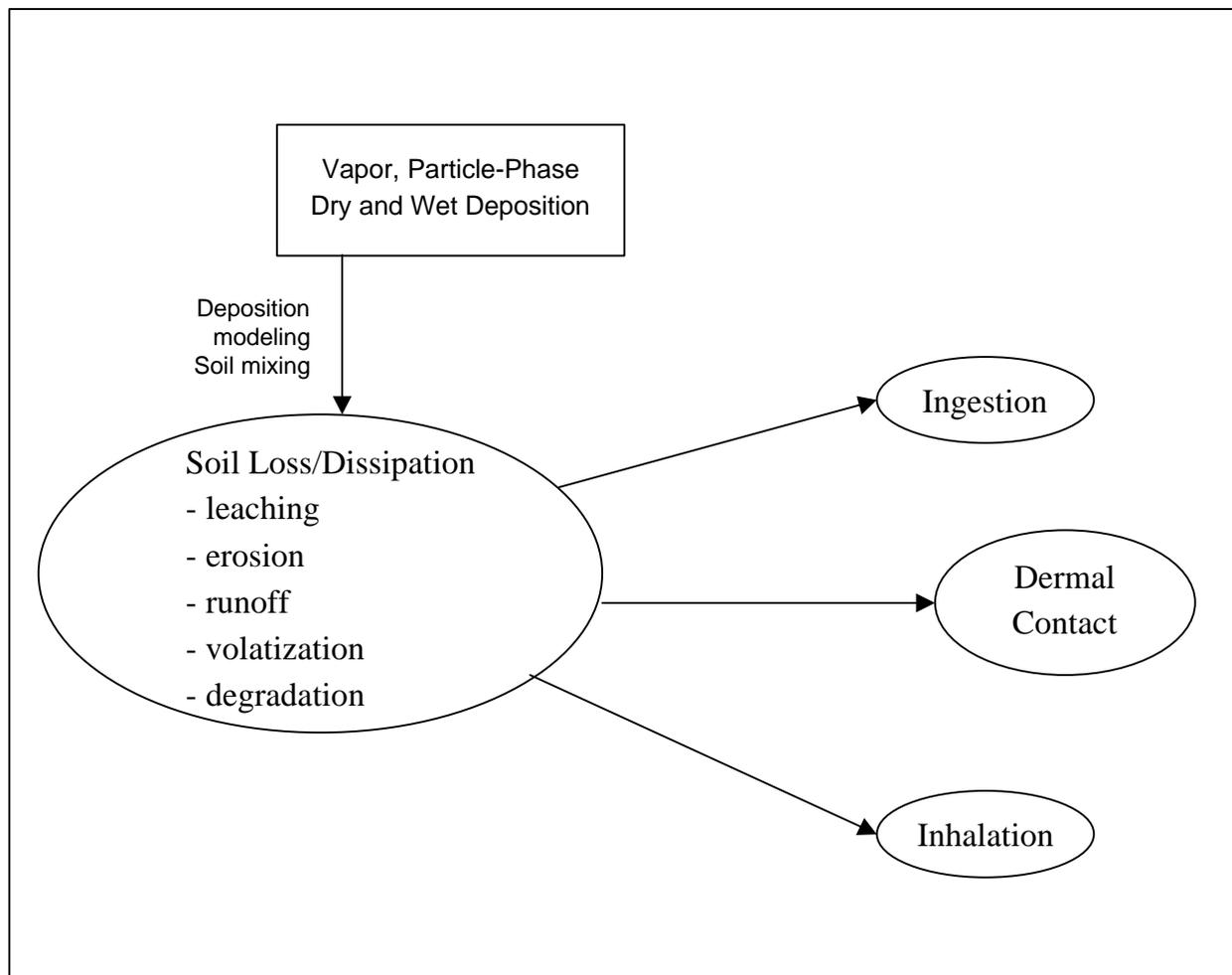


FIGURE 4-1

Overview of Soil Concentration and Exposure Pathway

and diffusion rates over the lifetime of the combustor and the contaminant loss rate from the soil. Contaminants may be lost from soils as a result of numerous factors,

including leaching, abiotic and biotic degradation, volatilization, soil erosion and surface water runoff. The equations used to estimate contaminant concentrations and losses in soil are adapted from Travis et al. (1983), Miller and Gardiner (1998), Hwang and Falco (1986), and Mills et al. (1985).

Key assumptions and limitations for soil concentration calculations are:

- ! Background soil concentration and the natural recycling of contaminated detritus are not considered. The calculated soil concentration is only the soil increment due to combustion fallout, and could under predict the actual soil concentration.
- ! Trace metal contaminants are assumed to be conserved indefinitely in the upper layer of soil unless loss constants are available. Although most heavy metals are tightly bound to the soil, measurements show that this assumption often over-predicts concentrations (i.e., at low pH metals become increasingly mobile and may be leached out of the upper soil layers).
- ! Loss processes occurring simultaneously are not taken into account. This could lead to an over-predict losses because contaminant concentration available for each loss process would be over-predicted.
- ! Degradation of organic contaminants is first-order. This assumption could over- or under-predict degradation rate, which is complex and not necessarily first-order.
- ! If soil incorporation of contaminant is assumed, incorporation depth is 20 cm and the upper 20-cm soil layer has a dry mass of 2.7×10^3 Mg/ha. A soil concentration of 1 $\mu\text{g/g}$ corresponds to a contaminant application of 2.7 kg/ha. If actual depth (and mass) was less, contaminant concentration could be under-predicted (and vice versa).

4.2.1. Calculating Cumulative Soil Concentration. The cumulative soil concentration of a pollutant (C_s) is calculated from the wet and dry particle deposition rates, diffusive flux into soil, and the soil loss constant, as described by Travis et al. (1983):

$$C_s = \frac{100 (D_{yd} + D_{yw} + L_{DIF}) [1.0 - e^{-ks tD}]}{Z_s BD ks} \quad (4-1)$$

where:

- C_s = concentration of contaminant in soil after total time period of deposition ($\mu\text{g/g}$)
- 100 = units conversion factor ($[10^6 \mu\text{g/g}]/[10^4 \text{cm}^2/\text{m}^2]$)
- D_{yd} = yearly dry deposition rate of contaminant to soil ($\text{g}/\text{m}^2\text{-yr}$)
- D_{yw} = yearly wet deposition rate of contaminant to soil ($\text{g}/\text{m}^2\text{-yr}$)
- L_{DIF} = atmospheric diffusion flux of contaminant to soil ($\text{g}/\text{m}^2\text{-yr}$)
- ks = soil loss constant (yr^{-1})
- tD = total time period over which deposition occurs (yrs)
- Z_s = soil mixing depth (cm)
- BD = bulk density of soil (g/cm^3)

Remember that the cumulative soil concentration (C_s) represents the concentration due to accumulation of contaminant deposited onto soil from the combustor, not the total concentration, because background concentrations are not included. For the steady-state soil concentration, the bracketed exponential term that contains a time-weighting factor is eliminated.

Another approach for calculating soil concentration (C_s) based on time period of deposition, exposure duration, and the toxicity characteristics (i.e., carcinogen or noncarcinogen) of the chemical are provided in U.S. EPA 1998.

4.2.2. Calculating Deposition Rates. Determination of annual deposition was discussed in Chapter 3. In the event that only ambient air concentrations are available, rather than stack emission rates, the dry deposition rate (D_{yd}) can be calculated from the dry deposition velocity and particle-phase air concentration:

$$D_{yd} = 0.31536 V_d C_{pa} \quad (4-2)$$

where:

- D_{yd} = dry deposition flux of contaminant sorbed to particles (g/m²-yr)
- 0.31536 = units conversion factor ([3.1536E+07 sec/yr]/[100 cm/m][10⁶ µg/g])
- V_d = dry deposition velocity (cm/sec)
- C_{pa} = particle-bound concentration of contaminant on settling particles (µg/m³)

Particles settle to the ground surface and plant surfaces through the forces of gravity. Gravitational settling velocity is a function of particle size, with more rapid settling occurring with larger particles. Seinfeld (1986) listed a gravitational deposition velocity of 1 cm/s for 10 -µm size particles. An assignment of V_d of 1.0 cm/s would be conservative because most particles depositing to ground surfaces (including particles originally emitted from the stack as well as particles of other origins in ambient air) are less than 10-µm diameter. In lieu of more site-specific data, this value should suffice for most assessments.

This equation must be modified in order to calculate a wet deposition rate (D_{yw}) using the volumetric washout ratio, and average annual moisture. Wet deposition is calculated as:

$$D_{yw} = X May Wp 10^{-8} \quad (4-3)$$

where:

- D_{yw} = yearly wet deposition rate of contaminant (g/m²-yr)
- 10⁻⁸ = units conversion factor [10⁻⁶ g/µg] [10⁻² m/cm]

- May = average annual moisture (precipitation: rainfall, snowfall) (cm/yr)
Wp = volumetric washout ratio for particulates (unitless)
X = contaminant air concentration ($\mu\text{g}/\text{m}^3$)

Geraghty et al. (1973) provide a map showing isolines of average annual rainfall throughout the United States. This map shows low rates of 10 to 50 cm/yr in the desert Southwest, moderate rates of 60 to 100 cm/yr in the Midwest cornbelt, 100 to 150 cm/yr in the South, and so on. If the deposition is onto irrigated cropland, it may also be appropriate to add irrigation amounts to rainfall amounts. Irrigation values range from 0 to 100 cm/yr (data from 69 selected cities) (Baes et al., 1984).

Washout ratios are generally defined as the concentration of contaminant in rain to the concentration of contaminant in air. Concentrations of contaminants in air and rainwater can be derived as a mass of contaminant divided by a mass or a volume of air/water. Mackay et al. (1986) show that volume-based washout ratios (mass of contaminant mixing in m^3 air or water) exceed mass-based washout ratios (mass of contaminant mixing in kg of air or water) by a factor 815, which is the ratio for water and air densities. The washout ratio used in this assessment is volumetric ratio which allows for direct use of contaminant concentrations estimated in this methodology, as they are already on a $\mu\text{g}/\text{m}^3$ volume basis.

Bidleman (1988) defines the overall washout ratio as: (mass contaminant/volume rain) / (mass contaminant/volume air). Bidleman (1988) also discusses that overall washout includes both wet deposition of particulates and scouring of contaminants in the vapor phase. A method is included for estimating the vapor particulate ratios for semi-volatile organic compounds (abbreviated SVOCs) and also for estimating the washout ratios for vapors. The study indicates that if Henry's law constant (H) is sufficiently high, vapor dissolution in droplets is negligible and only the particulate fraction is removed by wet deposition. On the basis of this work, it can be assumed that vapor scouring of contaminants emitted from combustors is small in comparison to

wet deposition, and that the washout ratio can be applied to the airborne particulate concentration of the contaminants.

Bidleman (1988) does not provide a chemical or site-specific equation to estimate the particle-phase washout ratio (as he does for the vapor-phase washout ratio). Rather, he summarizes available data and concludes that there is a wide range of particle-phase washout ratio, W_p for SVOC: between 2×10^3 and 1×10^6 . He says that a typical range is 10^5 to 10^6 , and uses a W_p of 2×10^5 in his exercises to estimate the overall washout ratio for several SVOCs. Koester and Hites (1992) list vapor and particle scavenging ratios for congener groups of dioxin-like compounds. To derive these ratios, they used air concentrations for congener groups that were taken at one time period in Bloomington and Indianapolis, IN, and rainfall depositions of these compounds at these sites measured at another. Using the Bidleman vapor/particle partitioning model in this assessment, they estimated the vapor/particle split for the air concentrations. With these observations and models, they concluded that the overall washout ratio (sum of vapor and particle ratios) ranges from 10^4 to 10^5 , contrasted with the typical range of 10^5 to 10^6 noted above in Bidleman (1988). Also, their calculations indicate that vapor scavenging of dioxin-like compounds is comparable to particle scavenging, also in contrast to the Bidleman analysis summarized above. However, they did not state whether their washout ratios were volume- or mass-based. If they were mass-based, then a conversion to volume based would put them in the 10^7 to 10^8 range, which seems improbable given the Bidleman summary presented above.

It is suggested that the user assign values of W_p based on data in Bidleman (1988). If ratios for specific contaminants of interest are not listed, a value of 10^5 should suffice for most contaminants.

The diffusive loading (L_{DIF}) refers to vapor-phase deposition or diffusion, and is governed by gas-phase mass transfer:

$$L_{DIF} = 0.31536 K_t C_{va} \quad (4-4)$$

where:

| | | |
|-----------|---|---|
| L_{DIF} | = | vapor-phase diffusion flux of contaminant to soil ($\text{g}/\text{m}^2\text{-yr}$) |
| 0.31536 | = | units conversion factor ($[(3.1536\text{E}+07 \text{ s}/\text{yr})/[100 \text{ cm}/\text{m}][10^6 \mu\text{g}/\text{g}]$) |
| K_t | = | gas phase mass transfer coefficient (cm/s) |
| C_{va} | = | vapor phase air concentration of contaminant ($\mu\text{g}/\text{m}^3$) |

The particle- and vapor-phase air concentrations that are appropriate for the above formulations are predicted by the air dispersion model. Chapter 3 details application of the air dispersion model to estimate vapor-phase concentrations.

The gas-phase mass transfer coefficient (K_t) is based on general soil properties (Hillel, 1980; Miller and Gardiner, 1998) which can be used to calculate the following equation:

$$K_t = \frac{D_a \theta_v}{Z_s} \quad (4-5)$$

where:

| | | |
|------------|---|--|
| K_t | = | gas phase mass transfer coefficient (cm/s) |
| Z_s | = | soil mixing depth (cm) |
| D_a | = | diffusion coefficient of contaminant in air (cm^2/s) |
| θ_v | = | soil void fraction (cm^3/cm^3) |

The soil void fraction (θ_v) is the volumetric fraction of a soil that does not contain solids or water.

$$\theta_v = 1 - \left(\frac{BD}{\rho_s}\right) - \theta_{sw} \quad (4-6)$$

where:

| | | |
|---------------|---|--|
| θ_v | = | soil void fraction (cm^3/cm^3) |
| θ_{sw} | = | volumetric soil water content ($\text{mL (=cm}^3\text{)}/\text{cm}^3$) |
| BD | = | soil bulk density (g/cm^3) |
| ρ_s | = | solids particle density (g/cm^3) |

The expression containing bulk density (BD) divided by solids particle density (ρ_s) gives the volume of soil occupied by pore space or voids (Miller and Gardiner, 1998). Blake and Hartge (1996) and Hillel (1980) both suggests that the mean density of solid particles is about 2.6 to 2.7 gm/cm^3 . Since soil water content is unique for each soil type, site-specific information is highly recommended. If site-specific information is not available, the volumetric water content of soil content can be obtained by multiplying the mass water content by BD (Miller and Gardiner, 1998). A more detailed discussion of θ_{sw} is presented in Section 4.3.7.1.

4.2.3. Calculating the Soil Loss Constant (ks). When available, an overall environmental dissipation rate can be used as the soil loss constant (Equation 4-1). This rate would be calculated from field data and would include all routes of dissipation and degradation. For example, the Dioxin Reassessment (U.S. EPA, 1994) reviewed the literature to arrive at a dissipation rate constant of 0.0693 yr^{-1} for dioxin residues depositing to a depth of 1 cm. Fries and Paustenbach (1990) suggested the use of a half-life of at least 10 years, and used a 15-year half-life in their example scenarios on the impact of airborne deposition of 2,3,7,8-TCDD originating from stack emissions. In a later publication, Paustenbach et al. (1992) reviewed the literature on the environmental half-life in soil. For surface soils, they cited the evidence from Eglin Air Force Base (Young, 1983) suggesting a half-life of 10 to 12 years for 2,3,7,8-TCDD, and the work of Cerlesi et al. (1989), who estimated a soil half-life of 9.1 years for 2,3,7,8-TCDD in Seveso soil. Paustenbach et al. (1992) also discussed the fact that the loss of TCDD from soil is predominantly through volatilization and photo degradation of residues at the soil surface, and that loss mechanisms are minimal

below the soil surface. They suggested that ultraviolet radiation penetrates the surface only to about 0.1 cm, which implies that photo degradation could be limited below that depth. They concluded that their review supported the concept that TCDD probably has a half-life of 9 to 15 years in surface soil and 25 to 100 years in subsurface soils.

If pertinent dissipation information is known for other compounds of interest, a k_s value can be calculated. Otherwise, the soil loss constant can be determined by summing the applicable contaminant losses due to the individual environmental processes of leaching, degradation, volatilization, soil erosion, and surface water runoff:

$$k_s = k_{sl} + k_{sg} + k_{sv} + k_{se} + k_{sr} \quad (4-7)$$

where:

- k_s = soil loss constant due to all environmental processes (yr^{-1})
- k_{sl} = loss constant due to leaching (yr^{-1})
- k_{sg} = loss constant due to abiotic and biotic degradation (yr^{-1})
- k_{sv} = loss constant due to volatilization (yr^{-1})
- k_{se} = loss constant due to soil erosion (yr^{-1})
- k_{sr} = loss constant due to surface water runoff (yr^{-1})

Equations for calculating soil losses due to leaching, erosion, and runoff have been adapted from Mills et al. (1985). The soil loss constant of contaminants due to leaching (k_{sl}) is obtained by calculating the water availability in the soil and the influence of soil properties on water and contaminant movement by the following equation:

$$k_{sl} = \frac{My + I - Ev - RO}{\theta_{sw} Z_l \left[1.0 + \frac{BD K_{d_s}}{\theta_{sw}} \right]} \quad (4-8)$$

where:

- k_{sl} = soil loss constant due to leaching (yr⁻¹)
- My = average annual precipitation (cm/yr)
- I = average annual irrigation (cm/yr)
- Ev = average annual evapotranspiration (cm/yr)
- RO = average annual surface runoff (cm/yr)
- θ_{sw} = volumetric soil water content (mL/cm³)
- Z_l = depth of soil where contaminant leaching occurs (cm)
- BD = bulk density of soil (g/cm³)
- K_{d_s} = soil-water partitioning coefficient (mL/g)

Losses due to degradation (k_{sg}) are chemical-specific and have been empirically determined from field studies. Values may be found in the literature. Degradation losses are discussed in more detail in Section 4.3.8.

The soil loss constant due to volatilization (k_{sv}) is based on gas equilibrium coefficients and gas phase mass transfer. The first order decay constant, K_{sv}, is obtained by adapting the Hwang and Falco equation for soil vapor phase diffusion (Hwang and Falco, 1986).

$$k_{sv} = K_e K_t \quad (4-9)$$

where:

- k_{sv} = soil loss constant due to volatilization (yr⁻¹)

- Ke = equilibrium coefficient (s/yr-cm)
 K_t = gas phase mass transfer coefficient (cm/s) (refer to eq. 4-5)

The equilibrium coefficient (Ke) is calculated using the following equation:

$$K_e = \frac{3.1536E+10 H}{Z_v K_{oc} f_{oc} R T BD} \quad (4-10)$$

where:

- Ke = equilibrium coefficient (s/yr-cm)
 3.1536E+10 = units conversion factor ([3.1536E+7 sec/yr][1000 L/m³])
 H = Henry's Law constant (atm-m³/mol)
 Z_v = depth of soil from which contaminants can volatilize (cm)
 K_{oc} = organic carbon partition coefficient (mL/g)
 f_{oc} = fraction of organic carbon in soil (unitless)
 R = ideal gas constant (L-atm/mol-K)
 T = temperature (°K)
 BD = bulk density of soil (g/cm³)

The soil loss constant due to erosion of soil (kse) is calculated using the following equation:

$$kse = \frac{0.1 X_e SD ER}{BD Z_e} \left(\frac{Kd_s BD}{\theta_{sw} + Kd_s BD} \right) \quad (4-11)$$

where:

- kse = soil loss constant due to erosion (yr⁻¹)
 0.1 = units conversion factor ([1000 g/kg][10⁴ cm²/m²])

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- X_e = unit soil loss (kg/m²-yr)
- SD = sediment delivery ratio
- ER = contaminant enrichment ratio
- Kd_s = soil-water partition coefficient (cm³/g)
- BD = bulk density of soil (g/cm³)
- Z_e = soil depth from which erosion occurs (cm)
- θ_{sw} = volumetric soil water content (mL/cm³)

The unit soil loss (X_e) is dependent on terrain and land management features and is calculated using the following equation:

$$X_e = 0.224 RF K LS C P \tag{4-12}$$

where:

- X_e = unit soil loss (kg/m²-yr)
- 0.224 = units conversion factor ([247.1 acres/km²][1 km²/1E+06 m²][907.18 kg/ton])
- RF = erosivity factor (yr⁻¹)
- K = erodibility factor (tons/acre)
- LS = topographic or slope length factor (dimension less)
- C = cover management factor (dimension less)
- P = supporting practice factor (dimension less)

The soil loss constant due to surface runoff (ksr) can be calculated by:

$$ksr = \frac{RO}{\theta_{sw} Z_r} \left(\frac{1}{1 + (Kd_s BD/\theta_{sw})} \right) \tag{4-13}$$

where:

- ksr = soil loss constant due to surface runoff (yr^{-1})
- RO = average annual surface runoff (cm/yr)
- θ_{sw} = volumetric soil water content (mL/cm^3)
- Z_r = depth of soil affected by surface water runoff (cm)
- Kd_s = soil-water partition coefficient (cm^3/g)
- BD = bulk density of soil (g/cm^3)

4.3. DESCRIPTION OF INPUT VARIABLES

Calculating cumulative soil concentration requires the input of site-specific data which must be calculated or derived from the available literature. This section defines the input variables required for the calculations, discusses the factors that affect the value of each variable, and outlines the typical range of values and sources of each variable.

4.3.1. Dry and Wet Deposition Rates (D_{yd} and D_{yw}). Site-specific dry and wet deposition rates are determined by air dispersion modeling. Several methods for determining deposition rates are described in Chapter 3. In cases where ambient air concentrations are used rather than stack emissions, deposition rates can be calculated from the respective deposition velocity and air concentration, described in Section 4.2.2. If the chemical is absorbed on the surface of the particle, the deposition velocity would be a function of particle size and several other methodological parameters. Deposition velocities can be found in the literature for specific chemicals or classes of chemicals.

4.3.2. Diffusive Loading (L_{DIF}). Vapor-phase deposition or diffusion also adds to the concentration of contaminants in soil. It is assumed that diffusive loading is driven by the same gas-phase mass transfer coefficient (K_t) as volatilization. It should be noted that this formulation pertains to diffusive flux into the soil and does not address entry into soil of vapor-phase contaminants via wet deposition. It is also not clear to what

extent this treatment of diffusive entry addresses the issue of dry deposition of vapors onto soils. Both areas are in need of further investigation.

4.3.3. Time Period of Deposition (tD). In this methodology, individuals are assumed to be exposed to contaminants in the soil following a time period in which there have been continuous combustor emissions. The lifetime of a combustion facility, such as a MWC, could be considered to be ≥ 30 years.

4.3.4. Soil Depth (Z_s). When modeling exposures to contaminants found in soils are modeled, the depth of assumed contamination is important in calculating the appropriate soil concentration. Contaminants deposited onto soil surfaces may be incorporated into lower soil profiles by tilling, whether done manually in a garden or mechanically in a large field. In general, if the area under consideration is likely to be tilled (e.g., agricultural soils), the soil mixing depth may be assumed to be 10 to 20 cm, depending on local conditions and the equipment used.

If soil incorporation does not occur, as in pastures or lawns, contaminants are assumed to be retained in a shallower, uppermost, untilled soil layer. Although the actual depth of this uppermost layer of mixing is unknown, a value of 1-cm is assumed as the untilled surface depth in which contaminants evenly mix. For soluble compounds, leaching might lead to movement below a 1-cm depth and perhaps justify a greater mixing depth. In any event, if more specific information is available on soil mixing depth for a particular site, a different value can be substituted.

Using the untilled soil concentration for soil-related exposures is a conservative assumption. If instead, it is felt that dermal exposures or soil ingestion exposures occur in conjunction with gardening or agricultural field crop production, then the tilled soil concentration should be used.

Volatilization and photodegradation are assumed to occur in the uppermost soil layer. Any volatile contaminants are likely to be desorbed from particles soon after emission from the combustor, prior to deposition onto the soil. However, semivolatile compounds (SVOCs) and volatile organic compounds (VOCs) emitted in sufficiently high concentrations may be deposited in particulate form and may undergo volatilization

losses from soils. Contaminants subject to volatilization losses may be incorporated to 20 cm by tilling and may not readily volatilize from this depth. The volatilization rate will reflect the contaminant concentration near the soil surface. For erosion and surface runoff, the affected soil layer will generally be the first few centimeters, while for leaching the entire tilled depth becomes involved. Care must be taken in assigning appropriate soil depths to each scenario.

For direct ingestion of soil and house dust by humans and herbivores, a depth of 1 cm is used. Surface soil is tracked into houses and incorporated into house dust. Strong correlations between soil concentrations and indoor dust levels have been found (Brunekeef, 1984; Berny et al., 1994; Fergusson et al., 1986; Ferguson and Kim, 1991); therefore, indoor dust concentrations are estimated from the surface soil concentration at 1 cm. Children can either intentionally or incidentally eat soil and are most likely to be exposed to contaminated soil from gardens, lawns, landscaped areas, parks, and recreational areas. Herbivorous animals are most likely to be exposed to contaminated soils while grazing pastures. Deposition onto hard surfaces, such as sidewalks, slides, swings, and other play areas may result in dust residues that have negligible dilution with other residues. Exposure may result via mouthing of these objects or dermal contact. If an exposure assessment is to include contact with dust that is on hard surfaces, it is recommended that the concentration of contaminants in that dust be assumed to be equal to soil concentrations estimated for the untilled depth of 1 to 2 cm.

For dermal exposure, the conditions and areas of likely exposure are similar to those of the soil ingestion pathway. Therefore, as in the soil ingestion pathway, the dermal exposure model usually assumes a depth of 1 cm in estimating risk due to contact with contaminated soil. This assumption overestimates soil concentrations where incorporation occurs to any depth greater than 1 cm, and need not be used if site-specific information is available.

For exposure through surface water, contaminants are assumed to travel from a watershed into a surface water body dissolved in runoff water and adsorbed to eroded

soil particles. The assumptions for soil depth for the watershed area are site-specific. If the area under consideration is an agricultural area that is likely to be tilled, soil depth is assumed to be 20 cm. In all other cases, soil depth is assumed to be 1 cm in order to be conservative.

4.3.5. Bulk Density of the Soil (BD). The bulk density of soil (BD) is the ratio of the mass of the soil to its total volume. Bulk density is affected by the soil structure (e.g., the looseness or compaction of the soil, depending on the water and clay content of the soil) (Hillel, 1980). Values range from 0.93 to 1.84 g/cm³, depending on soil type (Hoffman and Baes, 1979). It is recommended that bulk density of the soil at the study site be used, if available.

4.3.6. Soil Loss Constant (ks). Organic and some inorganic contaminants may be lost from the soil by many processes, which may occur simultaneously and/or at different rates. The rate at which a contaminant is lost from the soil is known as the soil loss constant and is determined by the physical, chemical, and biological characteristics of the soil. The processes that remove contaminants from the soil include leaching, biotic and abiotic degradation, volatilization, erosion, and surface water runoff.

Organics are subject to loss by leaching, degradation, volatilization, erosion, and runoff. Inorganics such as metals may be lost by leaching and, in some cases, by volatilization. This section discusses the kinetics of contaminant loss, including first-order processes, which this methodology generally assumes, and other types of kinetics that may govern loss of contaminants from soil.

First-order reaction rates depend on the concentration of one reactant (Bohn et al., 1985). The loss of a contaminant by a first-order process depends only on the concentration of the contaminant in the soil, and a constant fraction of the compound is removed from the soil over time.

Those processes that apparently exhibit first-order kinetics without implying a mechanistic dependence on a first-order loss rate are termed “apparent first-order” loss rates (Sparks, 1989). Some higher order kinetic processes appear to be first-order

because of the relative abundance of some reactants, such as water and oxygen, in comparison with one reactant. This type of reaction is limited by the concentration of only one reactant under the conditions at which the apparent rate law is applicable (Sparks, 1989).

The assumption that contaminant loss follows first-order kinetics may be an oversimplification because, at various concentrations or environmental conditions, the loss rates from soil systems will follow different kinetic expressions. However, at low concentrations, a first-order loss constant may be adequate to describe the loss of the chemical from the soil.

In addition to first-order kinetics, contaminant loss in soil could follow zero-order or second-order kinetics. Zero-order loss rates are independent of reactant concentrations (Bohn et al., 1985). Zero-order rates describe some processes in which the reactants are in very high concentration. Under zero-order kinetics, a constant amount of a contaminant is lost from the soil over time, independent of its concentration.

Processes that follow second-order kinetics are dependent on the concentrations of two reactants or on the concentration of one reactant squared (Bohn et al., 1985). The loss constant of contaminant disappearance following a second-order process can be contingent on its own concentration, or on both its concentration and the concentration of another reactant, such as an enzyme or catalyst.

Because contaminant loss from soil is dependent on many complex factors, it may be difficult to model the overall rate of loss. Combined soil loss rates by these processes can be derived experimentally, and values for certain compounds are presented in U.S. EPA (1986). If field data where soil concentrations have been followed over time are available, these data should be used in the calculation of soil concentration. Loss of the contaminant can be measured as the total loss by multiple processes. In this case it would not be necessary to calculate the constant as described in Section 4.2.2. If the loss constant must be calculated, the input variables described below should be used.

4.3.7. Contaminant Losses By Physical Processes. Leaching, erosion, and runoff represent the physical transport processes that remove contaminants from the area of soil contamination. Leaching refers to the downward vertical movement of entrained or water-soluble contaminants through the soil column. Erosion is the physical transport of soil, with adsorbed contaminants, by wind, runoff, or gravity to another location. Runoff refers to the lateral transport of contaminants from the soil surface (as particles or in solution) with flowing rain or flood waters. Often these losses from the soil compartment are inputs to the surface or groundwater compartments. This section is divided into three parts. The first part describes the soil properties upon which each of these three processes is dependent. The second part discusses how available water is used to determine leaching and runoff losses. Third is a discussion of how terrain and land management factor into the calculation of soil erosion losses. Last is a discussion on physical transfer processes associated with volatilization. The appropriate soil depths to use in the different calculations are provided in Section 4.3.4.

4.3.7.1. Soil Properties — Two variables take into account the soil properties that affect leachate formation, erosion and surface water runoff: bulk density (BD) and soil water content (Θ_{sw}). Bulk density is described in Section 4.3.5. The soil water content depends on the available water and on the soil structure. Values for Θ_{sw} range from 0.03 to 0.40 mL/cm³ depending on soil type (Hoffman and Baes, 1979). The lower values are typical of sandy soils, which cannot retain much water, and the higher values are typical of soils such as clays or loamy soils which can retain water.

For hydrophobic organic chemicals, the relevant soil property is the fraction organic carbon. For metals, relevant soil properties include pH and iron content.

4.3.7.2. Loss Due to Volatilization (ksv) — Equation 4-8 in Section 4.2.2. shows the calculation of ksv. Semivolatile and volatile compounds emitted in high concentrations may become adsorbed to soil particles and exhibit volatilization losses from the soil. The loss of a chemical from the soil by volatilization is dependent on the rate of movement of the chemical to the soil surface, the chemical vapor concentration

at the soil surface (due to soil conditions), and the rate at which the boundary layer between the soil and atmosphere is cleared at the contaminant (Jury, 1986).

Polar molecules are less volatile than slightly polar or nonpolar molecules because of their greater absorption to dry soil constituents and greater water solubility (Poe, 1988). Volatilization loss rates for specific chemicals may be found in the literature. Laboratory-measured volatilization rates for soil-incorporated chemicals adequately estimate the field-measured rates, because the rates are primarily dependent on soil factors that can be mimicked in the laboratory (Spencer et al., 1982). Such experimental values may be used if site-specific data are unavailable.

4.3.7.3. Soil-Water Partitioning Coefficient (K_{d_s}) — The soil-water partitioning coefficient (K_{d_s}) is used to calculate the infiltration rate, reflects the equilibrium sorption/desorption of chemicals to soil particles. Mean values for K_{d_s} for many chemicals can be found in Baes et al. (1984). Variations in soil properties, however, greatly affect K_{d_s} , which for inorganic chemicals can vary up to 3 orders of magnitude in soils ranging from pH 4.5 to 9.0. Partitioning coefficients for inorganic pollutants used in modeling may be derived from soil-to-plant transfer coefficients (Baes et al., 1984). For organic compounds, the soil organic carbon content is an important soil property. Partitioning coefficients for organics may be estimated as the product of K_{oc} and f_{oc} , where K_{oc} is the organic carbon-normalized partition coefficient and f_{oc} is the fraction of organic carbon in soil. Therefore, it is advisable to use site-specific data for K_{d_s} when available.

4.3.7.4. Available Water — Losses of soil contaminants through leaching and surface water runoff are dependent on the amount of water available and on the soil properties (e.g., bulk density, soil porosity and sorptive properties) that affect how water passes through the soil and how contaminants bind to it. The average annual volume of water available to generate leachate is the sum of the average annual precipitation (My) and the average annual irrigation (I) minus the average surface runoff (RO) and minus the average annual evapotranspiration (Ev). However, the

average annual volume of water available to create surface runoff is a function of just the annual surface runoff (RO) and average annual irrigation (I).

Precipitation values range from 18 to 164 cm/year (data for 69 selected cities; U.S. Bureau of the Census, 1987). Irrigation values range from 0 to 100 cm/year (data for 69 selected cities; Baes et al., 1984). The average annual runoff can be estimated given isopleths of surface runoff available in the *Water Atlas of the United States* (Geraghty et al., 1973). The isopleths give annual surface water contributions, which include interflow and ground water recharge, and would need to be adjusted downward to reflect surface runoff only. Another approach for estimating surface runoff is to use the curve number equation developed by the Soil Conservation Service (USDA, 1975). Isopleths of mean annual cropland runoff corresponding to various curve numbers have been developed by Stewart et al. (1975), as reported by Mills et al. (1985). Curve numbers are assigned to an area depending on the soil type, land use or cover, and the hydrologic condition of the soil. Evapotranspiration values range from 35 to 100 cm/year (Baes et al., 1984). The available water as calculated by $(My + I - RO - Ev)$ is assumed to be a mass balance of all water inputs and outputs from the area under consideration. Other mechanisms of removal or retention in the soil are not considered in this methodology.

4.3.7.5. Terrain and Land Management — While leaching and runoff losses depend on inputs of water, erosion loss is determined by the terrain and land management factors that set up erosion conditions. Seven factors describe the erosion of soil and contaminants: sediment delivery ratio, contaminant enrichment ratio, erosivity factor, erodibility factor, topographic or slope length factor, cover management factor, and support practices factor. The sediment delivery ratio (SD) reflects the sediment yield derived from erosion. In Chapter 7, SD is calculated based on the area of the watershed, although alternative methods are being investigated. A default value of 0.18 was chosen for this methodology. The contaminant enrichment ratio (ER) accounts for the increased tendency for erosion of soils that have higher organic matter

content and greater surface area-to-volume ratios. Sandy soils have a higher ER than silty or loamy soils. Because ER is dependent on soil characteristics it is site-specific.

The remaining five factors comprise the unit soil loss constant (X_e). The erosivity factor (RF) is the measure of the erosion potential due to the average rainfall at the site. Annual values range from <50 for the arid western U.S. to >300 for the southeast, as compiled by Wischmeier and Smith (1978). The erodibility factor (K) is experimentally determined based on the predominant soil type at the site. Values for K range from 0.02 for sand to 0.60 for silt. The topographic or slope length factor (LS) takes into account the steepness and slope of the site. Values for LS range from 0.1 to about 40 for slopes with inclines of 0.5 to 60% and slope lengths ranging between 20 and 800 m. The cover management factor (C) accounts for the vegetative cover, crop sequence, crop rotation, and tilling practices at a site. Values of C range from 0.001 for managed woodlands with 100% vegetative cover to 1.0 for bare soil with no coverage. The support practice factor (P) reflects the use of techniques such as surface conditioning, diking, contouring, and terracing to control runoff/erosion. Values for P range from 0-1.0 and should only be less than 1 when specific practices are in place to minimize erosion. The Parameters Guidance Document will provide ranges of input values for these soil parameters.

4.3.8. Losses by Chemical and Biological Processes. Chemical and biological processes of contaminant loss include biodegradation (e.g., microbial), chemical decomposition (e.g., hydrolysis, redox reactions, photolysis). Degradation loss is chemical-specific and is not applicable to most metals, which are transformed, but not degraded, by such mechanisms. The soil losses due to degradation and volatilization processes are based on field observations or empirical data as discussed below.

4.3.8.1. Loss Due to Biotic Degradation — The rate of biological degradation in soils depends upon the concentration and activity of the microbial populations in the soil, the soil conditions, and the contaminant concentration (Jury and Valentine, 1986). First-order loss rates often do not account for the high variability of these parameters in a single soil system. However, the use of simple rate expressions may be appropriate

at low chemical concentrations (ng/kg range), where a first-order dependence on chemical concentration may be reasonable.

The rate of biological degradation of contaminants is chemical-specific, depending on the complexity of the chemical and the usefulness of the chemical to the microorganisms. Some substrates are co-metabolized, that is not used by the organisms as a nutrient or energy source, but simply transformed along with other similar chemicals, which can be further utilized. Environmental and chemical factors that may limit the biodegradation of chemicals in the soil environment include availability of the chemical, nutrient limitations, toxicity of the compound, and inactivation or nonexistence of the enzyme capable of degrading the compound (Valentine and Schnoor, 1986).

4.3.8.2. Losses by Abiotic Degradation — Chemical and photodegradation of organic pollutants can be a significant mechanism of removal of these compounds from soil systems. Hydrolysis and oxidation-reduction (redox) reactions are the primary chemical transformation processes occurring in the upper layers of soils (Valentine, 1986). General rate expressions describing transformation of some contaminants by all nonbiological processes are available, and are helpful when division into component reactions is not possible.

Hydrolysis in aqueous systems is characterized by three reaction processes: acid-catalyzed, base-catalyzed, and neutral reactions (i.e., H^+ , OH^- , and H_2O -catalyzed hydrolysis). The overall rate of hydrolysis is the sum of the first-order rates of these processes (Valentine, 1986). In soil systems, sorption of the chemical can increase, decrease or not affect its rate of hydrolysis, as numerous studies cited in Valentine (1986) have shown. The total rate of hydrolysis in soil can be predicted by adding the rates in the soil and water phases, which are assumed first-order at fixed pH (Valentine, 1986). Methods for estimating these hydrolysis constants are described by Lyman et al. (1982). Organic and inorganic compounds also undergo redox reactions in the soil (Valentine, 1986). Organic redox reactions involve exchange of oxygen and hydrogen atoms by the reacting molecules. For example, glucose is oxidized to CO_2

and H₂O by oxygen and the oxygen is reduced to H₂O. Inorganic redox reactions may involve the exchange of atoms or electrons by the reactants.

In soil systems where the identities of oxidant and reductant species are not specified, a first-order rate constant can be obtained for describing loss by redox reactions (Valentine, 1986). Redox reactions involving metals do not constitute a degradative process, but may promote losses by making metals more mobile or more reactive. However, the effect of each redox reactions depends on the metal and on the soil conditions.

Photodegradation or photolysis can be significant for organic compounds found at the soil-atmosphere interface. Photolysis is generally restricted to the first millimeter of soil (Hebert, 1987), though this depth receives a large amount of pollutants through deposition. The presence of sunlight, atmospheric oxygen, and photosensitizing agents at the interface offer a strongly oxidizing environment. Sunlight directly affects the temperature and moisture content of soil, which can indirectly influence the soil's organic matter content, microbial activity, and physicochemical properties (Miller et al., 1989a). Drying of soil (caused by increased soil temperature and decreased moisture content) increases the sorption and retards movement of chemicals in soil. As with other biotic and abiotic degradation processes, photodegradation can result in products that are more toxicologically significant. In a study by Miller et al. (1989b), OCDD was photo-reduced to a variety of lower chlorinated, more toxic dioxins (e.g., 2,3,7,8-TCDD).

4.4. SOIL EXPOSURE PATHWAYS

The three soil exposure pathways described in this document include soil ingestion, dermal contact, and dust resuspension (Chapter 5).

Contaminants from combustor emissions deposited on soil can be ingested incidentally by hand-to-mouth transfer or intentionally by eating soil. Both adults and children may incidentally ingest small amounts of soil; young children (i.e., preschool, 1 to 6 years of age) will incidentally consume more soil than adults and older children. Some children with pica, the intentional ingestion or mouthing of nonfood items, may

consume larger quantities of soil. Both the rate of soil ingestion (i.e., amount/day) and the soil concentration of the contaminant affect exposure by this pathway. Dermal contact with contaminated soil represents a potential route of exposure to combustor emissions for both children and adults. Children can be exposed to contaminated soil when playing in the dirt, whereas adults might be exposed while gardening. The model presented in this chapter estimates human exposure resulting from skin contact with contaminants in the soil. The limited bioavailability of contaminants, both in the particulate fraction of combustor emissions (van den Berg et al., 1983), which are presumed to comprise a large fraction of the contaminant mass in soil, and in the soil, itself (Shu et al., 1988) may significantly reduce the overall importance of this exposure pathway. In addition, the general lack of adequate data for estimation of absorption fractions further limit the applicability of this model.

4.4.1. Soil Contaminant Concentration (C_s). People could possibly be exposed to combustor-emitted contaminants soon after deposition on soil and before contaminants are incorporated into soil layers. Therefore, for this pathway 100% of the deposited contaminant is assumed to be incorporated in the uppermost 1-cm of soil, and ingested soil is assumed to originate from the same 1-cm layer. Another depth of soil incorporation may be chosen if it is more appropriate for a site-specific assessment, such as agricultural activities. The soil concentration as determined in Equation 4-1 ($\mu\text{g/g}$) should be used as input into Equations 4-14 and 4-16.

4.4.2. Soil Ingestion — Human Daily Intake (DI_s). Because this methodology assesses only the risk associated with the increase in exposure due to combustor emissions (incremental risk), the background concentration of contaminants in soil is not included in the quantitation of daily intake.

Human daily intake (DI_s , mg/kg-day) resulting from ingestion of contaminated soil is a function of soil concentration and soil ingestion rate:

$$DI_s = \frac{C_s CR_s ED EF}{AT BW 1000}$$

(4-14)

where:

- DI_s = daily intake of contaminant from soil ingestion (mg/kg-day)
 C_s = concentration of contaminant in soil ($\mu\text{g/g}$ soil)
 CR_s = soil ingestion rate (g soil/day)
 BW = body weight (kg)
 ED = exposure duration (days/year)
 EF = exposure frequency (days/year)
 AT = averaging time (period over which exposure is averaged
(noncarcinogenic effects = $ED \times 365$ days/year) and carcinogenic
= 70 year lifetime $\times 365$ days/year) (U.S. EPA, 1989))
1000 = unit adjustment factor (μg contaminant/mg contaminant)

The DI_s for this pathway is compared with the RfD (reference dose for chronic oral exposure, mg/kg-day) for systemic toxicants to determine if the contaminant adversely affects human health. If the chemical is a carcinogen, the DI_s is used with the human cancer potency to determine excess risk. This is further discussed in Chapter 10.

Key assumptions and limitations for the soil ingestion exposure pathway are:

- ! Deposited emissions are not necessarily incorporated throughout the soil and may be concentrated in the uppermost soil layer. Deposited contaminant is assumed to be distributed within the uppermost 1 cm of soil, and ingested soil is assumed to originate from the same 1 cm layer. This technique over estimates exposure in situations where soil incorporation occurs to any depth >1 cm. If incorporation is to a lesser depth, exposure is underestimated. For example, if exposure is to fallout dust directly, ingested soil could approach 100% deposited particulate.

- ! Deposition-contaminated soil may be ingested intentionally by children at the rates observed in studies. This will over-estimate exposure to the extent the child frequents areas where deposition has not occurred.

4.4.2.1. Soil Ingestion Rate (Cr_s) — Studies of human soil ingestion were reviewed by U.S. EPA (1995). Table 4-1 contains brief summaries of the key studies conducted in children. The results of these studies are presented in Table 4-2. There are many uncertainties associated with these values. For one thing, the studies were all conducted over two weeks or less, which is too short to get a good estimate of usual intake and may not, therefore, be representative of long-term behavior. For another, experimental error in measuring soil ingestion values for individual children appears to have been considerable, such that the range of values seen in different children appears to represent uncertainty more than true variability in behavior; this is especially true of those studies that failed to sample all input and output tracer sources. Other uncertainties include extent of absorption of tracer elements in the body, degree of homogeneity of soil samples, and accuracy of parents' knowledge about their child's play areas.

The results of these studies need to be evaluated cautiously. There are several issues pertaining to study methodology that influence interpretation of the data. One

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TABLE 4-1

Studies of Soil Intake in Children*

| Study Type | Number of Observations | Age | Population Studied | Comments | Study |
|--|--|-----------|--|--|------------------------|
| Tracer study using aluminum, silicon, and titanium | 59 children | 1-3 years | Children living near lead smelter in Montana | Did not account for tracer in food and medicine; used assumed fecal weight of 15 g/day; short-term study conducted over 3 days | Binder et al., 1986 |
| Tracer - mass balance study using aluminum, barium, manganese, silicon, titanium, vanadium, yttrium, and zirconium | 64 children | 1-4 years | Children from greater Amherst area of Massachusetts; highly-educated parents | Corrected for tracer in food and medicine; study conducted over two-week period; used adults to validate methods; one pica child in study group. | Calabrese et al., 1989 |
| Tracer- mass balance | 1 pica child | 3.5 years | 1 pica child from greater Amherst area of Massachusetts | Child was observed as part of the Calabrese et al., 1989 study. | Calabrese et al., 1991 |
| Tracer study using aluminum, acid insoluble residue, and titanium | 18 nursery school children; 6 hospitalized children | 2-4 years | Dutch children | Did not account for tracer in food and medicines; used tracer-based intake rates for hospitalized children as background values; short-term study conducted over 5 days | Clausing et al., 1987 |
| Tracer - mass balance study using aluminum silicon and titanium | 104 children | 2-7 years | Children from 3-city area in Washington State | Corrected for tracer in food and medicine; short-term study conducted over seven-day period; collected information on demographic characteristics affecting soil intake. | Davis et al., 1990 |

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| | | | | | |
|---|--|-----------|--|--|------------------------------|
| Re-evaluation of Binder et al., 1986 data | 59 children | 1-3 years | Children living near lead smelter in Montana | Re-calculated soil intake rates from Binder et al., 1986 data using actual fecal weights instead of assumed weights. | Thompson and Burmaster, 1991 |
| Tracer study using aluminum, acid insoluble residue, and titanium | 292 daycare children; 78 campers; 15 hospitalized children | 1-5 years | Dutch children | Did not account for tracer in food and medicines; used tracer-based intake for hospitalized children as background values; evaluated population (campers) with greater access to soil; evaluated differences in soil intake due to weather conditions. | VanWijnen et al. 1990 |

*Source: U.S. EPA (1995)

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TABLE 4-2

Soil Consumption by Children as Measured by Various Tracer Elements in Key Studies (mg/day)^a

| Mean | | | | | Median | | | | | 95th Percentile | | | | Reference |
|------|-----|----------------------------|------|----|--------|-----|------------------|-----|----|------------------|------------------|-------------------|-----|---------------------------------|
| Al | Si | AIR ^b | Ti | Y | Al | Si | AIR ^b | Ti | Y | Al | Si | Ti | Y | |
| 181 | 184 | -- | 1834 | -- | 121 | 136 | -- | 618 | -- | 584 | 578 | 9590 | -- | Binder et al., 1986 |
| 97 | 85 | -- | 1004 | -- | 45 | 60 | -- | 293 | -- | 197 ^c | 166 ^c | 2105 ^c | -- | Thompson and Burmester, 1991 |
| 232 | -- | 129 | 1431 | -- | 71 | -- | 107 | 259 | -- | -- | -- | -- | -- | Clausing et al., 1987 |
| -- | -- | 162- 213 ^{d,e} | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | Van Wijnen et al., 1990 |
| 39 | 82 | -- | 246 | -- | 25 | 59 | -- | 81 | -- | -- | -- | -- | -- | Davis et al., 1990 |
| 153 | 154 | -- | 218 | 85 | 29 | 40 | -- | 55 | 9 | 223 | 276 | 1432 | 106 | Calabrese et al., 1989 |

^a Source: Adapted from U.S. EPA (1995)

^b AIR = Acid Insoluble Residue

^c 90th percentile

^d Based on limiting tracer (AIR was limiting tracer in about 80% of samples, but Al and Ti were also used)

^e Range according to activity (162 mg/day for children at daycare center, 213 mg/day for children camping)

issue relates to the tracer elements used. It is evident from Table 4-2 that estimates of soil ingestion based on Ti are consistently higher than estimates based on the other tracers, especially for the results reported by Binder et al. (1986), Thompson and Burmaster (1991), and Clausing et al. (1987). The especially high estimates based on Ti in these three studies occurred because the studies did not take into account dietary sources of the trace elements other than soil (e.g., food and medicine). This appears to have been especially significant for Ti, which may occur at relatively high levels in food. Even in the studies that did monitor intake of Ti through food and medicine, estimates of soil ingestion based on Ti were larger, and much more variable, than those for Al and Si (Davis et al., 1990; Calabrese et al., 1989). Calabrese et al. (1989) conducted a validation study in which known amounts of soil containing trace elements were administered to adult volunteers, and found that Ti was much less reliable as a tracer for soil ingestion than Al, Si, or Y.

Another issue relating to the study by Binder et al. (1986) is that fecal weight used to estimate soil ingestion was assumed to be 15 g/day, even though actual fecal weights were roughly half that value. The data reported by Thompson and Burmaster (1991) are those collected by Binder et al. (1986) reanalyzed using the measured fecal weights. The effect this adjustment has on the soil ingestion estimates is evident by comparing the results of these studies in Table 4-2.

The most reliable data, therefore, appear to be soil intake estimates based on Al and Si tracers in the studies by Davis et al. (1990) and Calabrese et al. (1989). Estimates of mean soil ingestion in the study by Calabrese et al. (1989) were considerably higher than those in the study by Davis et al. (1990) (153-154 mg/day versus 39-84 mg/day). Calabrese et al. (1989, 1991) noted that one child in their study exhibited soil pica during the second week of the 2-week study, consuming 10-14 g/day of soil during this time. It appears that mean values reported in this study were skewed by inclusion of a data point that does not represent normal behavior.

This conclusion is confirmed by comparing the median soil ingestion estimates for these two studies, which are very similar (29-40 mg/day for Calabrese et al., 1989,

versus 25-59 mg/day for Davis et al., 1990). The median is affected much less than the mean by inclusion of outlier data points. It is noteworthy that median soil ingestion estimates based on Al and Si tracers from Thompson and Burmaster (1991) and Clausing et al. (1987) are consistent with these values as well (45-71 mg/day), even though dietary intake from sources other than soil was not considered for these data (this may suggest that dietary intake of Al and Si from sources other than soil was not significant for the children in these studies).

Considering the high uncertainty associated with these experimental values, 100 mg/day (0.1 g/day) appears to be a reasonable estimate of central tendency for soil ingestion among non-pica children under 7 years of age. Based on 95th percentile soil ingestion estimates of 223 to 276 mg/day using Al and Si tracers (Calabrese et al., 1989), 300 mg/day (0.3 g/day) appears to be a reasonable estimate of upper percentile soil ingestion among non-pica children of this age group.

These recommendations apply to children with normal mouthing tendencies. Children who exhibit pica (abnormal mouthing behavior), and especially soil pica (deliberate mouthing or ingestion of soil) would have much higher ingestion rates. The child in the Calabrese et al. (1989, 1991) study who showed soil pica behavior consumed 10 to 14 g/day of soil during 1 week of the study. Although 10 to 14 g/day might be a reasonable estimate of short-term soil ingestion for a child displaying soil pica, insufficient information is available to produce a reasonable long-term estimate. For example, the child in the Calabrese et al. (1989, 1991) study displayed soil pica only during the second week of the study; the overall average soil ingestion for this child over the 2-week study period was 5 to 7 g/day. Few data are available regarding the frequency and duration of soil pica behavior in children (U.S. EPA, 1995). Thus, no quantitative basis can be offered to characterize long-term average or upper percentile soil ingestion among children displaying soil pica.

Data regarding soil consumption among adults are scarce. Only one preliminary experimental tracer study has been conducted in adults (Calabrese et al., 1990). This study calculated mean soil ingestion estimates of 110 mg/day based on Al, 30 mg/day

based on Si, 71 mg/day based on Ti, and 63 mg/day based on Y. Median soil ingestion estimates were 60, 31, 102, and 44 mg/day, respectively, based on the same tracers. This study included only six subjects, lasted only 1 week, and was not designed specifically to investigate soil ingestion by adults.

The only other source of an estimate for adult soil ingestion is a study by Hawley (1985), who estimated adult soil ingestion based on assumptions regarding activity patterns and related factors. Hawley estimated annual average adult soil ingestion to be 60.5 mg/day (57 mg/day due to outdoor work in the summer, 0.5 mg/day due to typical living space activities, and 3 mg/day due to periodic exposure to dust in the attic).

An average adult soil ingestion estimate of 50 mg/day (0.05 g/day) would be consistent with the estimate by Hawley (1985) and the preliminary data reported by Calabrese et al. (1990), and would satisfy the reasonable expectation that soil ingestion by adults should be less than that by young children, who were estimated above to have an average soil ingestion rate of 100 mg/day. Because the average soil ingestion recommended for adults is one-half that recommended for children, it may be reasonable to use one-half of the 95th percentile soil consumption for young children (300 mg/day) as an estimate of the 95th percentile soil consumption for adults (150 mg/day or 0.15 g/day).

Consult U.S. EPA (1997) for more detailed discussion of soil ingestion rates among adults and children, including issues related to consumption of indoor dust.

4.4.2.2. Body Weight (BW) — A body weight of 70 kg has traditionally been used by U.S. EPA to represent average adult body weight. Data reviewed by U.S. EPA (1995) support continued use of this value for adults. For children, age-specific body weights (means and upper 90th percentiles for males and females, and overall means for males and females together) are presented in Table 4-3. Consult U.S. EPA (1995) for more detailed information regarding human body weight.

4.4.3. Daily Dermal Intake From Soil. The daily dermal intake (DDI_s , mg/kg-day) represents the increase above background in daily human dermal intake of the contaminant due to combustor emissions. The DDI_s is determined as follows:

| TABLE 4-3 | | | | | |
|---|-------|-----------------|---------|-----------------|-----------------|
| Body Weights of Adults and Children (kg) ^{a,b} | | | | | |
| Age | Males | | Females | | Males + Females |
| | Mean | 90th Percentile | Mean | 90th Percentile | Mean |
| <1 | 9.4 | 10.9 | 8.8 | 10.4 | 9.1 |
| 1 | 11.8 | 13.6 | 10.8 | 12.7 | 11.3 |
| 2 | 13.6 | 15.8 | 13.0 | 14.9 | 13.3 |
| 3 | 15.7 | 17.9 | 14.9 | 17.4 | 15.3 |
| 4 | 17.8 | 20.9 | 17.0 | 20.2 | 17.4 |
| 5 | 19.8 | 23.7 | 19.6 | 24.7 | 19.7 |
| 6 | 23.0 | 28.3 | 22.1 | 28.9 | 22.6 |
| 7 | 25.1 | 29.6 | 24.7 | 30.3 | 24.9 |
| 8 | 28.2 | 35.5 | 27.9 | 33.2 | 28.1 |
| 9 | 31.1 | 38.6 | 31.9 | 43.3 | 31.5 |
| 10 | 36.4 | 46.3 | 36.1 | 45.8 | 36.3 |
| 11 | 40.3 | 57.0 | 41.8 | 56.6 | 41.1 |
| 12 | 44.2 | 58.9 | 46.4 | 60.5 | 45.3 |
| 13 | 49.9 | 64.2 | 50.9 | 66.4 | 50.4 |
| 14 | 57.1 | 68.9 | 54.8 | 67.6 | 56.0 |
| 15 | 61.0 | 72.8 | 55.1 | 65.5 | 58.1 |
| 16 | 67.1 | 82.2 | 58.1 | 73.3 | 62.6 |
| 17 | 66.7 | 82.3 | 59.6 | 71.6 | 63.2 |
| 18 | 71.1 | 83.5 | 59.0 | 70.1 | 65.1 |
| 19 | 71.7 | 86.8 | 60.2 | 74.8 | 66.0 |
| 18-74 | 78.1 | 95.7 | 65.4 | 84.4 | 71.8 |

^a Source: Adapted from U.S. EPA (1995) and NCHS (1987)

^b includes clothing weight, estimated as ranging from 0.09-0.28 kg

$$DDI_s = \frac{DA_{event} EF A}{BW 365} \quad (4-15)$$

where:

- DDI_s = daily dermal intake of contaminant from soil (mg/kg-day)
DA_{event} = absorbed dose per event (mg/cm²-event)
A = skin surface area available for contact (cm²)
EF = exposure frequency (events/year)
BW = body weight (kg)
365 = adjustment to calculate average daily dose (days/year)

The assumptions and uncertainties associated with each of these input parameters are discussed in the following sections.

To assess whether the contaminant poses a risk to human health by this pathway, the DDI_s may be compared with a dermal RfD (if available) or may be transformed to an equivalent oral DI_s (U.S. EPA, 1992; see also Chapter 10, Section 10.2.1.1.1.) and compared with the oral RfD for chronic exposure for systemic toxicants. In addition, the risk assessor is strongly encouraged to refer to the decision matrix found in Section 9 of the “Dermal Exposure Assessment” document (U.S. EPA, 1992). If the chemical is a carcinogen, the DDIs may be used with the dermal human cancer potency (if available) or may be transformed to an equivalent oral DI_s and used with the human oral cancer potency to determine excess risk (ER) Assessment of risk to humans is discussed in Chapter 10.

4.4.3.1. Estimating the Dermally Absorbed Dose per Event (Da_{event}) — The absorbed dose per event (DA_{event}) is estimated as follows:

$$DA_{event} = C_s AF ABS 10^3 \quad (4-16)$$

where:

| | | |
|---------------------|---|---|
| DA_{event} | = | absorbed dose per event (mg/cm ² -event) |
| C_s | = | concentration of contaminant in soil (µg/g soil) |
| AF | = | adherence factor of soil to skin (mg soil/cm ² -event) |
| ABS | = | absorption fraction |
| 10^3 | = | unit adjustment factor ((µg soil/g soil) |

U.S. EPA (1992) notes that theoretical models that estimate DA_{event} on the basis of a soil/skin permeability coefficient rather than ABS are being investigated. The permeability coefficient approach offers some advantages in that the coefficient should remain constant over a wider range of conditions, such as the amount of soil on the skin and the concentration of the chemical in the soil. This approach is also better suited to considering nonsteady-state conditions than ABS. However, since these procedures are not as well developed, it is currently recommended that the users first consider the ABS procedures for estimating dose.

A more complex two-layer dermal uptake model for soil exposure has been published (McKone, 1990). The model is a two-layer model which incorporates competing loss processes in addition to dermal absorption (see Text Box 4-1). As the dermal route of exposure is estimated to comprise only a small fraction of the total exposure, and the two-layer model requires significantly more data for the additional parameters, the simple absorption fraction model presented in Equation 4-16 is judged to be adequate in this application.

4.4.3.2. Absorption Fraction (ABS) — The absorption fraction (ABS) is the relative amount of a substance on the skin that penetrates through the epidermis into the body; it is generally reported as the unitless fraction of the applied dose or as the percent absorbed. The ABS is a chemical-specific quantity that depends on the physicochemical properties of the contaminant (e.g., lipid solubility, molecular size), but

may also be affected by soil characteristics (e.g., particle size, organic carbon content), skin characteristics (e.g., age, anatomical location, damage), physical factors (e.g.,

Text Box 4-1. The Next Generation of Dermal-Contact Soil Exposure Models:

McKone (1990) presents a two-layer model that shows the dependency of dermal absorption on chemical properties (4 parameters), soil properties (7 parameters), skin properties (4 parameters), and exposure conditions (4 parameters). The two-layer model was based on a previous model that showed that the efficiency of dermal uptake can decrease with increasing thickness of applied soil (Kissel and McAvoy, 1989; Kissel and Robarge, 1988). McKone (1990) presented results of the two-layer model and two less-complex linear models (Hawley, 1985; Sedman, 1989) applied to four compounds of widely varying K_{ow} and K_h : 2,3,7,8-TCDD, hexachlorobenzene (HCB), benzene, and trinitrotoluene (TNT). The two-layer model gave significantly different predictions than the linear models, with the linear models yielding both overestimates and underestimates (compared to the two-layer model) across the range of applied soil thickness of 0.5 to 2 orders of magnitude on the average. There was no specific range of applied soil thickness that yielded consistently better agreement among the models. McKone (1990) concluded that the efficiency of contaminant uptake depended strongly on the amount of soil on the skin surface. In addition, McKone (1990) suggested a few generalizations arising from the model results:

- 1) for compounds with a $K_{ow} \leq 10^6$ (e.g., TCDD), 100% absorption in 12 hours is a reasonable assumption;
- 2) for compounds with a $K_h \geq 0.01$, absorption is unlikely to exceed 40% in 12 hours and will be much less when $K_{ow} > 10$;
- 3) for compounds with a $K_h \geq 0.1$, absorption is unlikely to exceed 3% in 12 hours.

McKone (1990) identified a few remaining issues that need resolution with properly designed experiments, such as the assumption that soil on skin behaves as a matrix of soil particles mixed with air and water (as opposed to attaching to skin as individual particles) and the relationship between K_{ow} and skin permeability (the model predicted increasing permeability with decreasing K_{ow} , resulting from the assumption that transport through the skin occurs only in the aqueous phase).

Burmester and Maxwell (1991) ran the McKone (1990) model for a series of polyaromatic hydrocarbons with widely varying K_h and K_{ow} . For the most lipophilic ($\log K_{ow} > 4.5$) and least volatile of these compounds ($K_h < 10^{-3}$), the fraction absorbed was highly sensitive to the mass of the soil applied to the skin, varying from almost 100% to less than 1% for soil loadings of 0.1 mg/cm² and 100 mg/cm², respectively.

temperature, humidity), and extent of exposure (e.g., amount of soil on the skin, duration of soil contact with the skin). Therefore, there is a great deal of uncertainty associated with absorption fraction estimates. Some of this uncertainty is reflected in the available estimates being presented as ranges rather than single values. It should be noted that standard methods for adjusting experimental ABS do not exist and attempts to make adjustments should be done with caution.

When assigning an absorption fraction to a compound, first priority is given to values determined experimentally. However, experimentally derived values of percutaneous absorption from soil, expressed as the percentage of the applied dose absorbed, have been reported for only 16 chemicals (14 organic chemicals and 2 inorganic chemicals): 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), 3,3',4,4'-tetrachlorobiphenyl (PCB 77), benzo[a]pyrene (B[a]P), DDT, benzene, toluene, xylene, 2,4-D, PCBs(Aroclor 1242 and 1254), arsenic, phenol, pentachlorophenol, and cadmium (Bunge and Parks, *in press*). Even for these chemicals, experimental values generally cannot be used directly in exposure assessments because the experimental conditions are usually not completely consistent with conditions in the environment. Consequently, the results of each study must be scrutinized in light of the assumptions of the exposure assessment, and the experimental results must be adjusted to reflect likely percutaneous absorption under the conditions of the exposure assessment. U.S. EPA (1992) discusses the specific issues involved (e.g., use of *in vitro* data, use of animal data, quantity of soil in contact with skin, duration of soil contact with skin) and how these issues were addressed for the existing data set. After analyzing the available data, U.S. EPA (1992) was able to offer recommended absorption fractions from soil for only three chemicals based on experimental data. These recommendations are presented in Table 4-4.

Predictive procedures for estimation of the absorption fraction from soil include use of structural analogy, data on neat absorption, oral bioavailability data, and permeability coefficients. Most of these approaches are very limited, with some providing upper bound, rather than central tendency, estimates for ABS. For this reason, DI estimates should not be summed with exposures from other routes (as discussed in Chapter 10)

without a determination of representativeness of the central tendency. The more robust approach based on permeability coefficients has not been tested adequately.

Otherwise, because the absorption fraction is heavily dependent

| Chemical | Percent Absorbed |
|-------------------|------------------|
| TCDD ^b | 0.1 - 3% |
| TCB ^c | 0.6 - 6% |
| Cadmium | 0.1 - 1.0% |

^aSource: U.S. EPA (1992)

^bUpper bound of 3% considered appropriate for use with other PCDD/Fs

^cUpper bound of 6% considered appropriate for use with other PCBs and Aroclors

upon compound-specific properties, it may be possible to make qualitative judgments regarding likely significance of this route of exposure for some chemicals on the basis of properties. Relevant chemical-specific properties include lipophilicity, water solubility, polarity, volatility, and chemical structure. Discussion of how these properties might influence dermal absorption of a chemical is found in U.S. EPA (1992).

Structural Analogy. After analyzing the available data, U.S. EPA (1992) concluded that use of the upper bound absorption fraction for TCDD (3%) would be sufficiently conservative for use in assessments of other polychlorinated dibenzo-p-dioxins and polychlorinated furans (PCDD/Fs), and that use of the upper bound absorption fraction for PCB 77 (6%) would be appropriate for assessments of other PCBs and Aroclors.

Data on Absorption from Deposited Neat (undiluted or mixed) Chemicals. In some cases, percutaneous absorption of the neat compound will have been studied when data on absorption of the chemical applied in soil are not available. In these types of

studies, the chemical is usually applied in a solvent, such as acetone, which evaporates, leaving behind the pure compound. In such a study, the compound can usually be considered to be completely bioavailable in the sense that it is unbound to a vehicle and is in contact with the absorption barrier (i.e., the skin). Thus, the fraction of the neat compound that is absorbed will likely represent an upper bound on the fraction absorbed from soil, where the chemical may be bound to some extent to combustion particles and soil particles, and where not all of the chemical may be immediately in contact with the skin surface. In some cases, particularly for volatile organics, neat absorption data may actually underestimate absorption from soil, as thicker layers of soil may inhibit volatilization (see the modeling analysis of benzene and naphthalene in Burmaster and Maxwell, 1991). Also, experimentally-determined neat absorption fractions may be dependent on the thickness of the applied layer (U.S. EPA, 1992).

Data on Oral Bioavailability. The Agency is investigating the use of absorption fractions for chemicals in the gastrointestinal tract as upper bounding estimates for absorption via the dermal route. Such absorption fractions, sometimes referred to as oral bioavailability, are often available for chemicals administered in a variety of vehicles, including feed, water, and occasionally soil. When chemicals are administered in solid vehicles such as feed and soil, oral absorption fractions provide a combined estimate of the fraction of an administered dose that is extracted from the vehicle and subsequently absorbed. Absorption is generally believed to be greater via the oral route than via the dermal route.

Some issues need to be resolved in order to confidently use such data as upper estimates of bioavailability. If the chemical is administered in a vehicle other than soil, the affinity of the chemical for the vehicle may reduce absorption in the GI tract. Some studies report the fraction of the chemical excreted in feces as a measure of material that is not absorbed. However, because some chemicals are excreted in feces after absorption, the assumption that the fraction of the dose that is not in the feces was absorbed produces a minimum estimate rather than an upper bounding estimate of oral absorption.

Estimation of ABS from Permeability Coefficients and Soil loss Constants. For some chemicals, it may not be possible to derive a reasonable estimate of absorption fraction by any of these means. Theoretical models of dermal absorption from soil have been proposed, but generally rely upon permeability coefficients rather than absorption fractions, and in any case, are not well developed (see U.S. EPA, 1992). However, the model presented in Section 6.3.3. or U.S. EPA (1992) can be used to estimate ABS for a rough approximation of DA_{event} (Eq. 4-16), but the accuracy of such an estimate cannot be assessed at this time.

Because the absorption fraction is heavily dependent upon compound-specific properties, it may be possible to make qualitative judgments regarding likely significance of this route of exposure for some chemicals on the basis of properties. Relevant chemical-specific properties include lipophilicity, water solubility, polarity, volatility, and chemical structure. Discussion of how these properties might influence dermal absorption of a chemical is found in U.S. EPA (1992).

4.4.3.3. Adherence Factor (AF) — The adherence factor (AF) is defined as the amount of soil accumulating on the skin upon dermal contact with soil (mg/cm^2). Adherence of soil to skin can vary considerably, depending on the particular circumstances of exposure. For one thing, soil properties have been found to influence adherence. Adherence increases with increasing moisture content and decreases with increasing particle size, although it is only slightly affected by clay and organic carbon content (Kissel et al., 1996; Driver et al., 1989). Adherence is also affected by the type of activity in which the exposed individual is engaged and the region of the body contacted (Kissel et al., 1996). In general, adherence is highest in outdoor workers, followed by outdoor recreation (rugby played on a wet field) and gardening activities. The key factors are clothing, conditions (wet/dry) and level of activity. The hands, knees, and elbows tend to have the highest adherence values, while the face tends to have the lowest. Table 4-5 is a summary of the results obtained by Kissel et al. (1996) regarding influence of activity and body contact region on soil adherence. The very highest adherence values, 2 to 3 orders of magnitude higher than for other conditions

tested, were for children playing in mud. This suggests that individuals contacting wet soils, for example by wading or engaging in other shore area recreational activities, may have adherence values considerably higher than individuals engaged in other activities.

The results of other studies of dermal adherence reviewed by U.S. EPA (1992, 1995) are summarized in Table 4-6. Based on the data contained in Table 4-4, U.S.

| TABLE 4-5 | | | | | |
|--|------------|---------------|---------------|-------------|------------------|
| Mean Soil Adherence by Activity and Body Region (mg/cm ²)* | | | | | |
| Activity | Body Part | | | | |
| | Hands | Arms | Legs | Face | Feet |
| Tae Kwon Do | 0.0062 | 0.0019 | 0.0020 | -- | 0.0024 |
| Greenhouse Workers | 0.043 | 0.0064 | 0.0015 | 0.0051 | -- |
| Soccer Players | 0.035-0.11 | 0.0011-0.0043 | 0.0081-0.031 | 0.012-0.016 | -- |
| Grounds Keepers | 0.030-0.15 | 0.0021-0.023 | 0.0008-0.0012 | 0.0021-0.01 | 0.0041- 0.018 |
| Irrigation Installers | 0.19 | 0.18 | 0.0054 | 0.0063 | -- |
| Rugby Players | 0.4 | 0.27 | 0.36 | 0.059 | -- |
| Farmers | 0.41-0.47 | 0.059-0.13 | 0.0059-0.037 | 0.018-0.041 | -- |
| Reed Gatherers | 0.66 | 0.036 | 0.16 | -- | 0.63 |
| Kids-in-Mud | 35-58 | 11 | 9.5-36 | -- | 6.7-24 |

*Source: Adapted from Kissel et al. (1995) and U.S. EPA (1995)

EPA (1992) recommended using an average value of 0.2 mg/cm², and an upper percentile value of 1.0 mg/cm² to represent dermal adherence of soil. A site-specific approach, which takes into account the type of activity and the region of the body contacted, might be more appropriate. U.S. EPA (1995) recommends using the data presented in Table 4-6 (numerical values are geometric means and the numerical ranges reflect multiple group means) to select adherence values for activities that best match those of the population being assessed. The adherence factor in all the studies described above represents the amount of soil on the skin at the time of measurement. Assuming that the amount measured on the skin represents its accumulation between washings and that people wash at least once per day, then these adherence values could be interpreted as daily contact rates. However, because the residence time of soils on skin has not been studied, and because the adherence studies are independent of time, this is not recommended. Instead, U.S. EPA (1992, 1995) recommends that these adherence values be interpreted on an event basis (i.e., mg/cm²/event). Consult U.S. EPA (1992, 1995) for more detailed discussion of soil adherence values.

4.4.3.4. Exposure Frequency (EF) — Exposure frequency refers to how often the contact event occurs (i.e., events/year). A range of values for the frequency of soil contact has been developed in past exposure assessments. These estimates, shown in Table 4-7, were derived from consideration of seasonal factors that may influence human activity patterns and soil conditions. The upper end of the range presented in Table 4-7 is based on the rationale that in warmer climates, people who actively garden or play outdoors could have contact with soil almost every day. However, in cooler climates, outdoor activities involving soil contact may occur only during about half of the year. Where the contaminated soil is located outside the residential property, contact may only occur a few days/year. In summary, this is a highly site-specific value that could range from a few days/year to every day. For default purposes, a typical value for an adult who gardens or works outside 1 to 2 days/week during the warmer

months may correspond roughly to Hawley's estimate (after rounding) of 40 days/year.

For

| TABLE 4-6 | | | |
|--------------------------------------|--------------------|--------------------------------------|-----------|
| Soil Adherence Values ^a | | | |
| Reference | Size Fraction (µm) | Soil Adherence (mg/cm ²) | Body Part |
| Lepow et al., 1975 | -- | 0.5 | hands |
| Roels et al., 1980; Sedman, 1989 | -- | 0.9 | hands |
| Que Hee et al., 1985 ^b | -- | 1.5 | hands |
| Driver et al., 1989 ^c | <150 | 1.40 | hands |
| | <250 | 0.95 | hands |
| | unsieved | 0.58 | hands |

^aSource: Adapted from U.S. EPA (1995)

^bAssume exposed area = 20 cm²

^cFive different soil types and 2-3 soil horizons (top soils and subsoils)

| TABLE 4-7 | |
|---|--------------------------|
| Assumptions of Frequency of Exposure to Soil* | |
| Range | Reference |
| 350 days/year | U.S. EPA, 1989 |
| 247-365 days/year | U.S. EPA, 1984 |
| 180 days/year | Paustenbach et al., 1986 |
| 130 days/year (<2-5 years) | Hawley, 1985 |
| 130 days/year (older children) | Hawley, 1985 |
| 43 days/year (adults) | Hawley, 1985 |

*Source: U.S. EPA (1992)

consistency with the default value for the frequency of soil ingestion recommended by U.S. EPA (1989a), an upper estimate of 350 days/year was selected.

If the contaminated soil is carried into the house from the surrounding area, household dust may be contaminated at levels approaching those found outdoors. In certain instances, therefore, the risk assessor may need to consider the frequency of dermal contact with contaminated indoor dust in addition to the frequency of dermal contact with soil.

4.4.3.5. Skin Surface Area (SA) — Total dermal intake of a contaminant is approximately proportional to the exposed surface area. Data regarding total body surface area of human adults and children were reviewed by U.S. EPA (1992, 1995), and median and upper 95th percentile values are presented in Table 4-8. For dermal exposure to soil, it is not expected that the entire body will be exposed. Instead, the exposed surface area will be some percentage of the total surface area. U.S. EPA (1992, 1995) reported the exposed surface area associated with different soil exposure scenarios. Exposed surface area for these scenarios ranged from roughly 10% of total surface area when exposure was limited to the head and hands to roughly 25% of total surface area when the head, hands, forearms, and lower legs were considered to be exposed. Because some studies have suggested that exposure can occur under clothing (see U.S. EPA, 1992), and this type of exposure was not considered in the scenarios described above, U.S. EPA (1992, 1995) suggested using the upper end of this range (25%) to derive defaults for body surface area exposed to soil.

U.S. EPA (1992, 1995) recommended using values of 20,000 and 23,000 cm² to represent central tendency and 95th percentile adult total body surface areas, respectively. Applying 25% to these values for total body surface area produces default soil-exposed surface areas for adults of 5000 cm² (central tendency) and 5800 cm² (95th percentile). For children, default soil-exposed surface areas (50th and 95th percentile) can be derived by multiplying the 50th and 95th percentile total surface area values for the appropriate age group from Table 4-8 by 0.25.

| TABLE 4-8 | | | | |
|--|--------|-----------------|---------|-----------------|
| Total Surface Area of Adults and Children of Various Ages (m ²)* | | | | |
| Age | Males | | Females | |
| | Median | 95th Percentile | Median | 95th Percentile |
| 2 | 0.603 | 0.682 | 0.579 | 0.653 |
| 3 | 0.664 | 0.764 | 0.649 | 0.737 |
| 4 | 0.731 | 0.845 | 0.706 | 0.820 |
| 5 | 0.793 | 0.918 | 0.779 | 0.952 |
| 6 | 0.866 | 1.06 | 0.843 | 1.03 |
| 7 | 0.936 | 1.11 | 0.917 | 1.13 |
| 8 | 1.00 | 1.24 | 1.00 | 1.18 |
| 9 | 1.07 | 1.29 | 1.06 | 1.41 |
| 10 | 1.18 | 1.48 | 1.17 | 1.43 |
| 11 | 1.23 | 1.60 | 1.30 | 1.62 |
| 12 | 1.34 | 1.76 | 1.40 | 1.70 |
| 13 | 1.47 | 1.81 | 1.48 | 1.86 |
| 14 | 1.61 | 1.91 | 1.55 | 1.88 |
| 15 | 1.70 | 2.02 | 1.57 | 1.83 |
| 16 | 1.76 | 2.16 | 1.60 | 1.91 |
| 17 | 1.80 | 2.09 | 1.63 | 1.94 |
| | | | | |
| 3-5 | 0.728 | 0.876 | 0.711 | 0.879 |
| 6-8 | 0.931 | 1.14 | 0.919 | 1.13 |
| 9-11 | 1.16 | 1.52 | 1.16 | 1.56 |
| 12-14 | 1.49 | 1.85 | 1.48 | 1.82 |
| 15-17 | 1.75 | 2.11 | 1.60 | 1.92 |
| | | | | |
| Adult | 1.94 | 2.28 | 1.69 | 2.09 |

*Source: Adapted from U.S. EPA (1995)

Assessors may want to refine estimates of surface area exposed on the basis of seasonal conditions. For example, in moderate climates, it may be reasonable to assume that 5% of the skin is exposed during the winter, 10% during the spring and fall, and 25% during the summer. Consult U.S. EPA (1992, 1995) for more detailed discussion of dermal surface area of adults and children, including surface area data for specific parts of the body that may be exposed to soil under various conditions.

4.4.3.6. Uncertainty in the Soil Dermal Exposure Model — Some idea of the uncertainty can be obtained from the range of percent absorbed values reported. For example, the range of experimentally-determined absorption fractions for TCDD, PCB 77, and cadmium is an order of magnitude or larger. Absorption fractions will likely vary even more with varied soil loadings and exposure durations. An analysis of the McKone two-layer dermal absorption model (McKone, 1990) shows up to two orders of magnitude variation in uptake fractions across varied soil loadings and exposure durations for several (modeled) organic compounds (Burmester and Maxwell, 1991). The potential for introducing a conservative bias to the exposure assessment depending on the approach used to estimate ABS has already been mentioned (Section 4.4.3.2.).

Additionally, both the amount of soil adhering to skin and exposure frequency are highly uncertain. Finley et al. (1994) propose soil-to-skin adherence distributions (based on published studies) that show about an order of magnitude variation between the median and 95th percentile estimates. Exposure frequency could vary by almost an order of magnitude also (Table 4-7).

Model uncertainty is probably high, as well. The two-layer model gave significantly different predictions than the linear models, with the linear models yielding both overestimates and underestimates (compared to the two-layer model) across the range of applied soil thickness of 0.5 to 2 orders of magnitude on the average (McKone, 1990).

Accordingly, final dose and risk estimates must be considered highly uncertain. The overall magnitude of the range of uncertainty in the output of the dermal exposure

model can be appreciated by a Monte Carlo analysis as described in Chapter 10 of this document. Specification of the distributions assigned to each of the inputs, however, remains as a research exercise. Some idea of the range of possible values can be obtained by using central tendency (average or typical) values for each parameter (use the center of the percent absorbed range where available) to get a central tendency dose estimate. Then, by setting two or three of the most variable parameters to their upper values and the others to their central-tendency values, it is possible to get an approximation of an “upper-bound” estimate, but of unspecified probability. Otherwise, by varying each input parameter one at a time, the contribution of each input to the variability of the output can be investigated as a simple sensitivity analysis (see Chapter 10).

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DUST RESUSPENSION

5.1. INTRODUCTION

Dust resuspension may be considered an important exposure pathway under certain conditions because of the potential for deposited contaminants to be recycled into the air and subsequently inhaled by humans (Sehmel, 1980). Moosmüller et al. (1998) reported resuspended dust is largely responsible for high PM₁₀ (particles with diameters less than 10 micrometers) concentrations during warm months in urban and non-urban areas. This chapter evaluates the resuspension of dust particles from soils that contain contaminants emitted from combustion sources. Resuspension involves the deposition of substances from the air and their subsequent resuspension or re-entrainment into the atmosphere. As mentioned in Chapter 4, contaminant particles emitted from combustors are released in the atmosphere and subsequently deposited on soil, vegetation, and surface water downwind from the combustor. Contaminant particles deposited on soil may become aggregated with soil particles, which can be resuspended into the air by natural (i.e., wind erosion) and mechanical disturbances such as tilling of agricultural fields or vehicular traffic on paved or unpaved roads (Sehmel, 1980 and Scott et al., 1997) and construction and demolition of buildings and roads, and storage piles (Moosmüller et al., 1998)

Since the contribution of dust resuspension to human health risk may not always be important (U.S. EPA, 1990), only dust sources that are considered significant contributors are presented in this chapter: wind erosion, agricultural tilling, and vehicular traffic on paved and unpaved roads. Procedures for estimating dust emissions from these sources are based on *AP-42* (U.S. EPA, 1985, 1996a), *Control of Open Fugitive Dust Sources* (U.S. EPA, 1988), and *Air Quality Criteria for Particulate Matter* (U.S. EPA, 1996b) are described below in Sections 5.3., 5.4., and 5.5. Emission factors for other dust sources that might be considered important for a particular assessment may be found in *AP-42*. The algorithms that follow should be used to screen for the significance of this pathway in the site assessment. This is

accomplished in a two step process. First, an emission rate for each process is estimated. Second, the emission rate is used to calculate the contaminant resuspension flux.

5.2. OVERVIEW OF DUST RESUSPENSION

The risk assessor, in evaluating this pathway, must identify potential sources of dust generation within the study area (e.g., agricultural fields, roads) and assess the potential for exposure from these sources on the basis of environmental conditions (e.g., climate, soil, topography), location of the sources relative to receptors, and characteristics of the sources (e.g., size, traffic volume). Since the contribution of the dust resuspension pathway to human health may not always be significant (U.S. EPA, 1990), the algorithms presented in this methodology should be used for the initial screening of this exposure pathway. If dust emissions from identified sources seem likely to contribute to exposure, then these sources can be treated as area source inputs to the air dispersion model. In this way, the resuspended dust emissions can be added with the direct combustor emissions to determine air concentrations and deposition rates at downwind receptor locations. However, if the predicted air concentrations are less than 1% of the air concentration predicted to occur from stack emissions, then fugitive dust emissions may be neglected.

5.2.1. Sources of Dust. Atmospheric dust arises from natural or mechanical disturbances of eroded granular material. Resuspended dusts arise from many sources and a distinction is made between fugitive dusts, and reentrained dusts (U.S. EPA, 1995). Fugitive dust refers to dust put into the atmosphere by wind blowing over plowed fields, dirt roads, deserts, and areas with little or no vegetation. Reentrained dust is put into the air by agricultural operations (e.g., tilling) and by vehicles driving over dirt roads, dirty roads, and dusty areas (i.e., mechanical forces). This methodology considers the impact of stack emissions from an industrial source (Chapter 3) as well as dust sources (outside the industrial source being modeled) that may affect adjacent soils, surface waters, and vegetation. The key assumptions related to the dust resuspension pathway are:

- ! Resuspended dust (containing aggregated contaminant) can add to exposure by the direct inhalation and by indirect routes when the resuspended dust is deposited on soil, vegetation, or surface water.

- ! Transport is important in determining whether the resuspension changes the impact of the dust. Dust that is resuspended and deposited back onto the original area source will not impact the soil concentration at the source; there is no net effect. It is only when the dust is transported to physically distinct areas beyond the source (e.g., dust from roadways depositing onto adjacent soils or vegetation, dust from agricultural tillage depositing onto nearby residences) that it becomes important to evaluate the impact, since it increases the exposure at this point.

- ! Since the contribution of dust resuspension to human health risk may not always be important, only the most significant dust sources should be considered on a site-specific basis.

5.2.2. Environmental Conditions of Dust Generation. Environmental conditions are important in assessing resuspension of solid particles. In order for wind to cause erosion, the land surface must be sufficiently dry and have areas with little or no vegetative cover. The factors affecting dust resuspension due to wind disturbances include moisture content, presence of nonerodible surfaces (i.e., rocks and vegetation), wind velocity, particle size, surface crust stability, and soil roughness height.

Moisture hinders the resuspension of dust by forming a cohesive matrix among the dust or soil particles. When the soil is saturated, erosion will not occur (Sehmel, 1980). As the surface layer moisture is removed by evaporation, resuspension may occur. Evaporation is influenced by wind speed, temperature, and soil characteristics.

The presence of nonerodible surfaces reduces the amount of dust resuspension by decreasing the soil surface area exposed to the wind. Nonerodible surfaces include clumps of grass, and stones >1 cm in diameter.

Particle size influences the wind speed required to initiate dust resuspension by wind erosion. Particles ranging in diameter from 100 to 150 μm have the lowest threshold wind speeds (wind speed required to initiate soil erosion). As the particle size decreases below 100 μm the threshold speed increases. For particles larger than 150

μm , the threshold speed also increases. If particle sizes are mixed, the threshold wind speed is less than the speed required to erode the largest particle (Sehmel, 1980).

The surface crust, which is composed of small particles, hinders wind erosion and evaporation. Thus, crusted surfaces have greater threshold friction velocities. Soils without crusts, such as sandy or disturbed soils, are more erodible (U.S. EPA, 1985).

Soil roughness height is related to height, width, and spacing of clods and furrows. This parameter is required to convert the threshold friction velocity to a wind speed comparable with the wind speeds at 7 m above the surface (U.S. EPA, 1985). Cowherd and Guenther (1976) developed the roughness height scale for various conditions of ground cover, such as natural snow and plowed fields (U.S. EPA, 1976).

Various methodologies have been developed to determine the soil erosion caused by wind. However in applying these methods to deposited combustor emissions, the analyst should review the approaches discussed in U.S. EPA (1985), and Sehmel (1980) to select the most appropriate methodology for the exposure scenario.

5.2.3. Location of Dust Sources Relative to Receptor. When determining exposure to pollutants deposited onto the study area by resuspension processes, one must examine the proximity of the area source to the receptor. The resuspended dust pathway is considered only when particles are deposited onto adjacent, but physically distinct, water, land, or vegetation (e.g., dust from roadways depositing onto adjacent soils or vegetation, dust from agricultural tillage depositing onto nearby residences). In other words, dust that is resuspended and deposited back onto the original area source will not impact the soil concentration at the source; this process has no net effect. Only when the dust is transported beyond the source does it become important to evaluate the impact. Resuspension of dust can make an important contribution under certain circumstances. For example, an intervening area of agricultural fields between a combustor and a downwind residential community might lead to substantial exposure, particularly areas such as the west and southwest United States, which have characteristically high dust emissions.

5.3. GENERATION OF AGRICULTURAL DUST

5.3.1. Agricultural Wind Erosion. The terms used to describe soil movement by wind are suspension, saltation, surface creep, and resuspension. Suspension applies to small particles (ranging from $\leq 50 \mu\text{m}$ (Smith et al., 1982) to a maximum of $100 \mu\text{m}$ (Sehmel, 1980) that are kept airborne by wind forces. Saltation involves particles being bounces over the surface by the wind. These particles, ranging in size from 80 to $1000 \mu\text{m}$, are too heavy to be aloft and quickly fall back to the surface (Smith et al., 1982). When heavy particles (generally over $1000 \mu\text{m}$) are rolled or slide across the surface, this process is called surface creep. Resuspension describes the re-entry of previously deposited contaminants back into the atmosphere. Particle size distribution is an important parameter in the assessment of dust resuspension as a potential exposure pathway.

Although this section refers to an agricultural setting, the same concepts apply to dust generated by wind eroding exposed areas on public property or within an industrial setting (U.S. EPA, 1988). Nonuniform land surfaces (e.g., land surfaces interspersed with nonerodible elements such as stones or clumps of vegetation) are considered to have a finite or “limited” reservoir of erodible material. The presence of nonerodible surfaces reduces the amount of dust available for resuspension by decreasing the soil surface area exposed to the wind. On the other hand, bare surfaces of finely divided material, such as sandy or dry agricultural soil, are considered to provide an “unlimited” reservoir of erodible material. These surfaces require lower threshold wind speeds for erosion to take place. The cutoff threshold friction velocity separating “limited” and “unlimited” particle reservoirs has been defined at 50 cm/s (U.S. EPA, 1988) based on observations of highly erodible surfaces (e.g., sandy surface soils). This corresponds to an ambient wind speed of about 7 m/s (15 mph) measured at a height of about 7 m (U.S. EPA, 1988). Surfaces with friction velocities larger than 50 cm/s tend to be composed of aggregates too large to be eroded, mixed in with a small amount of erodible material or crusts that are resistant to erosion. For example, an area covered with a continuous layer of grass has minimal soil erosion by wind compared with a fallow agricultural field consisting of erodible particles.

For this methodology, wind erosion of open, plowed fields (agricultural wind erosion) is considered to present a potentially significant impact. Factors that affect whether wind will resuspend dust in agricultural fields include soil erodibility, surface roughness, climate (e.g., precipitation and evaporation), unsheltered field width, and vegetative cover (after harvest). The average emission rate per unit area of contaminated agricultural field with unlimited erosion potential (E_p) is calculated by U.S. EPA (1988):

$$E_p = 8E-6 \cdot k \cdot a_{sus} \cdot K \cdot KSR \cdot cf \cdot L' \cdot V'$$

(5-1)

where:

- E_p = emission of resuspended dust due to wind erosion (g/m^2 -sec)
- 8E-6 = conversion factor [(1.016E+6 g/ton) / (4.047E+3 m^2 /acre)(3.1536E+7 sec/yr)]
- k = particle size multiplier for total suspended particulate matter (unitless); 1.0 (U.S. EPA, 1985)
- a_{sus} = portion of total wind erosion losses expected to be measured as suspended particulate (unitless); 0.025 (U.S. EPA, 1988)
- K = soil erodibility (ton/acre-yr)
- KSR = surface roughness factor (unitless)
- cf = climatic factor (unitless)
- L' = unsheltered field width factor (unitless)
- V' = vegetative cover factor (unitless)

Soil erodibility (K) is a function of the amount of erodible fines in the soil, with aggregates ≤ 0.84 mm in diameter being considered erodible (U.S. EPA, 1988). This term is related to a rough size distribution of the soil and is usually associated with the soil texture. If the percentage of erodible aggregates ≤ 0.84 mm in diameter has been measured, then soil erodibility can be determined from the experimental plot provided in Figure 7-1 of the EPA document (U.S. EPA, 1988). When particle size distributions

are unknown, a value representative of the predominant soil type(s) from Table 5-1 can be used. It is important to note that seasonal variations are not considered in the values presented in Table 5-1. Gillette (1986) found that the value of K varies depending on the climatic conditions.

| Predominant Soil Textural Class | Soil Erodibility (tons/acre/yr) |
|---------------------------------|---------------------------------|
| sand ^b | 220 |
| loamy sand ^b | 134 |
| sandy loam ^b | 86 |
| clay | 86 |
| silty clay | 86 |
| loam | 56 |
| sandy clay loam ^b | 56 |
| sandy clay ^b | 56 |
| silt loam | 47 |
| clay loam | 47 |
| silty clay loam | 38 |
| silt | 38 |

^a Source: U.S. EPA, 1988

^b Very fine, fine, or medium sand

The K particle size multiplier for total suspended particles has been assigned a default value of 1. However, U.S. EPA (1988) provides a range of multipliers as a function of particle size.

The parameters KSR, cf, L', and V' act to reduce the erodibility (K) of a land surface. First, the surface roughness factor (KSR) accounts for the wind resistance caused by ridges, furrows, and large soil clods in an agricultural field. The resistance caused by furrows is related to the establishment of an aerodynamic roughness height and by sand being trapped in the furrows (Gillette, 1986). Its value ranges from 1.0 (no resistance) for a smooth-surface field to a minimum of 0.5 for a field with the optimum ratio of ridge height to ridge spacing. If the ridge dimensions are known, then a more precise estimate of KSR can be determined from Figure 7-3 provided in U.S. EPA (1988). Generally, it will be sufficient to use a value of 0.5 for a ridged surface and 1.0 for an unridged surface.

The climatic factor (cf) is a function of the wind velocity and the soil surface moisture. Climatic factors have been computed from available soil and precipitation data for many locations throughout the United States; maps showing annual climatic factors are provided in Figure 7-4 of U.S. EPA (1988) and, in more detail, the National Agronomy Manual (USDA, 1987). The climatic factor has been calibrated using the conditions in Garden City, KS (cf=1.00) and can be calculated at other geographic locations using the following equation (U.S. EPA, 1988):

$$cf = 0.345 \frac{W^3}{(PE)^2}$$

(5-2)

where:

- cf = climatic factor (unitless)
- 0.345 = empirical constant (1/mph³)
- W = mean annual wind velocity corrected to a standard height of 30 ft (mph)
- PE = Thornthwaite's precipitation-evaporation index (unitless)

Surface moisture is approximated using Thornthwaite's precipitation-evaporation index (PE); this can be calculated by multiplying the sum of 12 monthly ratios of precipitation to actual evapotranspiration by 0.83 (U.S. EPA, 1988). Mean wind speeds are available through local Weather Service offices or the National Climatic Data Center. Soil erodes across a field in the direction of the prevailing wind. The rate of erosion is zero at the windward edge of the field and increases approximately proportionately with distance downwind until, if the field is large enough, a maximum rate of soil movement is reached (U.S. EPA, 1988). Physical structures, such as trees and buildings, shelter portions of a field from wind and decrease its capacity for erosion. Therefore, the unsheltered field width (L') is the distance across a field (w , in the direction of the prevailing wind) less the distance from the windward edge of the field that is protected from wind erosion by a physical barrier. The distance protected by a barrier is equal to 10 times the height of the barrier (H), or $10 \times H$. For example, a row of 30-foot high trees along the windward side of a field reduces the effective width of the field by 10×30 or 300 feet (U.S. EPA, 1988).

The method presumes that the wind direction is perpendicular to the edge of the field. If the prevailing wind direction differs significantly (>25 degrees) from perpendicularity with the field, L' should be increased to account for this additional distance of exposure to the wind. The unsheltered distance across the field (L') is equal to the field width (w) divided by the cosine of the angle between the prevailing wind direction and the perpendicularity to the field (Ang):

$$L' = \frac{w}{\cos Ang}$$

(5-3)

where:

L' = unsheltered distance across field (ft)
 w = width of field (ft)

Ang = angle between prevailing wind direction and perpendicularity to field (unitless)

If wind barriers are present and the prevailing wind angle is >25 degrees, the increased distance due to angle is first calculated by Equation 5-3, then the resulting distance is decreased based on the configuration of the wind barrier. The unsheltered distance factor (L') can be determined if the soil erodibility (K) and surface roughness factor (KSR) are known. The product $K \cdot KSR$ and the unsheltered field width (L') are used to quantitatively estimate the unsheltered field width factor (L') from Figure 7-5 of U.S. EPA (1988).

The wind erosion equation (Equation 5-1) is configured so that individual crop types can be taken into account (by altering the value of KSR for specific crops). Crop-specific L' values have also been developed. These values are representative of field sizes in relatively flat terrain devoid of tall natural vegetation (U.S. EPA, 1988). The L' values should be divided by 2 in areas of moderately uneven terrain and by 3 in hilly areas before determining L' from Figure 7-5 in U.S. EPA (1988).

Vegetative cover on agricultural fields during periods other than the primary crop season greatly reduces wind erosion of the otherwise bare soil (U.S. EPA, 1988). This cover consists of residual matter from previous crops (e.g., standing stubble), which is eventually mulched into the soil. The effects of various amounts of residue in reducing erosion can be quantitatively estimated when the potential annual soil loss from a bare field ($K \cdot KSR \cdot cf \cdot L'$ in tons/acre-yr) is known. The product $K \cdot KSR \cdot cf \cdot L'$, along with an estimate of the amount of crop-specific residual vegetative cover (V , in lb air-dried residue/acre), can be used to quantitatively determine the resulting fractional amount of this potential loss (V') that results when the field has residual vegetative cover (Figure 7-6 of U.S. EPA, 1988).

5.3.2. Agricultural Tilling. Reentrained dusts can be generated by numerous agricultural operations, including soil preparation (e.g., tilling, fertilizing), soil maintenance (e.g., bedding, cultivating), and crop harvesting (U.S. EPA, 1988). This section focuses on dusts emitted from tilling, the operation with the most impact on the

adjacent terrain. Agricultural fields are mechanically plowed to create the desired soil structure for planting crops and to eradicate weeds (U.S. EPA, 1985). Most tilling is performed under dry soil conditions, causing dust particles to be resuspended into the atmosphere as the soil is loosened, pulverized, inverted, and dropped back to the surface (U.S. EPA, 1985, 1988). The quantity of dust generated from tilling is proportional to the area of land being tilled and depends on the surface soil texture (e.g., amount of silt, clay, sand, and loam) and the conditions of a particular field being tilled (U.S. EPA, 1985).

The quantity of dust emissions from agricultural tilling may be estimated using the following empirical expression (U.S. EPA, 1985, 1988):

$$E_f = (3.2E-9) (k) (5.38) s_c^{0.6}$$

(5-4)

where:

- E_f = emission of resuspended dust due to agricultural tillage ($\text{g/m}^2\text{- sec}$)
- $3.2E-9$ = conversion factor [$(1E+3 \text{ g/kg}) / (1E+4 \text{ m}^2/\text{ha})(3.1536E+7 \text{ sec/yr})$]
- k = particle size multiplier for total suspended particulate matter (unitless); 1.0 (U.S. EPA, 1985)
- 5.38 = empirical constant (kg/ha)
- s_c = silt content of surface soil (%)

Dust emissions from agricultural tilling have been found to vary directly with the silt content (defined as particles $<75 \mu\text{m}$ in diameter) of the surface soil (U.S. EPA, 1985). Soil silt content generally ranges from 1.7 to 88%, with a mean value of 18%; however, site-specific silt values should be used when possible (U.S. EPA, 1985).

5.3.3. Contaminant Emissions in Agricultural Areas. The emission rates ($\text{g/m}^2\text{- sec}$) presented in Sections 5.3.1. and 5.3.2. are used to estimate the dust resuspension flux. For this methodology, we are interested in emissions of contaminant aggregated with

the dust, not the dust itself. It is reasonable to assume that the concentration of contaminant in dust is the same as the concentration in the soil that is being resuspended (i.e., aggregation with contaminant does not influence whether or not a given particle will be resuspended). Therefore, the contaminant resuspension flux can be calculated for agricultural soils by multiplying the dust emission rate, E_d (Equations 5-1 [E_p] and 5-4 [E_f]), by the concentration of contaminant in the soil at the site of the dust source, and the enrichment ratio:

$$E_C = E_d \cdot C_s \cdot 10^{-6} \cdot ER$$

(5-5)

where:

- E_C = dust emission flux of contaminant in soil (g/m²-sec)
- E_d = dust emission rate (g/m²-sec)
- ER = enrichment ratio
- C_s = concentration of contaminant in soil (µg/g)
- 10^{-6} = conversion factor (µg to g)

The enrichment ratio refers to the fact that erosion favors the lighter soil particles. More information is provided in Section 7.2.10. of this methodology document.

The concentration of contaminant in soil at the dust source (C_s) is calculated using Equation 4-1, based on air dispersion modeling of the combustor emissions alone. For the agricultural soils, soil concentration is calculated assuming a mixing depth of 20 cm. A discussion of choice of mixing depth for various situations is presented in Section 4.3.4.

5.4. VEHICULAR TRAFFIC

Another source of reentrained dust is vehicular traffic. When a vehicle travels on an unpaved road, the force of the wheels on the surface causes the pulverization of surface material. Particles are lifted and dropped from the rolling wheels, and the road surface is exposed to strong air currents in turbulent shear with the surface. The turbulent wake behind the vehicle continues to act on the road surface after the vehicle has passed (U.S. EPA, 1996a).

5.4.1. Unpaved Roads. The quantity of dust emissions generated from an unpaved road depends on the volume of traffic, the silt content (particles <75 µm in diameter) in the road surface materials, and several correction factors including average vehicle speed, average vehicle weight, average number of wheels per vehicle, and road surface moisture (U.S. EPA, 1996b).

The following empirical expression may be used to quantify particulate emissions from an unpaved road (public or industrial), per vehicle kilometer traveled (VKT) (U.S. EPA, 1988, 1996b):

$$E_{uv} = k (1.7) \left(\frac{s}{12} \right) \left(\frac{S}{48} \right) \left(\frac{W}{2.7} \right)^{0.7} \left(\frac{w}{4} \right)^{0.5} \left(\frac{365-p}{365} \right)$$

(5-6)

where:

- E_{uv} = annual emission of dust due to travel on unpaved roads (kg/VKT-yr)
- k = particle size multiplier for total suspended particulate matter (unitless); 1.0 (U.S. EPA, 1996a)
- s = silt content of road surface material (%)
- S = mean vehicle speed, kilometers per hour (km/hr)
- W = mean vehicle weight, megagrams (Mg)

- w = mean number of wheels
p = number of days with at least 0.254 mm of precipitation per year

Table 5-2 summarizes measured silt values for industrial and rural unpaved roads (U.S. EPA, 1996a); mean values range from 4.3 to 24%. Since the silt content of a rural dirt road will vary with location, site-specific measurements are most appropriate; however, the silt content of the parent soil in the area can be used as a conservative approximation. Tests show, however that road silt content is normally lower than in the surrounding parent soil, because the fines are continually removed by the vehicle traffic, leaving a higher percentage of coarse particles (U.S. EPA, 1996a).

Equation 5-6 requires input of the average vehicle speed and weight, and average number of wheels of all vehicles traveling the road. For example, if 98% of

| TABLE 5-2 | | | | | |
|--|------------------------------|-------------|----------------|------------------|------|
| Typical Silt Content Values of Surface Material on Industrial and Rural Unpaved Roads* | | | | | |
| Industry | Road Use or Surface Material | Plant Sites | No. of Samples | Silt Content (%) | |
| | | | | Range | Mean |
| Copper smelting | Plant road | 1 | 3 | 16 - 19 | 17 |
| Iron and steel production | Plant road | 19 | 135 | 0.2 - 19 | 6.0 |
| Sand and gravel processing | Plant road | 1 | 3 | 4.1 - 6.0 | 4.8 |
| Stone quarrying and processing | Plant road | 2 | 10 | 2.4 - 16 | 10 |
| | Haul road | 1 | 10 | 5.0 - 15 | 9.6 |
| Taconite mining and processing | Service road | 1 | 8 | 2.4 - 7.1 | 4.3 |
| | Haul road | 1 | 12 | 3.9 - 9.7 | 5.8 |
| Western surface coal mining | Haul road | 3 | 21 | 2.8 - 18 | 8.4 |
| | Access road | 2 | 2 | 4.9 - 5.3 | 5.1 |
| | Scraper route | 3 | 10 | 7.2 - 25 | 17 |
| | Haul road (freshly graded) | 2 | 5 | 18 - 29 | 24 |
| Rural roads | Gravel/crushed limestone | 3 | 9 | 5.0 - 13 | 8.9 |
| | Dirt | 7 | 32 | 1.6 - 68 | 12 |
| Municipal roads | Unspecified | 3 | 26 | 0.4 - 13 | 5.7 |
| Municipal solid waste landfills | Disposal routes | 4 | 20 | 2.2 - 21 | 6.4 |

* Source: U.S. EPA, 1996a

vehicles on the road are 4-wheeled cars and trucks while the remaining 2% consists of 18-wheeled trucks, then the mean number of wheels (w) is 4.3 $[(0.98 \times 4) + (0.02 \times 18)]$. Equation 5-6 is *not* intended to be used to calculate a separate emission factor for each vehicle class; instead, only one emission factor should be calculated that represents the "fleet" average of all vehicles traveling the road (U.S. EPA, 1996a). Table 5-3 summarizes the range of conditions for sources used to derive Equation 5-6. For the most reliable application of this equation, inputs should fall within the displayed ranges.

| TABLE 5-3 Ranges of Source Conditions for Unpaved Roads* | | | |
|---|--------------------------------|----------------------------------|-----------------------|
| Road Silt Content (wt %) | Mean Vehicle Weight (Mg) | Mean Vehicle Speed (km/hr) | Mean No. of Wheels |
| 4.3 - 20 | 2.7 - 142 | 21 - 64 | 4 - 13 |

* Source: U.S. EPA, 1996a

The number of wet days per year (p) is defined as the number of days during which there is at least 0.254 mm (0.01 in.) of precipitation; (p) can be determined from local climatic data for the geographical area of interest. U.S. EPA (1996a) provides an illustration of the geographical distribution of the mean annual number of wet days per year in the United States. As noted in U.S. EPA (1996a), persons in dry, arid portions of the country may wish to base (p) on a greater amount of precipitation than 0.254 mm to account for rapid evaporation of moisture (and reduced dust mitigation) under these conditions. A worst-case condition of no wet days can be simulated by setting $p=0$.

The dust emission rate in Equation 5-6 is in units of kg/VKT-yr. In order to add these emissions to the air dispersion model, the emission rate must be converted to units of g/sec.

5.4.2. Paved Roads. Particles are deposited onto paved roadways from several sources, including pavement wear and decomposition, vehicle-related deposition, atmospheric dustfall, litter, mud and dirt carry out, erosion from adjacent areas, spills, biological debris, and ice control compounds (U.S. EPA, 1988, 1996a). Particles are resuspended whenever vehicles travel over paved surfaces and removed by wind erosion, displacement, surface runoff, and street sweeping (U.S. EPA, 1988, 1996a). Surface loading, as it is redistributed or removed, is continuously replenished by other sources. Several studies have shown that public and industrial streets and highways can be major sources of resuspended atmospheric particulate matter in an area (citations in U.S. EPA, 1988). Dust emissions from paved roads have been found to vary with the silt loading present on the road surface and the average weight of vehicles traveling the road. The quantity of dust emissions from vehicle traffic on a paved road may be estimated using the following empirical expression (U.S. EPA, 1996a):

$$E_p = k \left(\frac{sL}{2} \right)^{0.65} \left(\frac{W}{3} \right)^{1.5} \quad (5-7)$$

where:

- E_p = annual emission of dust resuspended from vehicular traffic on paved roads (g/VKT-yr)
- k = particle size multiplier for total suspended particulate matter (g/VKT);24 (U.S. EPA, 1996a)
- sL = road surface silt loading (g/m²)
- W = average weight (tons) of the vehicles traveling the road

This equation is based on a regression analysis of numerous emission tests of free-flowing (not stop and go) traffic (MRI, 1993). Silt loading (sL) refers to the mass of silt-size material (particles <75 µm in diameter) per unit area of the travel surface (U.S. EPA, 1996a) and is calculated as the product of the silt fraction and the total loading. In the event that site-specific values cannot be obtained, an appropriate value for an industrial road may be selected from the mean values given in Table 5-4. In the absence of site-specific sL data to serve as input to a public paved road inventory, conservatively high emission estimates can be obtained by using the figures in U.S. EPA (1996a). For annual conditions, median sL values of 0.4 g/m² can be used for high average daily traffic (ADT) roads (excluding limited-access roads) and 2.5 g/m² for low-ADT roads. Few sL data are available for limited-access roadways. For annual conditions, a default value of 0.02 g/m² is recommended for limited-access roadways (U.S. EPA, 1996b). Equation 5-7 also calls for the average weight of all vehicles traveling the road. For example, if 99% of vehicles on the road are 2 Mg cars/trucks while the remaining 1% consists of 20 Mg trucks, then the mean vehicle weight (W) is 2.2 Mg [(0.99 x 2) + (0.01 x 20)]. Equation 5-7 is an accurate estimate of emissions given that the input values fall within the ranges listed in Table 5-5 (U.S. EPA, 1996a).

5.4.3. Contaminant Emissions due to Vehicular Traffic. As mentioned earlier, this methodology is interested in emissions of contaminant aggregated with the dust, not the dust itself. The contaminant resuspension flux can be calculated unpaved roads by multiplying the dust emission rate, E_{uv} , (Equation 5-6) by the concentration of contaminant in the soil. Equation 5-8 is adapted from Scott et al., (1998):

$$E_{cv} = \frac{E_{uv} \cdot C_s \cdot TC \cdot AR \cdot 1 \text{ m}^2 \cdot 10^{-6}}{(3.1536E+7 \text{ sec/yr})}$$

(5-8)

where:

E_{cv} = vehicle related dust emission flux of contaminant in soil (g/sec)

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- E_{uv} = annual emission of dust due to travel on unpaved roads (g/VKT)
AR = area of the road (m^2)
TC = daily traffic count for the unpaved area (vehicles/day)
 C_s = concentration of contaminant in soil ($\mu\text{g/g}$)
 10^{-6} = conversion factor (μg to g)

TABLE 5-4
Typical Silt Content and Loading Values for Paved Roads at Industrial Facilities ^{a, b}

| Industry | No. of Sites | No. of Samples | Silt Content (%) | | No. of Travel Lanes | Total Loading x 10 ⁻³ (kg/km) | | Silt Loading (g/m ²) | |
|----------------------------|--------------|----------------|------------------|------|---------------------|--|-------|----------------------------------|------|
| | | | Range | Mean | | Range | Mean | Range | Mean |
| Copper smelting | 1 | 3 | 15.4-21.7 | 19.0 | 2 | 12.9-19.5 | 15.9 | 188-400 | 292 |
| Iron and steel production | 9 | 48 | 1.1-35.7 | 12.5 | 2 | 0.006-4.77 | 0.495 | 0.09-79 | 9.7 |
| Asphalt batching | 1 | 3 | 2.6-4.6 | 3.3 | 1 | 12.1-18.0 | 14.9 | 76-193 | 120 |
| Concrete batching | 1 | 3 | 5.2-6.0 | 5.5 | 2 | 1.4-1.8 | 1.7 | 11-12 | 12 |
| Sand and gravel processing | 1 | 3 | 6.4-7.9 | 7.1 | 1 | 2.8-5.5 | 3.8 | 53-95 | 70 |

| TABLE 5-5 Ranges of Source Conditions for Paved Roads* | | |
|---|--------------------------------|----------------------------------|
| Silt Loading (g/m ²) | Mean Vehicle Weight (Mg) | Mean Vehicle Speed (km/hr) |
| 0.02 - 400 | 1.8 - 38 | 16 - 88 |

* Source: U.S. EPA, 1996a

The concentration of contaminant in soil at the dust source (C_s) is calculated using Equation 4-1, based on air dispersion modeling of the combustor emissions alone. For the unpaved road, a mixing depth of 1 cm may be appropriate. A discussion of choice of mixing depth for various situations is presented in Section 4.3.4.

Calculation of contaminant emissions from paved roads is problematic. Equation 4-1 is not suitable for calculating the concentration of contaminant in dust on paved roads. It may be necessary to obtain measured values of contaminant concentrations in paved-road dust at the specific sites in question in order to include this pathway. A bounding estimate could be obtained by assuming that resuspended dust from the paved road consist entirely of contaminant particles, so that $E_c = E_p$.

5.5. ESTIMATING EXPOSURES TO RESUSPENDED DUST EMISSIONS

If dust emissions from identified sources seem likely to contribute to exposure, these sources can be treated as area-source inputs to the air dispersion model. In this way, the resuspended dust emissions can be added to the direct combustor emissions to determine air concentrations and deposition rates at downwind receptor locations. An alternative approach would be to convert the dust emissions to a screening-level estimate of air concentration rather than add the resuspended dust emissions to the air dispersion model. Both approaches would use the same value for dust emissions in contaminated soil (E_c), g/m²-sec and ($E_{c,v}$), g/sec.

5.5.1. Air Dispersion Modeling of Resuspended Dust Emissions. The ISC3 air model should be used (U.S. EPA, 1995). It is further assumed that all inputs needed to model dispersion based on the combustor itself have already been collected. In this case, just three additional types of information are needed to add a dust-generating site to the air dispersion model as an area source of contaminant emissions: the emission rate of contaminated dust from the site, the size distribution of dust particles emitted from the site, and the size and location of the site. Each of these variables is discussed below.

As mentioned above, there are many potential sources of resuspended dust. It is important to note that the emission rates calculated using the equations from *AP-42* are for dust, not contaminant. Calculation of contaminant emissions from resuspended dust is provided below.

5.5.1.1. Particle Size Distribution of Resuspended Dust — Size is a key determinant of the properties, effects, and fate of atmospheric particles (U.S. EPA, 1996b). The deposition rate of particles, and therefore the residence time in the atmosphere, is a function of particle size. Minimum deposition rates occur at particle sizes of 0.1-1.0 μm (diameter). Deposition rates increase with size for particles larger than 1.0 μm . Therefore, larger particles, which settle more rapidly, will have more of an effect on indirect routes of exposure via deposition to soil, vegetation, and surface water than smaller particles. Conversely, the smaller particles, because they remain suspended in the atmosphere for longer periods of time, have greater potential to influence direct inhalation exposure. (Smaller particles will settle, but at greater distances and after greater dilution in the atmosphere.) The ability of small particles to influence inhalation exposure also reflects the deposition of particles in the respiratory tract; smaller particles can penetrate deeper into the tract. Particles less than 10 μm in diameter are generally considered to be inhalable (i.e., able to penetrate beyond the nasopharyngeal region of the respiratory tract) in humans (U.S. EPA, 1996b).

Particles generated in uncontrolled conditions, in combustors and dust resuspension events, are not uniform in size. These uncontrolled sources produce a

range of sizes that can be described by a particle size distribution. Although the exact distribution will vary with the specific source and may be influenced by many factors, different types of sources generally produce characteristic distributions. A generalized particle size distribution for combustor emissions is shown in Table 5-6. The particle size distribution for resuspended dust differs markedly from that of combustors, with a much larger contribution by large particles. Data on resuspended dust suggest a log-normal bimodal distribution with one mode at 2-5 μm and the other at 30-60 μm (U.S. EPA, 1996b). The deposited pollutant particles may or may not become fully aggregated with their host soil particles (Sehmel, 1980). For the sake of simplicity, it will be assumed that the distribution of particle size found in resuspended dust applies to resuspended contaminant.

| TABLE 5-6 | | |
|--|-------------------|---------------|
| Particle Size Distribution for Resuspended Soils and Road Dusts* | | |
| Particle Diameter (μm) | | Mass Fraction |
| Range | Midpoint of Range | |
| <1.0 | 0.5 | 0.035 |
| 1.0 - 2.5 | 1.75 | 0.065 |
| 2.5 - 10 | 6.25 | 0.40 |
| 10 - 30 | 20 | 0.50 |

* Source: Chow et al., 1994; Houck et al., 1989

Because most studies of dust emissions have used total suspended particulate matter (TSP) or smaller size classes (e.g., PM_{10}) as the basis for their measurements, the emission factors presented in Section 5.2.1. represent emissions of TSP. Although

TSP, as typically collected with a high-volume sampler, can capture a small percentage of particles as large as 100 μm (the largest particles that can be resuspended by wind), it is not very efficient for particles larger than 30 μm (U.S. EPA, 1996a). Therefore, the emission rates for resuspended dust used in this methodology underestimate total dust emissions and effectively exclude particles larger than 30 μm . This is a limitation of the existing data, although it may be argued that particles larger than 30 μm are not likely to be suspended long enough to be transported off-site anyway. Only dusts that are resuspended and transported to physically distinct areas beyond the source will have any net effect on exposure.

Laboratory and field studies of resuspended soil and road dust have been conducted to estimate the size distribution as a percent of TSP mass (Chow et al., 1994; Houck et al., 1989, 1990). It was found that roughly 50% of TSP was contained in the PM_{10} fraction, 10% in the $\text{PM}_{2.5}$ fraction, and 3.5% in the PM_{10} fraction for soils and road dusts in both studies. In the absence of site-specific measured data, the generalized particle size distribution can be used to represent resuspended solid and road dusts in the ISC3 air dispersion model as shown in Table 5-6. For the alternate simpler screening level approaches suggested in Section 5.6.2., particle size distribution is not required as input.

5.5.1.2. Size and Location of Area Source — The size and location of the dust-generating area source must be entered into the model as described in U.S. EPA (1995). The ISC3 allows rectangular shaped areas with aspect ratios up to 10:1, which may be placed in any orientation. An irregularly shaped area source can be accommodated by subdividing it into smaller areas of varying shapes, sizes, and orientations. Line sources (e.g., roads) are accommodated by dividing the source into multiple rectangular (10:1 aspect ratio) segments. The PC version of the model is preset to include up to 300 sources. This number can be increased if adequate hardware resources are available.

5.5.2. Alternative to Air Dispersion Modeling of Resuspended Dust Emissions.

Once a dust-emission rate of contaminant due to dust resuspension has been

calculated, it can easily be converted into a screening level estimate of air concentration (screening-level in comparison to modeling with ISC3, at least). That estimate of particulate phase air concentration can be compared to the particulate phase air concentration at the exposure site predicted by the ISC3. In most cases, the concentration due to dust resuspension will be much lower than the concentration predicted to arrive at the exposure site from the stack emission. In situations where this may not be the case, such as in heavy traffic over dirt roads, or wind erosion over bare dry soils, the risk assessor should consider rerunning the ISC3 using the multiple source option. Since the MPE is limited to single source evaluations, no guidance on the use of ISC3 in modeling multiple sources will be offered here. The risk assessor should obtain the ISC3 code and User's Guide (U.S. EPA, 1995) to determine the procedures to model the transport and deposition of an area source emission.

The risk assessor should be cautious when comparing a screening-level estimate of air concentration due to dust resuspension and an ISC3 prediction of concentration resulting from the stack emission. Recall that the ISC3 prediction is an average over the course of a year. Depending on the process that caused the dust resuspension, an estimate of air concentration due to dust emissions may be short-lived in comparison to a year. Therefore, the screening-level air concentration predictions that can be made using the algorithms below are very specific to the time embedded in the calculation of the dust emission rate (the predicted flux of contaminant from the soil) used in the equations. A risk assessor should convert the predicted air concentration to an annual basis for a proper comparison with the ISC3 air concentration prediction.

Short- term impacts (e.g., from inhalation) from a dust resuspension event can also be examined through a screening approach. One such approach to estimating air concentrations from an area source emission is with a box model. This can be described mathematically as:

$$C_p = \frac{E_c A 10^6}{w V_w h}$$

(5-9)

where:

- C_p = particle phase air concentration due to dust resuspension ($\mu\text{g}/\text{m}^3$)
- E_c = dust emission rate of contaminant from soil ($\text{g}/\text{m}^2\text{-sec}$)
- A = area over which resuspension occurs (m^2)
- w = width of area perpendicular to wind direction (m)
- V_w = velocity of wind (m/sec)
- h = mixing height (m)
- 10^6 = converts g to μg

The assessor should be cognizant of what this rate term represents (e.g., a single event, an average over multiple events covering a long period of time), and also that the units should be properly converted to g/sec basis. The area term, A , refers to the land area over which dust resuspension occurs. This could be the area of a plowed field, the area of the road over which dust becomes resuspended, and so on. Since wind direction would not be known, the risk assessor can use judgment to assign a value to the width term, W . Perhaps this could be narrowest width associated with the area-source emission, so that the air concentration estimation can be maximized. The mean annual wind speed varies from 2.8 to 6.3 m/sec (U.S. EPA, 1985). On an event basis, the wind velocity could be higher. A first-estimate assumption for this screening model of 4.0 m/sec is probably reasonable. The mixing height, h , has often been assumed to be 2 m, which approximates the breathing zone. This would be appropriate in this application.

If the dust resuspension occurs at a distance from where the exposure occurs, a risk assessor can use a simple virtual point source model (Turner, 1970). This

approach treats the area source as though it were a point source. The model approximates the dispersion that occurs from an area source by using an imaginary point source. This point is located upwind of the actual source at a distance calculated to create a lateral dispersion at the site equal to its width:

$$C_p = \frac{2.03 E_c A FR 10^6}{VD D_{va} V_w}$$

(5-10)

where:

- C_p = particle phase air concentration due to dust resuspension ($\mu\text{g}/\text{m}^3$)
- E_c = dust emission rate of contaminant from soil ($\text{g}/\text{m}^2\text{-sec}$)
- A = area over which resuspension occurs (m^2)
- FR = frequency wind blows from area source to receptor, fraction
- VD = virtual distance, source center to receptor (m)
- D_{va} = vertical dispersion coefficient (m)
- V_w = velocity of wind (m/sec)
- 10^6 = converts g to μg

D_{va} is estimated as an empirical function of the distance from the source center to receptor:

$$D_{va} = 0.222 AD^{0.724} - 1.7, \quad AD < 1000 \text{ m}$$

(5-11)

$$D_{va} = 1.26 AD^{0.516} - 13.0, \quad AD > 1000 \text{ m}$$

(5-12)

where:

- D_{va} = vertical dispersion coefficient (m)
 AD = actual distance from source center to receptor (m)

Virtual distance, VD , is an empirical function of the width of the contaminated area and the actual distance from source center to receptor:

$$VD = 2.514 w + AD \quad (5-13)$$

where:

- VD = virtual distance, source center to receptor (m)
 w = width of area perpendicular to wind direction (m)
 AD = actual distance from source center to receptor (m)

In these equations, the E_c , A , W , and V_w are parameterized in a manner similar to the box model above. The frequency wind blows from the area source to the receptor, FR , can be assigned a value of 1.00 (100% of the time) as an absolute worst case, although it may be appropriate in evaluating the impacts of a single event. If the dust resuspension events occur frequently and it is desirable to obtain an annual average air concentration at the exposure site, a value of 0.50 or less is probably more reasonable, yet still conservative. The actual distance term, AD , is, as defined, the distance from the center of the area source to the receptor.

If a risk assessor has made a calculation of a particle-phase air concentration predicted to occur at a site because of dust resuspension from a distant site, and has judged it to be of importance, a few options are available. One is to rerun the ISC3, model as noted above. Otherwise, the air concentration prediction can be used in the assessment. First, it can be added to the other air concentration terms from the ISC3 model (the vapor- and particle-phase concentrations) to arrive at a total concentration

for inhalation exposures. Also, the assessor can assume that the particles redeposit back onto soils and vegetation at the exposure site. This particle deposition flux would be added to the particle deposition rate from the stack emission already predicted by ISC3. A particle deposition rate is easily calculated as the product of the air concentration times the deposition concentration, C_p ($\mu\text{g}/\text{m}^3$) * V_d (m/sec) (the units need to be converted to be compatible with output from ISC3).

The deposition velocity, V_d , can be assigned a value of 0.01 m/sec (1 cm/sec) as a reasonable screening-level estimate. Seinfeld (1986) lists a gravitational settling velocity of 1 cm/sec for 10 μm particles. These are the “inhalable” particles; the emission factor equations presented earlier were mostly developed to predict the dust resuspension rate for particles this size and smaller. Therefore, the 1 cm/sec assumption is reasonably conservative for this estimate.

As a final note, the risk assessor should not calculate resuspended contaminants that are redeposited at the site where exposure occurs. This will amount to double accounting. First, particles from a contaminated soil that fall back on the contaminated soil are not going to increase the soil concentration. Second, impacts to plants from soils are better handled with the use of a soil-to-plant algorithm, as described in Chapter 6.

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Chapter 5
Dust Resuspension

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DETERMINING EXPOSURE THROUGH THE TERRESTRIAL FOOD CHAIN

6.1. INTRODUCTION

The previous chapter describes how pollutants associated with combustor emissions are incorporated into soil. This chapter describes how contaminants enter the terrestrial food chain. The terrestrial food chain includes plants that animals consume, plants that humans consume, and animals that humans consume. Plants take up contaminants directly from the soil or from the atmosphere. Animals are exposed to contaminants by ingestion of plants and soils. In addition to contaminant fate modeling, this chapter shows how daily exposure to food chain contaminants is calculated and used to estimate human risk.

6.2. OVERVIEW OF TERRESTRIAL FOOD CHAIN

There are three general types of parameters in these fate algorithms. The first category includes media concentrations, or quantities, that have been calculated using other models of this assessment. Specifically, the soil and air concentrations and the atmospheric deposition fluxes were modeled using the approaches described in Chapters 3 and 4. A second category of parameters includes those that are specific to the contaminant. Included here, for example, are the bioconcentration/biotransfer factors used to translate an animal diet of the contaminant into an animal tissue concentration. The third and final category of parameters are the general physical parameters not related to the contaminants. These include, for example, plant yields and animal diet descriptors. The guidance presented for these parameters is general in nature and attempts to make important distinctions, such as guidance for inorganic versus organic contaminants, where pertinent.

Sections 6.3 and 6.4 describe the algorithms for estimating contaminant concentrations in plants and animals, respectively. Both sections follow a similar structure. First, the overall equations describing the fate pathway (e.g., the transfer of contaminants from the air to the plant, or the bioaccumulation of ingested contaminants in animal tissue) are given. These are generic equations pertinent to organic and

inorganic contaminants, soluble and insoluble contaminants, and so on. Then, general guidance is offered for assignment of the equations' parameters.

Section 6.5 presents algorithms for estimating human daily intake, given the food concentrations predicted using the algorithms in Sections 6.3 and 6.4. Section 6.6 provides an alternative approach for terrestrial food chain modeling.

It is important to understand that the algorithms for estimating terrestrial food chain impacts are relatively simple screening-level models. Simplifying assumptions often are made in order to arrive at the desired results, which are long-term average concentrations in the terrestrial foods. In summary, some of the key assumptions are as follows:

- ! The source strength remains constant throughout the period of exposure. The “sources” for terrestrial impacts include the deposition fluxes and air concentrations predicted by the air dispersion model. An assumption of a constant source strength also was used in air dispersion modeling, which predicted long-term average deposition fluxes and air concentrations assuming that the emissions of the contaminants from the combustion source were constant throughout the exposure period.
- ! Plant concentrations are modeled as a function of the deposition of contaminants that have been emitted from the combustion source and traversed to where the plants are growing; also considered is a component due to root uptake and translocation. Plant impacts do not consider the resuspension and redeposition of contaminants that have deposited onto soils (although the use of the “plant biotransfer factor,” Br , for lipophilic compounds may inherently model this process—see discussion in Section 6.3 below on this parameter). These resuspension/redeposition phenomena could occur where processes such as tillage, wind erosion, vehicular resuspension, and/or rainsplash might be important. Models are available to estimate plant impacts from these processes, but they are not discussed in this chapter.
- ! Previous analysis has suggested that the exposure of terrestrial animals to bioaccumulating contaminants is primarily via ingestion of food and soil. Therefore, other possible routes of exposure, such as inhalation or water ingestion, are not considered. There may be special circumstances where an animal's exposure is significantly influenced by pathways not considered in this assessment (other than water ingestion or inhalation). One example could be the impact of worms or other biota consumed by free-ranging chickens. Another example would be the exposure of farm animals to wood

that has been treated with pentachlorophenol or other preservatives. Fries et al. (1996) found very high levels of dioxins in cattle in an experimental setting that could not be explained by their diet but that correlated very well with concentrations of dioxins in the pentachlorophenol-treated wood in their environment.

Figure 6-1 shows the general structure of the modeling algorithms of this chapter. The box shows the air reservoir and the quantities used to model the terrestrial food chain impacts. For the terrestrial impact model, this box represents the “source” of the contaminants. The circles show the media compartments that are impacted by the source and to which humans are exposed (vegetables/fruits, animal food products) or to which animals are exposed (forages, soil). The arrows show the pathways between media compartments, and the terms near the arrows describe the processes of importance in the terrestrial food chain.

6.3. CALCULATING CONTAMINANT CONCENTRATION IN PLANTS

This section examines three mechanisms by which contaminants can bioaccumulate in plants: root uptake and translocation, deposition of particle-bound contaminants to exposed plant tissues, and deposition of vapor-phase contaminants to exposed plant tissues (deposition of vapor-phase contaminants also has been called “air-to-plant transfer” of vapor-phase contaminants; one algorithm described below does not contain a “deposition velocity” term, but rather is based on an empirical vapor “transfer” factor). The relative importance of each mechanism depends on both the characteristics of the plant and the characteristics of the contaminant. Plant characteristics of importance include the surface-area-to-plant-volume relationship (i.e., leafy vegetations are likely to accumulate more than bulky vegetations) and whether the edible portion (edible by humans or by animals as part of the food chain) is exposed, such as the skin of an apple or grass leaves, or protected, such as peas or grain for animal feeds. Contaminant characteristics include the degree of partitioning between a particle and a vapor phase and the persistence of the contaminant in the environment.

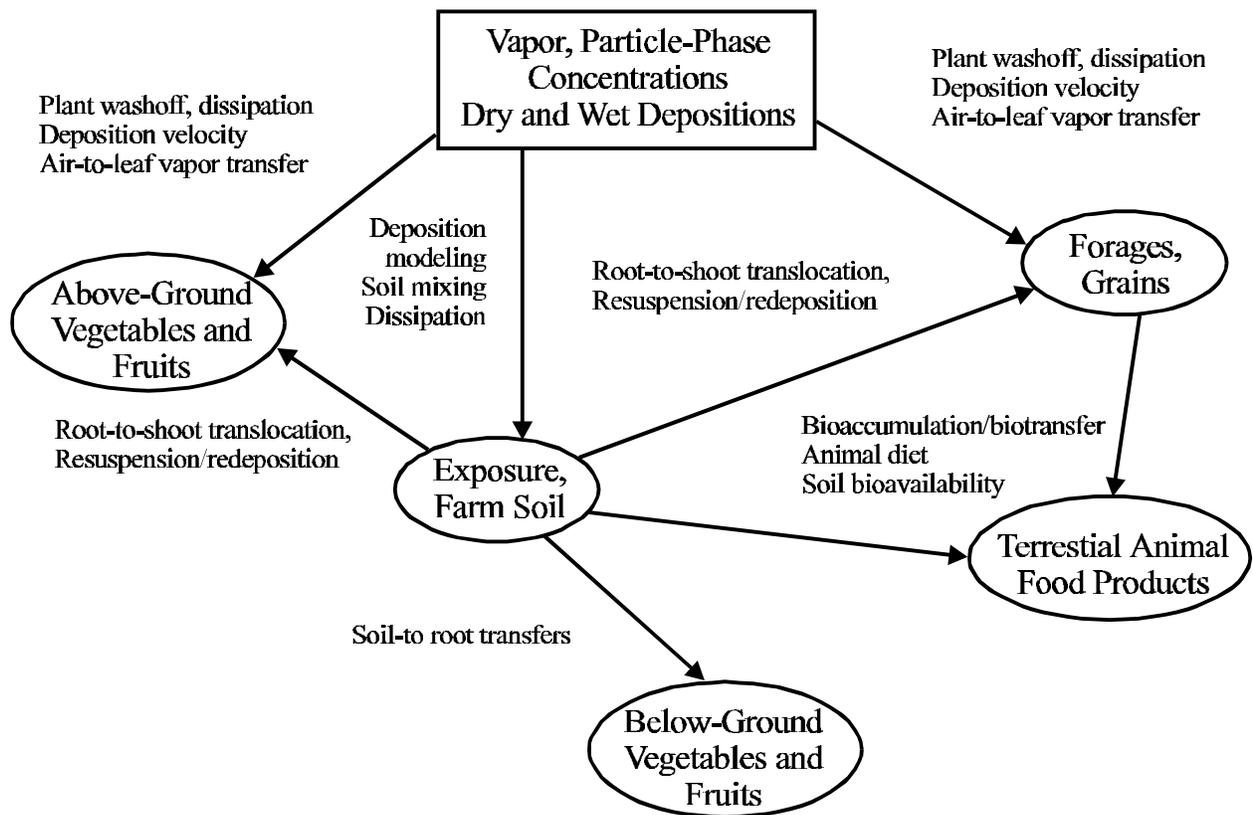


Figure 6-1

Overview of Terrestrial Food Chain Modeling Compartments and Processes

The food chain model calculates the contaminant concentration in each plant group due to the appropriate mechanisms and sums them to obtain the total contaminant concentration:

$$P_i = Pr_i + Pd_i + Pv_i \tag{6-1}$$

where:

- P_i = total concentration of contaminant in i th plant group ($\mu\text{g/g DW}$)
- Pr_i = concentration of contaminant in above-ground parts of i th plant group due to translocation from roots ($\mu\text{g/g DW}$)
- Pd_i = concentration of contaminant in i th plant group due to particle-phase deposition ($\mu\text{g/g DW}$)
- Pv_i = concentration of contaminant in i th plant group due to vapor-phase deposition ($\mu\text{g/g DW}$).

Vegetations consumed by humans can be grouped into five categories: exposed fruits, protected fruits, vegetables, protected vegetables, and root vegetables. The terms “exposed” and “protected” refer to whether or not the edible portion is exposed to the atmosphere. For example, apples are an exposed fruit, whereas peas are considered a protected vegetable. Vapor-phase transfers and particle-phase depositions are calculated for exposed fruits and vegetables but not for protected fruits or vegetables or root vegetables, since these vegetations are not in direct contact with the air. For protected vegetables and fruit grown above ground, accumulation could occur by root uptake followed by translocation. Root vegetables could be impacted by passive uptake of contaminants through transpiration water or by absorption onto the outer parts of the root vegetables. Table 6-1 summarizes the mechanisms of impact that are assumed for each of the categories of vegetation. Table 6-2 lists some of the more common items from each category of produce consumed by humans.

| TABLE 6-1 | | |
|---|--|-------------------------------|
| Uptake Mechanisms Based on Plant Morphology Assumed in this Methodology | | |
| Edible portion is: | Edible portion is: | |
| | Exposed | Protected |
| | Uptake mechanisms | |
| Above ground | Direct deposition Vapor deposition Root uptake and translocation | Root uptake and translocation |
| Below ground | Root uptake | Not applicable |

| TABLE 6-2 | | | | |
|---|---|---|--|------------------------------------|
| Common Items from Each Category of Produce Consumed by Humans | | | | |
| Category | Common fruits and vegetables | | | |
| Exposed fruits | apples pears apricots | strawberries cherries nectarines | plums grapes rhubarb | peaches berries dates |
| Protected fruits | citrus kiwi passion fruit | melons avocados pomegranates | bananas mangoes figs | pineapples papayas guava |
| Exposed vegetables | tomatoes celery pea pods peppers | string beans summer squash cabbage mushrooms | cucumbers asparagus cabbage brussels sprouts | eggplant cauliflower lettuce |
| Protected vegetables | peas pumpkin artichoke hearts | corn winter squash | lima beans kidney beans | soybeans cactus |

| | | | | |
|-----------------|-----------------------------------|---|--------------------------------|--|
| Root vegetables | potatoes garlic horseradish | beets sweet potatoes rutabagas | carrots turnips parsnips | onions radishes water chestnuts |
|-----------------|-----------------------------------|---|--------------------------------|--|

Vegetations consumed by animals can be grouped into three categories: grains, forage, and silage. Animal grains are categorized as protected vegetations, while forage (e.g., pasture plants and grasses) is considered to be exposed vegetation. In this document silage is used in a generic sense to refer to plants harvested for animal consumption that could be partly protected and partly exposed. An example here is corn silage fed to the animal as whole plants. Here, the corn grain could be considered protected, the leaves of the plant could be considered unprotected, and the stalks are in part protected and unprotected. Particle depositions and vapor transfers are calculated for silage. As described below, the VG_{ag} empirical parameter for vapor transfer is given a unique value for silage, based on the fact that silage is part protected and part exposed.

Some uptake mechanisms can be excluded based on what is known about the contaminant. For example, dioxin-like compounds will sorb to outer portions of below-ground vegetation, but inner translocation has been shown to be negligible in EPA's Exposure Reassessment Document for Dioxin-Like Compounds. This reassessment, when completed, will replace EPA's current draft exposure document on dioxin entitled *Estimating Exposures to Dioxin-Like Compounds* (EPA/600/6-88/005 Ca-Cc, June 1994). As it is still under development, it will be referred to throughout this exposure pathways document as the "dioxin exposure reassessment." Therefore, risk assessors may choose not to consider an algorithm to estimate above-ground plant impacts as a function of soil concentrations for risk assessments involving dioxins. This was the approach taken for the site-specific methodologies developed for the dioxin-like compounds in EPA's dioxin exposure reassessment. Risk assessors may want to consider site-specific data when developing appropriate plant groups. Note that

separate P_i values must be calculated for each contaminant to be considered in the risk assessment.

6.3.1. Plant Contaminant Concentration Due to Root Uptake (Pr_i). Contaminants in soil may enter a plant via uptake through the roots, where they may accumulate in the below-ground mass (e.g., tuber, bulb) and/or be translocated to the above-ground shoots. The concentration of contaminant in plant tissue due to root uptake is determined from the concentration of contaminants in soil and a chemical-specific biotransfer/ bioconcentration factor.

For above-ground crops (e.g., spinach), translocation from roots may contribute to the contaminant concentration in the plant. A general model relating soil concentrations to above-ground plant concentrations using a simple soil-to-plant biotransfer factor (Br) was developed by Travis and Arms (1988):

$$Pr_i = C_s Br \tag{6-2}$$

where:

- Pr_i = concentration of contaminant in above-ground parts of i th plant group due to translocation from roots ($\mu\text{g/g DW}$)
- C_s = concentration of contaminant in soil ($\mu\text{g/g}$) [see Equation 4-1]
- Br = soil-to-plant bioconcentration factor for contaminant ($[\mu\text{g contaminant/g DW plant}]/[\mu\text{g contaminant/g soil}]$).

In this equation, it would be inappropriate to assume that the Br is modeling translocation from root to shoot in all cases, however. Some of the experiments gathered by Travis and Arms (1988) to develop the Br term involved soluble pesticides while others involved compounds of very low solubility whose transport is dictated more by soil rather than by water movement, such as DDT. For the former class of soluble compounds, translocation would explain the above-ground concentrations found in the experiments, while in the latter case of sorbed contaminants, other mechanisms such as resuspension followed by redeposition would be cause for above-ground plant

impacts. Therefore, it may be assumed that in the modeling of above-ground plant impacts from soluble compounds in soil, the Br represents root uptake and translocation, while in the modeling of above-ground plant impacts from tightly sorbed contaminants, the Br represents resuspension followed by redeposition onto the plants.

A second approach to modeling above-ground plant impacts for soil reservoirs of contaminants was suggested by the work of Briggs et al. (1982), who grew barley plants in a growth solution in a laboratory setting and added O-methylcarbamoyloximes and substituted phenylureas to the growth solution. From their data, they calculated the Transpiration Stream Concentration Factor (TSCF), which they defined as the concentration in the transpiration stream divided by the concentration in the solution in which the barley plants were growing. For highly soluble contaminants, the TSCF would approach 1.0. Otherwise, the TSCF would be less than 1.0. If one assumes that the experimental solution concentration is analogous to soil pore water concentration and that the concentration in the transpiration stream is equivalent to the concentration in the moisture fraction of the actively growing plant, then the Briggs et al. (1982) TSCF can be used for estimating above-ground plant concentrations:

$$Pr_i = \frac{\frac{C_s}{Kd} TSCF F_{ts}}{\frac{100 - M_{ag}}{100}} \quad (6-3)$$

where:

- Pr_i = concentration of contaminant in above-ground parts of *i*th plant group due to translocation from roots ($\mu\text{g/g DW}$)
- C_s = concentration of contaminant in soil ($\mu\text{g/g}$)
- TSCF = transpiration stream concentration factor ($[\mu\text{g contaminant/mL transpiration stream}]/[\mu\text{g contaminant/mL pore water}]$)
- M_{ag} = percentage moisture content of above-ground vegetation (% water)
- Kd = soil-water partition coefficient (mL/g).
- F_{ts} = fraction of whole weight which is transpiration stream water, unitless

In this equation, C_s/Kd solves for the concentration in soil pore water. Therefore, multiplication of the soil pore water concentration by TSCF yields the concentration of the contaminant in the transpiration stream water. The concentration of the contaminant in transpiration stream water will, by definition, be higher than the concentration in the whole plant, assuming transpiration is what brought the contaminant from the soil to the above ground parts of the plant; hence the need to include the F_{ts} , which converts the concentration of the contaminant in transpiration stream water to a concentration in the whole plant on a fresh weight basis. An assumption of 50%, or a F_{ts} of 0.50, would be reasonable. Finally, the term in the denominator, $(100 - M_{ag})/100$, converts the whole-plant fresh-weight concentration into a whole-plant dry-weight concentration, which are the appropriate units for Pr_j .

Either of the two approaches for estimating above-ground impacts from the contaminants in the soil is acceptable for any class of contaminants considered in this assessment methodology. A risk assessor also can choose not to consider above-ground impacts from tightly sorbed contaminants depositing onto the soil in which the plant is growing. In a modeling assessment for dioxin-like compounds, EPA's dioxin exposure reassessment did not consider this pathway when modeling the impacts of dioxins emitted from combustion sources. The assumption was that the direct deposition of dioxins onto plants led to a much greater impact as compared with the impacts from the resuspension/redeposition of dioxins already deposited onto the soil.

Briggs et al. (1982) also suggested a framework for calculating the concentration in roots as a function of concentration in their experimental solution. They developed a Root Concentration Factor (RCF), which they defined as the concentration in the roots divided by the concentration in soil pore water. Using the RCF, the algorithm used to estimate the concentration in root vegetables is:

$$Pr_{rv} = \frac{C_s RCF VG_{bg}}{\frac{(100 - M_{bg})}{100} Kd}$$

(6-4)

where:

- Pr_{rv} = concentration of contaminant in root vegetables due to root uptake ($\mu\text{g/g DW}$)
- C_s = concentration of contaminant in soil ($\mu\text{g/g}$)
- RCF = root concentration factor ($[\mu\text{g contaminant/g plant FW}]/[\mu\text{g contaminant/mL pore water}]$)
- VG_{bg} = empirical below-ground vegetation correction factor (dimensionless)
- M_{bg} = percentage moisture content of below-ground vegetation (% water)
- Kd = soil-water partition coefficient (mL/g)

As in Equation 6-3, C_s/Kd solves for the concentration in soil pore water, and the division by $[100 - M_{bg}]/100$ converts the whole-plant fresh-weight concentration into a whole-plant dry-weight concentration.

All these algorithms for soil impacts require, of course, the soil concentration of the contaminant, C_s . Methods for calculating soil concentration are presented in Chapter 4. When considering root uptake for root vegetables, above-ground fruits and vegetables, or crops grown for animal feed, soil concentration should be calculated assuming a tilled depth since the ground is usually tilled or disturbed in some manner to plant food and grain crops. For vegetations that are not tilled, such as forage for the terrestrial animal food chain, the soil concentration should equal that calculated for the untilled condition. As described in Chapter 4, tilled depths are typically 15 to 20 cm and untilled depths are typically 1 to 2 cm, depending on site-specific conditions and the risk assessor's judgment.

The VG_{bg} is introduced on the basis of data on the transfer of dioxin-like compounds into below-ground vegetables, including carrots and potatoes (Muller et al., 1994; Hulster and Marschner, 1991). These data suggest that the whole barley root concentrations would be similar to concentrations near the skin of a bulky below-ground vegetable, but not the whole vegetable. Further, these experiments suggest that the concentrations found on the outer parts of the vegetable are due more to adsorption than to passive uptake via transpiration water. To adjust for the volume

differences between barley roots (used in Briggs et al. [1982] experiment) and bulky below-ground root crops, the empirical below-ground correction factor, VG_{bg} , is used. EPA's dioxin exposure reassessment derived a value of 0.25 for VG_{bg} for all the dioxin-like compounds for all root vegetables from these data. Unless better data are available, it would be appropriate to similarly assign a value of 0.25 for compounds similar to the dioxins—lipophilic (near $\log K_{ow}$ 6.0 and higher) and persistent. Other factors that reduce vegetation concentrations, such as peeling, cooking, or cleaning, can be considered in this empirical correction factor for site-specific assessments. Soluble compounds would be taken into the plant via transpiration water and would tend to distribute more uniformly throughout the entire plant. Therefore, this adjustment would not be appropriate, that is, the VG_{bg} would be set equal to 1.0. For purposes of VG_{bg} assignments, a value of 1.0 can be assumed for organic contaminants with $\log K_{ow}$ less than 2.0.

The plant-soil bioconcentration factor, Br , is a measure of a contaminant's tendency to accumulate in plant tissue and is defined as the contaminant concentration in the plant divided by the contaminant concentration in the soil. Bioconcentration factors may be derived differently for inorganic and organic pollutants, but they generally are related to the bioavailability of the pollutant in the soil.

Data on uptake of inorganics by plants may be available in the form of bioconcentration factors, which are discussed in Baes et al. (1984). The *Parameters Guidance Document* (under development by EPA) will contain values for Br_i for numerous inorganics.

However, in some cases, accumulation of inorganics is measured by “uptake response slopes” rather than by bioconcentration factors. The term “uptake response” is used to denote the difference between pre- and postexposure plant tissue concentrations. As defined in the literature, “exposure” here refers to the exposure of the plants to specific applications of the inorganic to the land, such as in fertilization or sludge application. In this case, the soil instantaneously achieves the long-term average soil concentration. In the case of combustion depositions, the long-term

average soil concentration builds up over time. Uptake response slopes have not typically been derived for these long-term buildup situations, and it is not known if the inorganic contaminants translocate into plants differently depending on whether the soil is amended with one swift application or the concentration builds up over time. However, there does not appear to be any immediate justification for not using uptake response curves for evaluating soil-to-plant impacts from depositions, as long as the risk assessor makes the appropriate unit conversions. Uptake response slopes have been derived from data sets where changes in plant concentration and contaminant application rate have been determined; the units often are expressed as (μg contaminant/g DW plant)/(kg contaminant applied/ha). Uptake response slopes can be converted to bioconcentration factors by converting the term in the denominator, kg contaminant applied/ha, to a concentration in similar units to the numerator, μg contaminant applied/g soil. If the contaminant has been tilled into the ground, then the conversion considers the mass of a 15- to 20-cm slice of a hectare. Assuming a 1.35 g/cm^3 soil bulk density, the mass of 20 cm/ha is $2.7 \cdot 10^9 \text{ g}$. Therefore, the denominator is converted to appropriate units by the multiplication of $[\text{kg/ha}] \cdot [10^9 \mu\text{g/kg}] \cdot [\text{ha}/2.7 \cdot 10^9 \text{ g}]$.

Uptake response slopes of metals by plants, reviewed by the Council for Agricultural Science and Technology (CAST) (1980), Ryan et al. (1982), and Logan and Chaney (1983), are influenced by application rate, soil pH, and soil organic matter content. Ryan et al. (1982) used linear regression of plant tissue cadmium concentration against cadmium application rate to derive uptake response slopes for various crops. The authors stated that, given constant soil conditions, cadmium plant tissue concentration had a highly significant positive linear correlation with the amount of cadmium added to the soil.

More recent work, as reviewed by Page et al. (1986), has shown that plant response to metals from sludge-amended soil is curvilinear, approaching a plateau concentration in tissue as sludge application rate increases. However, metal-

adsorptive materials present in the sludge matrix are thought to be responsible for this effect.

Soil pH is probably the most important characteristic influencing metal retention, and thus availability, by soils (LaBauve et al., 1988). The pH of soils varies greatly, from 2.0 or less in acid soils to 9.0 or more in alkaline soils (Hillel, 1980). Agricultural soils usually are limed to maintain the pH at approximately 6.5, the pH at which plant nutrients are most readily available for plant uptake.

Metal cations exhibit a pH-dependent adsorption behavior, probably due to several different adsorption mechanisms (Elliott et al., 1986). At pH less than 6.0, some metal cations tend to be more mobile. For example, cadmium mobility tends to increase as soil pH decreases; lead is less pH dependent (Harter, 1983). As soil pH increases, generally above 6.0, metal cations are adsorbed more strongly and become less available for uptake by plants. Several studies have demonstrated that, generally, plant uptake of metals decreases with increasing pH (Lagerwerff, 1971; Ryan et al., 1982; Giordano et al., 1983). However, the effects of liming acid soils to increase pH are unclear. While Giordano et al. (1983) and Ryan et al. (1982) report decreased cadmium concentration in plants after soil has been limed to pH 6.5, several studies cited in CAST (1980) indicate that using lime to raise soil pH from 5.0 to 6.6 had little or no effect on metal uptake by plants.

Ideally, site-specific data on soil pH and organic matter content should be used to assist in the assignment of a bioconcentration factor of inorganic contaminants, since these factors greatly influence the uptake of inorganic contaminants into plants. If literature data are used to derive bioconcentration factors, the data should be from studies in which the pH and organic matter content of the experimental soils are similar to those of soils at the site. Where evidence suggests that the response may be other than linear, a slope derived from soil concentrations similar to those predicted for the site in question is preferred. In general, it is probably reasonable and, at least, conservative to assume that there is no uptake-limiting effect for deposited metals, as was shown for sludge-amended soils (Page et al., 1986). Data derived from studies of

deposited emissions are preferable, if available. If data on depositions are unavailable (which is the case most of the time), bioconcentration factors (or uptake response slopes converted to bioconcentration factors) derived from other types of chemical application (such as sludge or pesticide additions) can be assumed to apply to deposited contaminants.

A linear uptake response also is assumed for organic chemicals, although as with inorganics, there may be situations where uptake could be nonlinear and a function of the soil concentration or characteristics of the plant. Given this assumption of linearity, a bioconcentration factor for organics can be derived from any data set that includes both tissue concentration ($\mu\text{g/g DW}$) and soil concentration ($\mu\text{g/g}$).

As for inorganics, the most accurate factor would be derived from interpolation of values for soil concentration similar to those predicted for the site of concern. Ideally, factors determined using local soil data should be used. However, if literature data are used, the experimental soils should be of similar type, pH, and organic matter as soils on the site.

For organics, uptake from soil and transport to above-ground plant parts is dependent on the solubility of a chemical in water, which is inversely proportional to the octanol-water partition coefficient, K_{ow} . Travis and Arms (1988) developed the following empirical relationship from field experiments on 29 organic chemicals, mostly pesticides, to estimate the bioconcentration factor ($r = 0.73$):

$$\log Br_i = 1.588 - 0.578 \log K_{ow} \quad (6-5)$$

where:

- Br_i = soil-to-plant bioconcentration factor for i th plant group ($[\mu\text{g contaminant/g DW}]/[\mu\text{g contaminant/g}]$)
- K_{ow} = octanol-water partition coefficient (dimensionless).

The TSCF is the other parameter that is used to model concentrations in above-ground vegetations as a function of soil concentration. Like the Br_i , it is a function of the contaminant octanol-water partition coefficient (Briggs et al., 1982; n=17, r not given):

$$TSCF = 0.784 e^{-[\log K_{ow} - 1.78]^2 / 2.44} \quad (6-6)$$

where:

TSCF = transpiration stream concentration factor ($[\mu\text{g contaminant/mL transpiration stream}]/[\mu\text{g contaminant/mL pore water}]$)

K_{ow} = octanol-water partition coefficient (unitless).

The range of $\log K_{ow}$ for which this relationship was derived was -0.57 to 4.6. Root-to-shoot translocation will be minimal for strongly sorbed compounds, that is, those with higher $\log K_{ow}$, perhaps above 4.5. The TSCF at $\log K_{ow} = 4.5$ is 0.038, meaning that the concentration in the transpiration stream water is less than 4% of what it is in soil water. Similarly, the Br at $\log K_{ow} = 4.5$ is 0.097, meaning that the above-ground plant concentration in fresh weight is less than 10% of the soil concentration. EPA's dioxin exposure reassessment did not consider root-to-shoot translocation for the dioxins, whose $\log K_{ow}$ exceeds 6.00. In general, it is recommended that root-to-shoot translocation need not be considered for organic contaminants with $\log K_{ow}$ s near to or greater than 6.0.

The *Parameters Guidance Document* will contain values for Br_i for numerous organics.

Briggs et al. (1982) developed the following relationship for RCF, considering compounds with a range of $\log K_{ow}$ s from -0.57 to 4.6 (n=18; r not given):

$$\log (RCF - 0.82) = 0.77 \log (K_{ow}) - 1.52 \quad (6-7)$$

where:

RCF = root concentration factor ($[\mu\text{g contaminant/g plant FW}]/[\mu\text{g}$

$$K_{ow} = \frac{\text{contaminant /mL pore water}}{\text{contaminant octanol-water partition coefficient (unitless)}}$$

When evaluating only the lipophilic compounds (which the authors defined as contaminants having $\log K_{ow}$ greater than 2.0), they derived the following variation (n=7, r=0.981):

$$\log (RCF) = 0.77 \log (K_{ow}) - 1.52 \quad (6-8)$$

Equation 6-7 should be used for organic compounds with $\log K_{ow} < 2.0$, whereas Equation 6-8 should be used for organic compounds with $\log K_{ow} > 2.0$.

The highest $\log K_{ow}$ of the seven for which the relationship in Equation 6-8 was derived is 4.6. This could mean that the relationship may not hold for compounds with $\log K_{ow}$ s greater than 4.6. However, a validation test done for dioxin-like compounds, which have $\log K_{ow}$ s ranging from about 6.0 to greater than 8.0, showed this relationship to perform fairly well. This exercise is summarized in Chapter 14 on Model Validation.

The *Parameters Guidance Document* will contain values for RCF for numerous organics. RCFs for inorganics have been devised from field studies and will be found in the *Parameters Guidance Document*.

The soil-water partition coefficient, K_{ds} , reflects the sorption tendencies of the contaminant, in combination with the sorption capabilities of the soil. K_{ds} is a function of the contaminant organic-carbon partition coefficient, K_{oc} , and the soil organic carbon fraction, OC_{sl} . Further information on this parameter can be found in Section 4.3.6.1.1.

6.3.2. Plant Concentration Due to Deposition of Particle-Bound Contaminants

(Pd_i). Contaminants are deposited on exposed plant surfaces by both dry and wet deposition of particle-bound contaminants. Contaminant concentration due to deposition is calculated for exposed produce but not for protected produce, grains, or

root vegetables, which are not directly exposed to deposition. The concentration of contaminant in plant tissue due to deposition onto plant surfaces is calculated as:

$$Pd_i = \frac{1000 [Dy d_p + (Fw Dy w_p)] Rp_i (1.0 - e^{-kp Tp_i})}{Yp_i kp}$$

(6-9)

where:

- Pd_i = concentration of contaminant in i th plant group due to deposition of particle-bound contaminants ($\mu\text{g/g DW}$)
- 1000 = conversion factor ($[10^6 \mu\text{g/g}]/[10^3 \text{g/kg}]$)
- $Dy d_p$ = yearly dry deposition rate of particle-based contaminants ($\text{g contaminant}/\text{m}^2/\text{yr}$)
- Fw = fraction of wet deposition that adheres to plant surfaces (dimensionless)
- $Dy w_p$ = yearly wet deposition rate of particle-based contaminants ($\text{g contaminant}/\text{m}^2/\text{yr}$)
- Rp_i = interception fraction of edible portion of plant tissue for i th plant group (dimensionless)
- kp = plant surface loss coefficient (yr^{-1})
- Tp_i = time of plant's exposure to deposition per harvest of edible portion of i th plant group (yr)
- Yp_i = yield or standing crop biomass of edible portion of i th plant group ($\text{kg DW}/\text{m}^2$).

The air dispersion model provides values for wet and dry deposition, $Dy w$ and $Dy d$. Information on these terms can be found in Chapter 3 on Air Modeling and Chapter 4 on Soil Concentration.

All of the contaminants that come in contact with plant surfaces as a result of dry deposition are assumed to remain on the surfaces until removed by weathering. However, only a fraction of contaminant material that intercepts plant surfaces as a result of wet deposition adheres; the remainder is assumed to wash off almost

immediately. F_w is a measure of the amount of wet deposition that adheres to the plant surface.

In a simulated precipitation study by Hoffman et al. (1992), retention on leaf surfaces was measured for radiolabeled particles of varying sizes (3, 9, and 25 μm). The authors found the “interception fractions” (equivalent to $R_{p_i} \cdot F_w$ in this document) for the three particle sizes ranged from 0.24 to 0.37 (mean=0.3). Assuming an R_{p_i} of 0.47 for forage (Baes et al., 1984), the F_w for organic contaminants sorbing to particles is assumed to be 0.6. Upon completion other values for F_w will be found in the *Parameters Guidance Document*.

Baes et al. (1984) define the interception fraction as a “factor which accounts for the fact that not all of the airborne material depositing within a unit area will initially deposit on edible vegetation surfaces.” Models developed for the Nuclear Regulatory Commission assumed the interception fraction was a constant of 0.2 for dry and wet deposition of particles (Boone et al., 1981). However, Shor et al. (1982) suggest that the diversity of plant growth indicates the need for vegetation-specific interception fractions. Baes et al. (1984) present equations for interception fractions for pasture grasses (forage), leafy vegetables, and exposed produce. Based on an empirically derived relationship to standing crop biomass, interception fractions for pasture grasses (forage) can be calculated as:

$$R_{pg} = 1 - e^{-2.88 Y_{pg}}$$

(6-10)

where:

R_{pg} = interception fraction for pasture grasses (dimensionless)

Y_{pg} = standing crop biomass for pasture grasses ($\text{kg DW}/\text{m}^2$).

Baes et al. (1984) estimated the average interception fraction for forage at 0.47.

Interception fractions for mature leafy vegetables can be calculated as:

$$Rp_{lv} = \frac{n_r r_n \pi r_f^2}{[(n_r - 1)d_p + 2r_f] [(r_n - 1)d_r + 2r_f]}$$

(6-11)

where:

- Rp_{lv} = interception fraction for mature leafy vegetables (dimensionless)
- n_r = number of plants per row
- r_n = number of rows of plants
- r_f = radius of individual fruit or plant (mm)
- d_p = distance between plants in a row (mm)
- d_r = distance between rows of plants (mm).

The average interception fraction for mature leafy vegetables was calculated to be 0.3. Interception fractions for exposed produce are based on the five most commercially important noncitrus fruit and field crops (apples, snap beans, tomatoes, peaches, cherries) (Baes et al., 1984) and are calculated by determining the total fruit cross-sectional area per unit area:

$$Rp_{rf} = \frac{n \pi r_f^2}{l w}$$

(6-12)

where:

- Rp_{rf} = interception fraction of round fruit (dimensionless)
- n = number of fruit per unit area
- r_f = radius of individual fruit or plant (mm)
- l = length of unit area (mm)
- w = width of unit area (mm).

For long rather than round exposed produce (e.g., snap beans), the above equation is modified to:

$$Rp_{lf} = \frac{2 n r_f l_f}{l w} \quad (6-13)$$

where:

- Rp_{lf} = interception fraction of long fruit (dimensionless)
- n = number of fruit per unit area
- r_f = radius of individual fruit or plant (mm)
- l_f = length of long fruit (mm)
- l = length of unit area (mm)
- w = width of unit area (mm).

Interception fractions for leafy vegetables and exposed produce also can be calculated based on an empirical relationship to standing crop biomass (Yp_i) as for pasture grasses:

$$Rp_{lv} = 1 - e^{-0.0846 Yp_{lv}} \quad (6-14)$$

$$Rp_e = 1 - e^{-0.0324 Yp_e} \quad (6-15)$$

where:

- Rp_{lv} = interception fraction for leafy vegetables (dimensionless)
- Yp_{lv} = standing crop biomass for leafy vegetables (kg DW/m²)
- Rp_e = interception fraction for exposed produce (dimensionless)

Yp_e = standing crop biomass for exposed produce (kg DW/m²).

Risk assessors may wish to choose the appropriate set of equations for interception fractions depending on the availability of site-specific data. In addition, values for number of plants per row, number of fruit per square meter, etc., should be selected from site-specific data, if possible.

Once contaminants are deposited onto plant surfaces via particle deposition processes, several environmental processes, including wind removal, water removal, and growth dilution, work to reduce the amount of contamination on the plant surface (Miller and Hoffman, 1983). The plant-surface loss coefficient is a measure of the amount of contaminant lost to these processes over time.

Miller and Hoffman (1983) derived a half-life of 14 days for particles depositing onto vegetation. This value represented the mid-range of experimental half-lives ranging from 2.8 to 34 days. These half-lives can be converted to the surface loss coefficient value of Equation 6-9, k_p , by first converting the half-lives to an equivalent annual basis (i.e., 2.8 days = 0.00767 yr), and then dividing them into 0.693 (i.e., 0.693/0.00767). Half-life values of 34 and 2.8 days correspond to k_p values ranging from 7.44 to 90.36 yrs⁻¹.

U.S. EPA's dioxin exposure reassessment used a k_p of 18.07 yr⁻¹, corresponding to a half-life of 14 days, to model the surface loss of particle phase of all dioxin-like compounds depositing onto all plant types, following the analysis of Miller and Hoffman (1983). However, this parameter is perhaps the most uncertain of the parameters for modeling the impacts of particle-phase contaminants depositing onto vegetation. This half-life corresponds to the half-life of the particles themselves on the plants. It is certainly possible that contaminants sorbed to particles would desorb and then resorb onto the plants. In this case, the particles could be weathering off the plants but the contaminants could be staying behind. Umlauf and McLachlan (1994) discuss the phenomena of the transfer of semivolatile organic compounds (SOCs) from depositing particles onto the leaf. The particles themselves may weather off the leaves with a

half-life of 14 days, but the SOCs would transfer from the particle and not weather off the leaves. Umlauf and McLachlan (1994) could not find information on the transfer of SOCs from particles to leaves, but they speculated that the lipid covering of the cuticle would facilitate a rapid particle-to-leaf transfer. In their modeling of several SOCs to spruce leaves, they assumed that the SOCs completely transferred from the particles to the leaves in both wet and dry particle-bound deposition with no subsequent loss of contaminant via weathering or degradation. This is equivalent to assuming an infinite half-life rather than a 14-day half-life. Umlauf and McLachlan (1994) also modeled the wet and dry deposition of vapor-phase SOCs. They could not find reasonable model agreement between modeled and measured leaf concentration. Still, their assumptions demonstrate the uncertainty of the weathering dissipation constant, k_p . For some compounds where evidence suggests a rapid photodegradative loss on plant surfaces, a surface loss coefficient corresponding to a half-life of less than 14 days may be appropriate.

Few data could be found in the literature to derive chemical-specific or plant-specific surface loss coefficients, k_p . For this reason, it is recommended that a value of 18.07 yr^{-1} be used unless experimental data can be found to support different values.

The time of a plant's exposure to deposition per harvest of the edible portion of the plant, TP_i , is treated as a constant and differs by crop type. For animal forage, a time period of 45 days is recommended based on an average of typical periods between successive hay harvests (60 days) and successive grazing by cattle (30 days) (Belcher and Travis, 1989). Since the units of T_p are years, this 45-day period is divided by 365 days to give a T_p of 0.123 years. For the remaining animal foods, time between successive hay harvests is divided by 365 days to give a T_p of 0.164 (Belcher and Travis, 1989). A T_p of 0.164 also is used in this document for foods consumed by humans. This value can be easily refined based on site-specific information on local food crops and growing seasons.

The standing crop biomass, Y_{p_i} , also has been termed "productivity" (Baes et al., 1984; Shor et al., 1982). Belcher and Travis (1989) have calculated average

productivity values for several animal and human foods. From their data compilations, productivities for forage and silage are estimated at 0.31 kg DW/m². In addition, Shor et al. (1982) present average U.S. productivity values for several exposed produce varieties averaging 0.24 kg DW/m².

6.3.3. Plant Concentration Due to Deposition of Vapor-Phase Contaminants (P_v).

In addition to the root uptake and deposition routes, plants can accumulate vapor-phase contaminants by the processes of wet and dry deposition. Plant impacts from vapor-phase contaminants, therefore, also can be modeled using Equation 6-9, which was the particle impact deposition algorithm. However, the current version of ISC3, the air dispersion model recommended for use in Chapter 3, does not have fully developed dry or wet vapor-phase deposition algorithms. A test-version dry deposition algorithm available in ISC3 is most appropriate for use on inorganic contaminants (metals). The dry and wet deposition of mercury, for example, has been modeled recently for an EPA assessment of the impacts of mercury emissions from combustors. It is not appropriate for use with organic vapor-phase deposition. The wet deposition algorithm is only for wet deposition of particle-bound contaminants.

In the absence of wet and dry deposition fluxes modeled by the ISC3 or another dispersion/deposition model, these fluxes can be estimated from the ambient air concentrations of the contaminant in the vapor phase:

$$Dy_{w_v} = 10^{-8} May Wv C_{va} \quad (6-16)$$

$$Dyd_v = 0.31536 Vd C_{va} \quad (6-17)$$

where:

Dy_{w_v} = yearly wet deposition rate of vapor-phase contaminants (g contaminant/m²/yr)

| | | |
|-------------|---|---|
| D_{y,d_v} | = | yearly dry deposition rate of vapor-phase contaminants (g contaminant/m ² /yr) |
| 10^{-8} | = | units conversion factor (g/μg) (m/cm) |
| C_{va} | = | vapor-phase concentration of contaminant in air due to stack emissions (μg/m ³) |
| May | = | annual average moisture (m/yr) |
| Wv | = | washout ratio for vapor-phase contaminants (unitless) |
| 0.31536 | = | units conversion factor ([m/yr]/[cm/sec] and [g/μg]) |
| Vd | = | vapor-phase dry deposition velocity (cm/sec). |

In these equations, the vapor-phase air concentration, C_{va} , is predicted by the air dispersion models.

Geraghty et al. (1973) provide a map showing isolines of annual average moisture, the May in term in Equation 6-16, throughout the United States. This map shows low rates of 5 to 20 in/yr in the desert Southwest, moderate rates of 25 to 40 in/yr in the Midwest cornbelt, 40 to 60 in/yr in the South, and so on.

Washout ratios, Wv of Equation 6-16, are generally defined as the concentration of contaminant in rain to the concentration of contaminant in air. Concentrations of contaminants in air and rainwater can be derived as a mass of contaminant divided by a mass of air/water or a volume of air/water. Mackay et al. (1986) show that volume-based washout ratios (e.g., mass of contaminant mixing in m³ air or water) exceed mass-based washout ratios (mass of contaminant mixing in kg of air or water) by a factor of 815, which is the ratio of water and air densities.

The washout ratio in Equation 6-16 is a volume-based ratio. Bidleman (1988) defines the overall washout ratio as: [mass contaminant/volume rain] ÷ [mass contaminant]/[volume air]. Bidleman (1988) also discusses the fact that overall washout includes both wet deposition of particulates and scouring of contaminants in the vapor phase. However, he claims that if H (Henry's Law Constant) is sufficiently high, vapor dissolution in droplets is negligible and only the particulate fraction is removed by wet deposition. He claims this to be the situation for n-alkanes, PCBs,

chlordane, DDT, and 2,3,7,8-TCDD. Developing overall washout ratios for these and several other SOCs, he estimates that vapor scouring accounts for 1% of the overall washout ratio for 2,3,7,8-TCDD. For PCBs, he estimates similar percentages of 2%, 4%, and 28% for Aroclors 1260, 1254, and 1248, respectively. Based on this work, it may be assumed that the washout of highly sorbed contaminants in the vapor phase will be negligible in comparison with the wet deposition of particle-bound contaminants, and it can be neglected. As given in Bidleman (1988), the washout ratio for soluble contaminants can be estimated as:

$$W_v = \frac{R T}{H} \quad (6-18)$$

where:

- W_v = washout ratio for vapor-phase contaminants (unitless)
- R = ideal gas constant (8.205·10⁻⁵ atm·m³/mol/°K)
- T = ambient temperature (°K)
- H = Henry's Law Constant (atm m³/mole).

In Equation 6-18, the ambient temperature can be assumed to be equal to 298°K (25°C) in the absence of site-specific temperatures. The Henry's Law Constant is a commonly available parameter.

The dry deposition velocity, V_d, for vapor-phase contaminants can be solved as the inverse of the sum of the resistances to transfer to the plant surface as:

$$V_d = \frac{1}{R_a + R_b + R_c} \quad (6-19)$$

where:

- V_d = vapor-phase dry deposition velocity (cm/sec)
- R_a = atmospheric resistance, a function of vertical turbulent transport (sec/cm)
- R_b = surface boundary layer resistance, a function of molecular diffusivity (sec/cm)
- R_c = plant canopy/leaf resistance, a function of vegetative density, stomatal uptake, surface effects, humidity, and so on (sec/cm).

Assignment of values for V_d , or for the resistance terms of Equation 6-19, is very difficult, and data are limited. Smith et al. (1995) assigned values of $R_a = 0.4$ sec/cm, $R_b = 0.38$ sec/cm, and $R_c = 0.5$ sec/cm, leading to an overall V_d of 0.78 cm/sec. Their modeling exercise was for the deposition of vapor-phase dioxins onto grass leaves. Trapp and Matthies (1995) modeled the dry deposition of dioxins onto a meadow and developed a value of V_d of 0.5 cm/sec based on a leaf area index of 5 and a “conductance” term of 0.1 cm/sec. The leaf area index is in units of m^2 leaf area/ m^2 ground area and would vary as a function of the canopy onto which the vapor-phase contaminant was depositing. The conductance term is in units similar to deposition velocity of cm/sec. Trapp and Matthies (1995) stated that it ranged from 0.01 cm/sec to 0.5 m/sec, with the upper boundary term appropriate for lipophilic compounds (high K_{ow}) and plants with relatively permeable cuticles, and the lower boundary conductance is where uptake is mainly via stomata and the compounds are less lipophilic. Deposition of vapor-phase mercury to soils used either a velocity deposition of 0.3 cm/sec or 1.0 cm/sec, depending on wind turbulence. Deposition velocities for several vapor-phase inorganics are displayed in Table 6-3. Sehmel (1980) recommends the use of 1 cm/sec for V_d for both organics and inorganic vapor-phase contaminants, in the absence of data, and that is the recommendation made here as well.

The final term to consider if using the deposition framework for modeling the vapor impacts to plants (Equation 6-9) is the rate of degradation of the contaminant on the plant, k_p . Smith et al. (1995) and Trapp and Matthies (1995) included a leaf surface loss term for the dioxins, k_p . Smith et al. (1995) derived a value of 0.495 day^{-1} (or on

an annual basis, 180.7 yr^{-1}), and Trapp and Matthies (1995) derived a value of 0.159 day^{-1} (58.0 yr^{-1}). This is a very uncertain term for the modeling of the deposition of vapor-phase contaminants to plants.

It may be appropriate to assume that certain vapor-phase contaminants, such as metals or other inorganics, do not degrade once depositing onto plants. In that case, Equation 6-9 is rewritten as:

| TABLE 6-3 | | | |
|--|--|----------------------------------|-----------------------|
| Dry Deposition Velocities for Gases (compiled in Bodek et al., 1988) | | | |
| Depositing Material | Deposition Surface | Deposition Velocity, Vd (cm/sec) | Reference |
| Cl ₂ | Alfalfa | 1.8, 2.1 | Sehmel (1971) |
| CO ₂ | Alfalfa | 0.3 | Sehmel (1971) |
| Fluorides | Forage | 1.9 ± 0.5 | Sehmel (1971) |
| HF | Alfalfa | 3.5 | Sehmel (1971) |
| H ₂ S | Sandy loam soil | 0.015 H ₂ S | Sehmel (1971) |
| Iodine | Grass | 7.2 ± 0.9 | Sehmel (1971) |
| NO _x | Pine needles | 0.4 - 0.8 (average) | Voldner et al. (1986) |
| NO _x | Crops and grassland (soybeans, summer day, unstable conditions) | 0.6 | Voldner et al. (1986) |
| HNO ₃ | Crops and grassland (summer day, 1 m reference height) | 2.5, 0.9 | Voldner et al. (1986) |
| O ₃ | Deciduous forest (leafless, during winter day) (during winter night) | 0.19 - 0.37 0.05 | Wesely (1983) |
| O ₃ | Soybean canopy (midday, appr. 25% of soil exposed) (windy conditions) | 0.85 1.2 | Wesely (1983) |
| SO ₂ | Water (neutral stability, 0.2 m reference height) | 0.5 ± 0.1 | Voldner et al. (1986) |
| SO ₂ | Snow (unstable conditions) | 0.17 | Voldner et al. (1986) |
| SO ₂ | Forest (dry) (wet) | 0.8 1.5 | Voldner et al. (1986) |

| TABLE 6-3 | | | |
|--|--|----------------------------------|-----------------------|
| Dry Deposition Velocities for Gases (compiled in Bodek et al., 1988) | | | |
| Depositing Material | Deposition Surface | Deposition Velocity, Vd (cm/sec) | Reference |
| SO ₂ | Grass and crops (unstable conditions; u = 0.11 - 0.26 m/sec, 2 m reference height) | 0.33 ± 0.30 | Voldner et al. (1986) |

$$Pv_i = \frac{1000 [Dyd_v + (Fw Dyw_v)] Rp_i Tp_i}{Yp_i} \quad (6-20)$$

where

- Pv_i = concentration of contaminant in *i*th plant group due to deposition of vapor-bound contaminants (µg/g DW)
- 1000 = conversion factor ([10⁶ µg/g]/[10³ g/kg])
- Dyd_v = yearly dry deposition rate of vapor-phase contaminants (g contaminant/m²/yr)
- Fw = fraction of wet deposition that adheres to plant surfaces (dimensionless)
- Dyw_v = yearly wet deposition rate of vapor-phase contaminants (g contaminant/m²/yr)
- Rp_i = interception fraction of edible portion of plant tissue for *i*th plant group (dimensionless)
- Tp_i = time of plant's exposure to deposition per harvest of edible portion of *i*th plant group (yr)
- Yp_i = yield or standing crop biomass of edible portion of *i*th plant group (Kg DW/m²).

The term "vapor deposition" can be misleading for some bioaccumulating contaminants such as the highly lipophilic dioxin compounds. Evidence has shown that these compounds can be essentially stripped from the air simply by coming in contact

with vegetation. In other words, the visual image of deposition can be misleading. An alternative model for the dry deposition of these vapor-phase lipophilic compounds is termed the “transfer” approach. As noted above, wet deposition of vapor-phase lipophilic compounds can be considered negligible. Therefore, this transfer approach can be used to model the overall vapor-phase impacts to plants.

The air-to-plant transfer algorithm solves for plant concentrations as a function of vapor-phase air concentrations, a “transfer factor,” and an empirical factor:

$$Pv_i = \frac{C_{va} Bv_i VG_{ag}}{\rho_a} \quad (6-21)$$

where:

- Pv_i = concentration of contaminant in i th plant group due to air-to-plant transfer of vapor-phase contaminants ($\mu\text{g/g DW}$)
- C_{va} = vapor-phase concentration of contaminant in air due to stack emissions ($\mu\text{g}/\text{m}^3$ air)
- Bv_i = air-to-plant biotransfer factor for i th plant group ($[\mu\text{g contaminant}/\text{g DW}]/[\mu\text{g contaminant}/\text{g air}]$)
- VG_{ag} = empirical above-ground vegetation correction factor (dimensionless)
- ρ_a = density of air ($1190 \text{ g}/\text{m}^3$).

Chapter 3 describes the air dispersion modeling and the vapor/particle partitioning algorithm used to model the vapor-phase air concentration term, C_{va} . The density of air term, ρ_a , converts this air concentration from mass/volume units to mass/mass units appropriate for use with the air-to-leaf transfer factor, Bv_i .

The air-to-plant biotransfer factor is defined as the ratio of contaminant concentration in aerial plant parts ($\mu\text{g/g DW}$) to the vapor-phase concentration of contaminant in air ($\mu\text{g/g}$). Little is known about the mechanisms of vapor uptake by leaves, and few experimentally derived air-to-leaf biotransfer factors are available in the literature. Bacci et al. (1990, 1992) conducted chamber studies on the transfer of

vapor-phase concentrations of 14 organic contaminants to azalea leaves. He correlated the results to the octanol-water partition coefficient (K_{ow}), Henry's Law Constant (H), ideal gas constant (R), and ambient temperature (T) in the following manner (Bacci et al., 1992):

$$\log (B_{vol}) = 1.065 \log K_{ow} - \log \left(\frac{H}{R T} \right) - 1.654$$

(6-22)

where:

- B_{vol} = volumetric air-to-leaf biotransfer factor ($[\mu\text{g contaminant/L leaf FW}]/[\mu\text{g contaminant/L air}]$)
- 1.065 = empirical constant (dimensionless)
- K_{ow} = octanol-water partition coefficient (dimensionless)
- H = Henry's Law Constant for contaminant ($\text{atm/m}^3/\text{mol}$)
- R = ideal gas constant ($8.205 \cdot 10^{-5} \text{ atm/m}^3/\text{mol}/^\circ\text{K}$)
- T = temperature ($298.1 \text{ }^\circ\text{K}$)
- 1.654 = empirical constant (dimensionless).

An earlier study by Bacci et al. (1990) showed that the volumetric transfer factor can be transformed to a mass-based transfer factor considering leaf density, density of air, and percent of wet leaf that is dry matter:

$$B_v = \frac{\rho_a B_{vol}}{\frac{(100 - M_d)}{100} \rho_p}$$

(6-23)

where:

- B_v = mass-based air-to-leaf biotransfer factor ($[\mu\text{g contaminant/g DW}]/[\mu\text{g contaminant/g air}]$)
- ρ_a = density of air (1.19 g/L)

- B_{vol} = volumetric air-to-leaf biotransfer factor ($[\mu\text{g contaminant/L leaf FW}]/[\mu\text{g contaminant/L air}]$)
- M_l = moisture content of wet leaf (% water)
- ρ_p = leaf density (g/L FW).

In his application of this equation to azalea leaves, Bacci et al. (1990) assumed a moisture content of 70% and a leaf density of 890 g/L. A moisture content of 85% and plant density of 770 g/L was recommended by McCrady and Maggard (1993) for grass. McCrady and Maggard (1993) also empirically determined a B_{vol} for 2,3,7,8-TCDD in their chamber experiments of the transfer of this compound to grass leaves and found that their B_{vol} was 40 times lower than a B_{vol} calculated for 2,3,7,8-TCDD from Equation 6-22. They attributed the difference mainly to differences in the plants used (grass leaves vs. azalea leaves) and to the fact that the Bacci experiments did not consider photodegradation whereas their experiments did include a phase where the grass was kept in sunlight, allowing for photodegradative loss of 2,3,7,8-TCDD from the leaves.

Based on this evidence, EPA developed B_{vol} for the dioxin-like compounds in the following manner (U.S. EPA, 1994). The Bacci algorithm in Equation 6-22 was used for all the compounds, but then each value calculated was divided by a factor of 40 based on the McCrady and Maggard (1993) experiments. The mass-based transfer factor, B_v , assumed the McCrady and Maggard (1993) moisture content of 85% and the grass density of 770 g/L, on the basis that grass was more pertinent to vegetations of the terrestrial food chain than azalea leaves.

Lorber (1995) developed B_v for dioxins on the basis of field data that included air concentrations and grass concentrations. He found that the B_v calculated empirically from these data was still lower than the B_v calculated using the Bacci algorithm and a division by 40. Specifically, the field-derived B_v s were about 2 to 5 times lower than the Bacci amended B_v s for the dioxin congeners.

For determination of B_v for organic contaminants other than dioxins (which should be assigned the values derived in Lorber [1995]), the following is recommended. Values should be determined using the original Bacci algorithm as in Equations 6-22

and 6-23. B_v values determined this way should be reduced by a factor of 100. This empirical reduction factor is based on the dual evidence described above for dioxins: that a reduction is necessary, and that the reduction is very likely going to be more than the factor of 40 derived from the McCrady and Maggard (1993) chamber experiments for 2,3,7,8-TCDD. It is recommended that a leaf density of 770 g/L and a leaf moisture of 85% be used for all vegetations, following the justification used by U.S. EPA (1994).

The B_v developed this way will allow for the prediction of impacts of vapor-phase organic contaminants to leafy vegetation. For bulky vegetation, however, this term is not fully appropriate because most organic contaminants that bioaccumulate (i.e., the semivolatile, lipophilic, persistent compounds such as PAHs, dioxins, PCBs, and so on) will not translocate from outer surfaces to inner plant parts. In other words, the B_v is appropriate for calculating the concentration in the outer surfaces of an apple but not the inner pulp.

The VG_{ag} was introduced by U.S. EPA (1994) to consider the difference between outer-surface and whole-plant concentrations for the dioxins when calculating plant impacts to vapor-phase dioxins using the B_v as developed above. The experiments by McCrady (1994) demonstrate the concept behind the VG_{ag} parameter. He measured the uptake rate of vapor-phase 2,3,7,8-TCDD into several vegetations. He found that the uptake rate for an apple divided by the uptake for the grass leaf was 0.02 (where uptake rates were from air to whole vegetation on a dry-weight basis). The ratio of the uptake rates of tomato and pepper to that of grass was similarly 0.03 and 0.08.

U.S. EPA's dioxin exposure reassessment used a VG_{ag} of 0.01 for the general category of unprotected fruits and vegetables, rather than a value in the range of 0.03 to 0.08, on the assumption that washing or peeling would further reduce outer surface residues of dioxins. The Agency also used a VG_{ag} of 0.50 for the animal food category of "silage" on the assumption that silage (as described earlier) is part protected and part unprotected. No correction for leafy vegetation (or a VG_{ag} of 1.00) is required since the B_v was developed from data on leafy vegetation. For site-specific applications, more refined values for VG_{ag} can be derived for specific vegetations for

human or animal consumption. Otherwise, these values for fruits/vegetations, silage, and grass are recommended for general use.

It is important to understand that the VG_{ag} is required only when the B_v used was based on the transfer of vapor-phase contaminants to leafy vegetation. This was the case in the Bacci experiments (Bacci et al., 1990, 1992), the McCrady experiments (McCrady and Maggard, 1993; McCrady, 1994), and the field experiments by Welsch-Pausch et al. (1995) that Lorber (1995) used to refine the B_v for the dioxins. If the B_v is developed from data on the transfer of vapor-phase contaminant to whole plant, then a VG_{ag} is not required.

The same B_v approach can be used for inorganic contaminants, if appropriate data are available to empirically determine B_v .

The deposition velocity approach for estimating dry deposition of vapors recognizes fundamental processes while the Bacci algorithm is a simple empirical treatment of a complex process. For both models, assessors face the practical concern of assigning parameters when selecting the appropriate model for use at a particular site. The vapor deposition algorithm has been parameterized in two separate research efforts for 2,3,7,8-TCDD vapor deposition onto grass plants (Smith et al., 1995; Trapp and Matthies, 1995). However, in a model validation exercise described in Chapter 13, it was shown that the parameterization by these two research teams led to a significant underprediction in a field site where the appropriate data for model testing had been gathered. The Bacci algorithm was amended by adding an empirical reduction factor of 100. This was based on field experiments which showed that the Bacci B_v , when applied to 2,3,7,8-TCDD, would overpredict measured grass concentrations by about 100. This overprediction was attributed to the fact that the idealized laboratory conditions in which the transfer of several organic contaminants to azalea leaves was measured in Bacci's experiments did not mimic outdoor conditions, particularly in that sunlight could degrade contaminants in the air or after they transferred to leaves. However, when this general framework was applied to PAHs in a model validation exercise described in Chapter 13, it was seen that plant concentrations were

underpredicted, sometimes up to a factor of 10. In other words, while the empirical reduction of factor of 100 may be appropriate for 2,3,7,8-TCDD, it may not be appropriate for all organic contaminants.

Therefore, both models for predicting the impact of vapor phase contaminants onto plants may have flaws. Chapter 13 provides a tabular summary of the B_v as assigned to the 17 congeners of dioxin and furan which have dioxin-like toxicity. These values were shown to successfully reproduce measured grass concentrations in the validation exercise in that chapter. It is recommended that the B_v framework has more validity for use with the dioxins and furans based on this model validation exercise. For other contaminants, the choice may not be as straightforward. If possible, assessors should attempt to evaluate the validity of their predicted vegetation concentrations by comparing predicted concentrations of their contaminants with measurements in the literature. This could be done in the context of a simple “reality check” by comparing predicted concentrations with those that can be found in the literature, or more vigorously as a model validation exercise where air and grass concentrations are concurrently available for such an exercise (see the air-to-leaf validation exercise in Chapter 13). Certainly, the prediction of vegetation concentrations should be identified as a key uncertainty in site assessments, since vegetation comprises the principal diet component for terrestrial animals, and therefore drives the potential human health risk posed by emissions of bioaccumulating contaminants from stacks.

6.4. CALCULATING CONTAMINANT CONCENTRATION IN ANIMAL TISSUES

The animals that humans usually consume as food take up contaminants from the food chain by ingesting plants and soil while grazing. The food chain model calculates the concentration of contaminant in animal tissues as a function of the concentration of contaminant in plants and soil, the diet of the animal in plants and soil, and the chemical- and animal tissue-specific bioconcentration or biotransfer factor. Two quite analogous approaches have been used, one termed the “biotransfer” approach and the other a “bioconcentration” approach. The biotransfer approach is expressed as:

$$A_j = \left[\sum_{i=1}^n (P_{ij} Qp_{ij} F_{ij}) + (C_s Qs_j Bs) \right] Ba_j \quad (6-24)$$

where:

- A_j = concentration of contaminant in j th animal tissue group (mg contaminant/kg animal tissue whole weight)
- P_{ij} = concentration of contaminant in i th plant group eaten by j th animal (mg/kg plant tissue DW)
- Qp_{ij} = quantity of i th plant group eaten by j th animal each day (kg plant tissue DW/day)
- F_{ij} = fraction of i th plant group grown on contaminated soil and eaten by j th animal (dimensionless)
- C_s = concentration of contaminant in soil (mg/kg)
- Qs_j = quantity of soil eaten by j th animal each day (kg soil/day)
- Bs = bioavailability of contaminant in soil vehicle relative to vegetation vehicle (dimensionless)
- Ba_j = contaminant biotransfer factor for j th animal tissue group [(mg contaminant/kg animal tissue whole weight)/(mg contaminant ingested/day)].

The units of the biotransfer factor, Ba_j , often are expressed as day/kg, which is the simplification of the units as expressed above. The bioconcentration algorithm is expressed as:

$$AF_j = \left[\sum_{i=1}^n (P_{ij} DF_{ij} F_{ij}) + (C_s DFs_j Bs) \right] BCF_j \quad (6-25)$$

where:

- AF_j = concentration of contaminant in lipid (or fat) portion of j th animal group (mg contaminant/kg animal lipid)
- P_{ij} = concentration of contaminant in i th plant group eaten by j th animal

- (mg/kg plant tissue DW)
- DF_{ij} = diet fraction of i th plant group eaten by j th animal each day (fraction)
- F_{ij} = fraction of i th plant group grown on contaminated soil and eaten by j th animal (dimensionless)
- C_s = concentration of contaminant in soil (mg/kg)
- DFs_j = diet fraction of soil eaten by j th animal each day (fraction) (note: $\sum DF_{ij} + DFs_j = 1.00$)
- Bs = bioavailability of contaminant in soil vehicle relative to vegetation vehicle (dimensionless)
- BCF_j = contaminant bioconcentration factor for j th animal tissue group ([mg contaminant/kg lipid]/[mg contaminant/kg DW diet]).

Risk assessors need to be very careful in their use of Equations 6-24 and 6-25 to consider the units for the parameters and the derivation of the biotransfer/bioconcentration factors. The A_j of Equation 6-24 calculates animal tissue on a whole-weight basis, not a dry-weight basis or a lipid basis. The Ba_j of Equation 6-24 transforms a contaminant input in a mass ingested/day basis to this whole-weight tissue concentration. Risk assessors should verify that their Ba_j will do this as well. Some literature values of the biotransfer factors for specific contaminants could be derived to predict animal tissue concentration on a dry-weight or lipid basis. Risk assessors should also verify that their plant mass ingested and their plant concentrations are on the same basis. In Equation 6-24, both are on a dry weight basis. Similarly, the AF_j of Equation 6-25 is on a lipid basis. The BCF_j of Equation 6-25 transforms an average concentration in the animal diet to a lipid-based concentration. Some BCF_j s in the literature transform the concentration in the diet of an animal to a whole weight rather than lipid concentration. Finally, the average concentration required in Equation 6-25 is calculated on a dry-weight rather than a fresh-weight basis.

General information on animal dietary habits and bioconcentration/biotransfer factors will be presented principally in the *Parameters Guidance Document* for beef, pork, poultry, eggs, and dairy products. In site-specific applications, risk assessors

should ascertain whether these foods are locally produced or consumed. Other animal food products may be included if they are consumed in significant quantities at a particular site. However, information will not be provided on biotransfer/bioconcentration factors or animal dietary habits for other animals.

The plant concentrations, P_{ij} , are calculated using the equations in Section 6.3 for each relevant plant group. Animals raised for food are fed a variety of plants, including grain (corn, oats, wheat, etc.), forage (pasture grass, hay), and silage. In addition, grazing animals ingest soil that clings to plants or incidentally while they are grazing. Plant ingestion generally is expressed as a rate, that is, the amount of plant tissue (kg dry weight) consumed per day. This is the $Q_{p_{ij}}$ term in Equation 6-24. These ingestion rates, plus the soil ingestion rate, Q_{s_j} , can be directly used to calculate animal tissue concentrations if a “biotransfer” factor approach is used. If a “bioconcentration” factor approach is used, all animal dietary components, including soil, need to be summed to obtain a total daily intake in units of kg/day. Then each component can be converted to a fraction for the Df_{ij} (plant dietary fraction) and DF_{s_j} (soil dietary fraction) of Equation 6-25. Note that the sum of the plant dietary fractions and the soil dietary fraction should equal 1.00. The *Parameters Guidance Document* will provide detail on the assignment of QP_{ij} and DF_{ij} for cattle (for beef or dairy), poultry (for meat or eggs), and swine. The *Parameters Guidance Document* will also provide guidance on the assignment of the animal soil ingestion parameters, Q_{s_j} and DF_{s_j} .

Default values of 1.0 should be assumed for the assignment of F_{ij} , or the fraction of the i th plant group grown on contaminated soil and eaten by the j th animal. Values less than 1.0 should be based on information regarding the portion of grain, silage, and other feeds that is imported from sites not impacted by the stack emission source.

The contaminant soil concentration, C_s , should be the concentration in the untilled soil layer. This is typically 1 to 2 cm, as described in Chapter 4. The relevant assumption is that the animals come in contact with soils during grazing or other activities on untilled soils (e.g., swine rooting). If, instead, it is assumed that the animals’ principal contact with soil is soil residue on plants that have been harvested

(i.e., grains or silages) or other contact with tilled soils, then it would be appropriate to assume a tilled soil concentration. Unless otherwise stated and known, the conservative assumption of contact with untilled soils should be assumed.

Soil bioavailability, B_s , can be thought of as the ratio between bioconcentration (or biotransfer) factors for soil and vegetation for a given contaminant. The efficiency of transfer from soil may differ from efficiency of transfer from plant material for some chemicals. If the transfer efficiency is lower for soils, then this ratio would be less than 1.0. If it were equal or greater than that of vegetation, the B_s would be equal to or greater than 1.0. U.S. EPA's dioxin exposure reassessment reviewed the evidence that 2,3,7,8-TCDD was less available to rats when rats were fed soil as compared with feed. Similarly, the Agency showed that the transfer of 2,3,7,8-TCDD from corn oil was more efficient than that of feed or soil. The evidence was in terms of absorption into the rat's gut rather than bioconcentration. The ratio of absorbed dose to administered dose was 0.70 to 0.83 when corn oil was the carrier, 0.50 to 0.60 when feed was the carrier, and 0.30 to 0.40 when soil was the carrier. Therefore, U.S. EPA assigned a value of 0.65 to B_s , based on the ratio of soil absorption to feed absorption, or $[0.3-0.4]/[0.5-0.6]$.

It is also important to note that the bioconcentration factors for dioxin-like compounds were developed from data on animal feeds in U.S. EPA's dioxin exposure reassessment. Stephens et al. (1995) determined bioconcentration factors for dioxins into chickens based on soil concentrations. Their dosing experiments verified that the chicken feed was free of dioxins (i.e., less than the detection limits). They dosed the animals with 10% soil and 90% chicken feed, and after analyzing various matrices (eggs, thigh meat, liver, and adipose tissue) they developed bioconcentration factors based on lipid concentrations and soil concentrations. Therefore, their bioconcentration factors were soil based rather than vegetation based. Since U.S. EPA defined the dioxin bioconcentration factors in terms of animal vegetation instead of soil, all the Stephens et al. (1995) soil concentration factors had to be converted to vegetation-based bioconcentration factors. To do so, U.S. EPA assumed a B_s of 0.65 and divided all the Stephens et al. (1995) bioconcentration factors by 0.65. In this way,

the bioconcentration factors of Stephens et al. (1995) for dioxins into poultry became vegetation based and a B_s of 0.65 was assigned.

This discussion implies the following regarding the proper assignment of the soil bioavailability term, B_s , in relation to bioconcentration factors. The risk assessor should first ascertain the basis of the bioconcentration/biotransfer factors. If they are based on vegetation (i.e., grains, forage, or silage), then a risk assessor has to decide whether the contaminant is less bioavailable (i.e., $B_s < 1.0$), equally bioavailable ($B_s = 1.0$), or more bioavailable ($B_s > 1.0$) on soil. The assessor should determine the value for B_s based on this decision. If the bioconcentration/biotransfer factors are based on soil, then the risk assessor has two choices. One is to convert the soil-based factor to a vegetation-based factor, as was done in U.S. EPA's dioxin exposure reassessment, and then assign a B_s value in keeping with this conversion. The other is to retain the soil-based bioconcentration factor, make the same decision as above with regard to whether the contaminant is less, equal, or more bioavailable on vegetation as compared with soil, and then define a " B_p ," or a plant bioavailability term, to use in Equations 6-24 and 6-25 in place of the " B_s ."

In most cases, bioconcentration factors developed from empirical data are based on vegetation rather than soil. If this is the case, it is recommended that a B_s be assigned a value of 0.65, in keeping with the data on 2,3,7,8-TCDD, unless other chemical-specific data are available. It seems reasonable to assume that vegetation is a more efficient vehicle of transfer of organic and inorganic contaminants than is soil, since vegetation is digested and soil passes through the system.

In general, risk assessors need to be very careful in the use of the bioavailability factor and the biotransfer/bioconcentration factors derived in the literature. The precise derivation of these factors, with particular attention to the definition of the units of the animal tissue and feed concentrations, need to be ascertained and converted to appropriate units, if necessary. The *Parameter Guidance Document* will contain bioconcentration and biotransfer parameters for several organics and inorganics.

For organic compounds, the octanol-water partition coefficient, K_{ow} , can be used to estimate biotransfer factors for beef and milk if experimental data are not available. Travis and Arms (1988) derived the following empirical relationships between K_{ow} and biotransfer factor for beef and milk (for beef, $n=36$, $r=0.81$; for milk, $n=28$, $r=0.74$):

$$\log Ba_{beef} = -7.6 + \log K_{ow} \quad (6-26)$$

$$\log Ba_{milk} = -8.1 + \log K_{ow} \quad (6-27)$$

These equations produce estimates of Ba that predict whole-beef and whole-milk concentrations on a fresh-weight basis given dietary input of organic contaminant in terms of mass ingested/day, as appropriate for use in Equation 6-24.

Equations 6-26 and 6-27 were derived from experimental data for milk (28 chemicals, primarily pesticides, with $\log K_{ow}$ values ranging from 2.8 to 6.9) and beef (36 chemicals, primarily pesticides, with $\log K_{ow}$ values ranging from 1.3 to 6.9). Their applicability to chemicals with $\log K_{ow}$ values outside this range is not recommended.

For example, these empirical relationships are not appropriate for dioxins. Data in a mass balance study of dioxins in lactating cows by McLachlan et al. (1990) suggest that these equations will greatly overestimate the transfer of dioxins into milk. This is shown in Table 6-4, which displays the Ba_{milk} determined by Equation 6-27 using $\log K_{ow}$ for the dioxin compounds as given in U.S. EPA's dioxin exposure reassessment and the Ba_{milk} determined directly from the data of McLachlan et al. (1990). Specifically, the data show that biotransfer of dioxin-like compounds decreases as the $\log K_{ow}$ increases, which is the opposite of the trend embodied in Equation 6-27. Failure of the Travis and Arms (1988) equations to accurately predict dioxin biotransfer is due, in part, to the fact that most of the organic compounds in their derivation had $\log K_{ow}$ less than that of the dioxins. The range of $\log K_{ow}$ for the Travis and Arms data set was 2.8

to 6.9, with only 6 of 28 data points from compounds with $\log K_{ow}$ greater than 6.0. The dioxin-like compounds have $\log K_{ow}$ that range from 6.5 to 8.0. For these compounds, it is recommended that the biotransfer factors calculated from McLachlan et al.'s (1990) data be used to predict milk concentrations. Note that these biotransfer factors in Table 6-4 are in the appropriate units for use in Equation 6-24.

The Ba_{milk} based on the data of McLachlan et al. (1990) can be transformed to Ba_{beef} . McLachlan (1994) argues that it is reasonable to assume that dioxins bioconcentrate almost equally in the fat of commercial beef and milk. This is because excretion of dioxins in the milk of the lactating animals is expected to be matched (approximately) by dilution of the contaminant reservoir due to rapid growth in the commercially raised beef cattle during their short lifespan (approximately 1.5 years).

| TABLE 6-4 | | |
|---|-------------------------|------------------------|
| Comparison of Predicted and Observed Biotransfer Factors for Dioxin-like Compounds in Beef and Milk | | |
| Congener | Predicted Ba_{milk}^a | Observed Ba_{milk}^b |
| 2,3,7,8-TCDD | 0.05 | 0.01 |
| 1,2,3,7,8-PCDD | 0.03 | 0.01 |
| 1,2,3,4,7,8-HxCDD | 0.50 | 0.006 |
| 1,2,3,6,7,8-HxCDD | 0.16 | 0.005 |
| 1,2,3,7,8,9-HxCDD | 0.16 | 0.005 |
| 1,2,3,4,6,7,8-HpCDD | 0.79 | 0.001 |
| OCDD | 1.26 | 0.001 |
| 2,3,7,8-TCDF | 0.01 | 0.003 |
| 2,3,4,7,8-PCDF | 0.05 | 0.009 |
| 1,2,3,7,8-PCDF | 0.03 | 0.002 |
| 1,2,3,4,7,8-HxCDF | 0.08 | 0.007 |
| 1,2,3,6,7,8-HxCDF | 0.08 | 0.006 |
| 1,2,3,7,8,9-HxCDF | 0.08 | 0.006 |
| 2,3,4,6,7,8-HxCDF | 0.08 | 0.005 |
| 1,2,3,4,6,7,8-HpCDF | 0.20 | 0.001 |
| 1,2,3,4,6,7,8-HpCDF | 0.79 | 0.003 |
| OCDF | 5.01 | 0.001 |

^a These predictions use the Travis and Arms (1988) empirical relationship for milk displayed above in Equation 6-27 in conjunction with $\log K_{ow}$ for the dioxins as given in EPA's dioxin exposure reassessment.

^b These observations were derived from data in McLachlan et al. (1990).

Assuming this to be generally true, the milk biotransfer factors for dioxins listed in Table 6-4 can be converted to beef biotransfer factors by making assumptions regarding the fat contents of beef and milk. U.S. EPA's dioxin exposure reassessment assumed that milk is 3.5% fat and that beef is 19% fat for its modeled scenarios. Biotransfer factors for beef would be 5.4 times higher ($19/3.5$) than for milk with these fat content assumptions. Therefore, the Ba_{beef} can be calculated as the McLachlan (1994) Ba_{milk} multiplied by 5.4.

Risk assessors should be aware, however, that beef biotransfer factors estimated this way will generally tend to underestimate beef concentrations in cattle that have not lactated and have lived longer than typical commercial beef cattle. This is expected to be only a small fraction of the total beef supply in America. However, this could be critical for certain site-specific circumstances. For example, bulls raised for breeding generally live longer lives and, of course, have not lactated. If subsistence cattle raising occurs in the vicinity of a stack emission source, assessors should determine the prevalence of home slaughter of bulls.

Equations similar to 6-26 and 6-27 are not available for animal tissues/products other than beef and milk, and the applicability of these equations to other types of animal tissues is unknown. However, in the complete absence of data, assessors may choose to apply the Ba_{beef} algorithm for organic contaminants with $\log K_{ow}$ less than 6.0 (or thereabouts) with a fat content adjustment, as was recommended above when using the McLachlan Ba_{milk} to calculate a Ba_{beef} . This presumes, of course, that other terrestrial animals such as poultry or swine tend to bioconcentrate organic contaminants in the same way cattle do.

6.5. CALCULATING HUMAN DAILY INTAKE

Human daily contaminant intake from consumption of contaminated plants is calculated by multiplying the concentration of contaminant in each plant group by the amount of contaminated plant group consumed daily. Similarly, daily contaminant intake from the consumption of meat, dairy products, or eggs is determined from the

concentration of contaminant in the animal tissue and the amount of each contaminated animal tissue that is consumed daily.

The sections below describe the equations used to calculate human daily intake. Before that, an overview is given of the critical exposure parameters, the consumption rates of vegetables, fruits, and terrestrial animal food products. However, this information is not provided as site-specific guidance. The risk assessor should ascertain local food production and consumption patterns, if possible. If that is not possible, then the appropriate reference for obtaining information on exposure factors is the *Exposure Factors Handbook* (U.S. EPA, 1996). Overview information provided is from that reference.

6.5.1. An Overview of Terrestrial Food Consumption Rates. Of most importance in site-specific assessments is the proximity of food production to the stack emission source. Existence of home gardening can be ascertained by visual inspection and with the help of local agricultural extension agents, the local health department, or other organizations. Similarly, prevalence of agricultural operations for larger scale production of vegetable/fruit crops or terrestrial animals should be ascertained for site-specific assessments. Once this information is at hand, the next decision is on the fraction of food consumed by individuals that is impacted by the stack emissions sources. Options for consideration range from subsistence behaviors (all of one or more food products is produced at the exposure site) to consuming a small portion of one or more food products that are locally produced. Finally, the risk assessor needs to determine rates of consumption of specific food items. These issues are explored in more depth in Chapter 2 on Human Exposure.

Of the issues identified, the rates of consumption are perhaps the most difficult to ascertain for a site-specific assessment. The other information just outlined — identification of terrestrial food production, prevalence of home gardening or agricultural operations, and even judgments on the fraction of consumed food that is home- or locally produced—can be ascertained with a degree of reasonableness with some effort and assistance from local authorities. Only a site-specific food

consumption survey can ascertain site-specific consumption rates, and this effort is usually beyond the scope of a site-specific assessment. In the absence of this information, risk assessors need to rely on data from existing food consumption surveys.

The *Exposure Factors Handbook* (U.S. EPA, 1996) summarizes food consumption surveys, most importantly, the U.S. Department of Agriculture's (USDA, 1975) Nationwide Food Consumption Survey (NFCS) and the USDA Continuing Survey of Food Intakes by Individuals (CSFII). The subset of data from these surveys described below includes an NFCS household survey conducted between 1987 and 1988 and a CSFII 3-day individual consumption survey conducted between 1989 and 1991. For simplicity, these will be abbreviated as the 1987-88 NFCS and the 1989-91 CSFII. A substantial amount of analysis of these data was conducted by U.S. EPA in order to interpret the information and display consumption rates for use in assessments such as the indirect exposure assessments of this methodology. Following are some of the more important issues and interpretative analyses done for the *Exposure Factors Handbook*, which should be considered by the assessor in conducting site-specific assessments.

6.5.1.1. Consumption Rates in Units of Mass Consumed/Body Weight/Time — The earlier version of the *Exposure Factors Handbook* (U.S. EPA, 1989) and, in fact, most exposure assessments through the latter 1980s and early 1990s, considered consumption rates in terms of mass consumed per day and then would assign body weight with a standard factor such as 70 kg for an adult and 16 kg for a child. Since there is a relationship between rates of consumption and body weight, it is more technically accurate to link the two by using a consumption rate expressed in terms of mass consumed/body weight/day and then not include the body weight as a separate factor in the calculation of average daily dose (ADD). The NFCS and the CSFII data included individual body weights with the consumption data. With this information, the consumption rates were derived in the *Exposure Factors Handbook* (U.S. EPA, 1996) on a more appropriate g consumed/kg body weight/day.

6.5.1.2. Proper Consideration of Fresh Versus Dry Weight and Lipid Versus Whole Weight Concentrations — Most food consumption surveys express consumption in fresh-weight terms, whereas the plant concentration algorithm typically solves for concentrations on a dry-weight basis. The rate of consumption needs to be on the same basis as the vegetation concentration, so that the mass of contaminant ingested can be properly calculated. A risk assessor can convert the concentration from a dry-weight to a fresh-weight basis, or alternately, the consumption rate from a fresh-weight to a dry-weight basis. These two options are expressed mathematically as:

$$P_i^{FW} = P_i^{DW} \left(\frac{100 - M_i}{100} \right) \quad (6-28)$$

$$Cp_i^{DW} = Cp_i^{FW} \left(\frac{100 - M_i}{100} \right) \quad (6-29)$$

where:

- P_i^{FW} = plant concentration of i th plant group in terms of fresh weight ($\mu\text{g/g}$ fresh weight)
- P_i^{DW} = plant concentration of i th plant group in terms of dry weight ($\mu\text{g/g}$ dry weight)
- Cp_i^{DW} = consumption rate of i th plant group in terms of dry weight (g DW/kg/ day)
- Cp_i^{FW} = consumption rate of i th plant group in terms of fresh weight (g FW/kg/ day)
- M_i = percent moisture for i th plant group (%).

Animal food products can be modeled in terms of lipid concentrations, as described above, whereas food consumption is most often in terms of whole weight. The

following equation converts an animal food product concentration in lipid terms to whole-weight terms:

$$A_j = AF_j F_j \quad (6-30)$$

where:

- A_j = concentration of contaminant in j th animal tissue group (mg contaminant/kg animal tissue whole weight)
- AF_j = concentration of contaminant in lipid (or fat) portion of j th animal group (mg contaminant/kg animal lipid)
- F_j = fat content of animal tissue.

The *Exposure Factors Handbook* provides information on food-specific moisture contents and lipid fractions. Vegetables and fruits are typically between 80% and 90% moisture. Animal tissue lipid concentrations range from 1% to 2% fat (low-fat milk or cheese) to greater than 20% (ground beef).

6.5.1.3. Consumers Only Versus Per Capita Consumption — If an individual reported consumption of a food product in the USDA surveys (or in general), then he/she was considered for the calculation of a “consumers-only” consumption rate. This is the rate of consumption calculated only for those who consumed the food product during the survey period. The “per capita” consumption rate includes consideration of all individuals in the survey, whether they reported consumption or not. Intuitively, a consumers-only rate will be higher than a per capita rate. It is not immediately obvious which rate to use in a site-specific assessment. For estimating average exposures, a per capita consumption rate is most appropriate since it considers individuals consuming and not consuming the food product (although nonconsumers may consume the product at some time), and it is therefore the best measure of “average” behaviors. A consumers-only rate may be more appropriate when assessing individual impacts in site-specific exposure assessments. After all, if a beef consumption exposure pathway is appropriate for a given site, it makes sense to

use a rate of consumption derived from individuals known to consume beef. When using consumers-only rates, other considerations include seasonal variations (e.g., during what season were the data obtained from survey participants, and does their consumption during particular seasons reflect availability of the food product) and the proper consideration of annual averages, realizing that all “consumers” in a survey may not consume the food product 52 weeks a year.

6.5.1.4. USDA Individual Surveys Versus Household Surveys — The 1989-91 CSFII surveys included an “individual” survey where individuals kept 3-day records of all food consumed. The *Exposure Factors Handbook* (U.S. EPA, 1996) used this survey to derive per capita and consumers-only consumption rates for a wide variety of food products, including vegetable/fruit and terrestrial animal food products, that could be considered for indirect exposure assessments. The 1987-88 NFCS surveys included a “household” component that was used by U.S. EPA to generate per capita and consumers-only consumption rates that were different from the individual consumption rates and potentially more useful for site-specific assessments. Specifically, the head of the household completed a survey reporting all food brought into and used within a household for a week. The term “used” does not necessarily mean consumed. The reported values do not account for food that is spoiled or discarded, food that is fed to pets, or inedible portions that get discarded during preparation or cooking. Included in this survey was information as to whether the food product brought into the house was “home produced” or store bought. The 1989-91 CSFII individual survey did not include the question of whether the consumed food was home produced or not. The rate of consumption of home-produced food products can be very important if scenarios considered for site-specific assessment include subsistence behaviors, which they often do. Below are a few other considerations for each type of survey.

6.5.1.4.1. Individual Surveys. The consumption rates are defined in this survey as “as eaten,” which means that losses due to cooking, peeling, nonconsumption of bones, and other preparations have been considered. This

contrasts the categorization of food brought into the house and “used,” where adjustments are necessary (as noted above and described in more detail below). Furthermore, components in food mixtures (e.g., the tuna in tuna casserole) are separated so that full consumption of the various components was estimated in the *Exposure Factors Handbook* (U.S. EPA, 1996). The data from the individual surveys of the NFCS are considered among the most robust for general assessment purposes and are quite often used. Unfortunately, consumption of home or locally produced foods is often of most importance in site-specific assessment, and the individual surveys do not provide information on the sources of the foods eaten.

6.5.1.4.2. Household Surveys. The identification of foods brought into the home as “home produced,” and the generation of consumption rates based on this information, is the principal benefit from this survey. A second advantage of these data over the individual survey data is that they cover behaviors over the course of a week, rather than only 3 days as in the individual consumption surveys. The identification of home-produced foods allows for the calculation of two quantities that are informative and may be used in site-specific assessments. One is the fraction (or percent) of all people who consume home-produced foods, and the second is the fraction of total food consumed in households that is home produced. Although these quantities appear to be similar, in fact they are developed differently and have different meanings. The fraction of individuals who consume home-produced foods is calculated as the fraction of all people in the 1987-88 NFCS who reported consumption of a specific home-produced food item divided by all people in the survey, whether or not they consumed the food product. The derivation of the fraction of food consumed that is home produced is a little more complicated. The total amount of a specific food item consumed is calculated as the total number of individuals in the survey multiplied by the surveywide per capita consumption rate. The total amount of home consumption of a specific food item is calculated as the total number of individuals reporting consumption of that food item multiplied by their consumer-only consumption rate for that food item. The ratio of this latter quantity (total amount of consumer-only

consumption of a specific home-produced food item) over the former quantity (total amount of per capita consumption of a specific food item whether home-produced or not) defines the fraction of food consumed that is home produced. Examples of these two slightly different fractions is given below in the sections on daily intake from contaminated plants and terrestrial animal food products.

Even though the 1987-88 NFCS home consumption data appear very pertinent to site-specific assessments, the raw data as supplied by the head of the household need interpretative analyses before arriving at individual consumption rates for home-produced foods. First, the total food brought into the house needs to be portioned to the various members of the household according to age (and hence portion size, etc.) and sex. Next, the data are grouped in terms of total amounts of raw commodity brought into the house and “used” (not “as eaten”). Consideration includes what the *Exposure Factors Handbook* (U.S. EPA, 1996) has termed “preparation loss,” “net cooking loss,” and “net postcooking loss,” which are defined as the percentages of weight loss (1) before cooking due to preparations such as coring, peeling, and stemming; (2) during cooking, such as water loss; and (3) after cooking, such as drainage of liquids from canned or frozen foods or removal of skin for fruits and vegetables. Table 6-5 presents meat weight losses due to cooking. This includes dripping and volatile losses, and postcooking losses include cutting, shrinkage, excess fat, bones, and juices. Preparation loss, cooking loss, and postcooking loss are not considered for dairy and eggs. Procedures for consideration of these factors and the delineation of consumption rates for home-produced foods are included in the *Exposure Factors Handbook* (U.S. EPA, 1996).

| Meat Type | Mean Net Cooking Loss (%) ^a | Mean Net Post Cooking Loss (%) ^b |
|-----------|--|---|
| Beef | 27 | 24 |
| Chicken | 30 | 30 |
| Lamb | 29 | 34 |
| Pork | 28 | 36 |
| Turkey | 31 | 28 |
| Veal | 30 | 25 |

^a Includes dripping and volatile losses during cooking. Averaged over various cuts and preparation methods.

^b Includes losses from cutting, shrinkage, excess fat, bones, scraps, and juices. Averaged over various cuts and preparation methods.

Source: USDA (1975).

The following sections discuss the consumption of vegetables/fruits and terrestrial animal food products. Some limited information on consumption rates is provided here, but only as overview information. More detailed information, such as the consumption of specific homegrown vegetables, the rates of consumption of beef as a function of geography or demographics, or even specific percentiles of food consumption, should be obtained from the *Exposure Factors Handbook* (U.S. EPA, 1996).

6.5.2. The Impact of Cooking on Food Concentrations. As indicated in the previous section, an assessor may need to introduce food preparation factors if the consumption rate that is used does not already account for losses in weight due to food preparation.

Another issue is the impact of cooking on the concentration of the contaminant in the food. This becomes important because essentially all the algorithms in this chapter to predict vegetative and terrestrial animal food concentrations were developed by using raw, and not cooked, food product. Therefore, predictions of contaminants in foods are valid for raw foods, and by not adjusting the concentration of the contaminant based on cooking practice, an assessor is assuming that the concentration of the contaminant is not effected by cooking. While weight loss of the food product from cooking is clear (due mainly to loss of water when cooking), it is not clear that the *concentration* of the contaminant should change as well.

In most cases, it should be assumed that cooking does not change the concentration because, as will be shown, there is very little data in the literature regarding the impact of cooking on the concentration of bioaccumulating contaminants in food products, and it is not all uniform. If an assessor makes an adjustment to the predicted concentration in food based on the impact of cooking, there should be a good reason for this adjustment and the assessor should be clear in the rationalization for this adjustment factor. An example might be, "Outdoor barbequing is an important aspect to the behaviors in this scenario, and several experiments have shown a reduction in lipid concentrations of contaminant X when barbequing."

If considering a change in concentration due to food preparation, the assessor first needs to understand the basis of the food concentration prediction: whether the concentration prediction was on a whole weight or on a lipid basis. This is important for bioaccumulating contaminants which are associated with the lipid portion of the food product, as are most contaminants that will be considered in this assessment methodology. If the modeled concentration was on a whole weight basis, than the assessor needs to consider the impact of cooking and other preparations on the lipid content of the fully prepared product. Say, for example, that predictions of the contaminant in beef on a whole weight basis were made, and it was assumed that the raw beef was 20% lipid. After broiling, evidence suggests that a substantial amount of the lipid is cooked out of the beef, or the fat is trimmed off the beef, such that the final

eaten beef product is 10% lipid. In this case, one would have reason to reduce predicted concentrations, that were made on a whole weight basis, by one-half. If, on the other hand, raw and cooked product have approximately the same percent lipid content (proportionally as much or more water was lost from cooking as was fat, e.g), than there would be no basis for a reduction in a predicted whole weight concentration.

If the concentration prediction was on a lipid basis, than it may not be important what cooking does to the lipid content. What becomes important is simply the assumption used for lipid content of the final prepared product (so that lipid-based concentrations can be converted to whole weight concentrations to be consistent with consumption rates expressed in whole weight terms; see Section 6.5.1.2.).

On the other hand, there is some evidence that cooking can reduce the concentration of some contaminants due to volatile loss of the contaminant from the lipid reservoir. Armbruster et al. (1989) concluded that losses of PCBs by vaporization best explained a 7.5% loss in concentration when cooking bluefish. Schechter et al. (1996, 1997) conducted studies on the impact of cooking on final concentrations of dioxins and coplanar PCB in hamburger, bacon, and catfish. Although they noted about a 40-50% loss in the amount of the dioxins and PCBs in these food products, this was found to be roughly equal to the decrease in overall weight of these products during cooking, so that the final concentrations were roughly the same. Like these studies, other studies have not been consistent or conclusive with regard to the impact of cooking on volatile loss of contaminants.

In summary, then, the assessor should assume that cooking and other preparations do not affect the lipid-based concentration of contaminants in animal food products, unless they have good reason to assume an increase or a reduction in concentration. Assessors should be cognizant of the basis of the food concentration prediction to be sure that the predicted concentrations are in units consistent with the food consumption rates used.

6.5.3. Calculating Daily Intake from Contaminated Plants. The human daily intake of contaminants due to consumption of a specific plant group is calculated by:

$$Dlp_i = P_i CP_i \quad (6-31)$$

where:

- Dlp_i = daily intake of contaminant from consumption of i th plant group ($\mu\text{g}/\text{kg}/\text{day}$)
- P_i = concentration of contaminant in i th plant group ($\mu\text{g}/\text{g DW}$)
- Cp_i = daily human consumption of locally grown items of i th plant group (g DW/kg/day).

Total daily intake from consumption of all plant groups is calculated by summing the contributions of each individual plant group:

$$Dlp = \sum_{i=1}^n Dlp_i \quad (6-32)$$

where:

- Dlp = total daily intake of contaminant from consumption of plant tissue ($\mu\text{g}/\text{kg}/\text{day}$)
- Dlp_i = daily intake of contaminant from consumption of i th plant group ($\mu\text{g}/\text{kg}/\text{day}$).

The total plant concentration, P_i , is the total concentration of the contaminant in the i th plant group, calculated according to the equations in Section 6.3. for each plant group. For use in this section, plant contaminant concentration is reported in units of μg contaminant/g plant tissue DW, as calculated in Section 6.3.

As discussed in Section 6.3., plants consumed by humans may be grouped into five categories: exposed vegetables, protected vegetables, root vegetables, exposed fruits, and protected fruits. Some consumption rates of vegetable/fruit consumption that

were developed in the *Exposure Factors Handbook* (U.S. EPA, 1996) include the following:

- ! The recommended per capita fruit intake rate for the general population is 3.4 g fresh weight/kg/day, and the recommended per capita vegetable intake rate for the general population is 4.3 g fresh weight/kg/day. The 95th percentiles for these two categories are 12 g/kg/day (fruit) and 10 g/kg/day (vegetables). These data are from the individual surveys of the 1989-91 CSFII and cover all categories of fruits and vegetables.
- ! The mean per capita consumption rates for exposed fruits, exposed vegetables, and root vegetables is 1.435 g fresh/kg/day, 1.490 g fresh/kg/day, and 1.245 g/kg/day, respectively. These data are also from the 1989-91 CSFII.
- ! Of all respondents in the household component of the 1987-88 NFCS, 7.8% reported consumption of homegrown fruits with an average consumers-only consumption rate of 2.68 g fresh/kg/day. The percentage of total fruits used in the household that were home produced was 4%. The distinction in the percentage of individuals consuming a home-produced product (in this case, 7.8% consuming home-produced fruits) and the percentage of a total product consumed that is home produced (in this case 4% of all fruits consumed were home produced) is described above. Of all respondents from this survey, 18.3% reported some consumption of homegrown vegetables with an average consumers-only rate of 2.08 g fresh/kg/day. Seven percent of all vegetables used in the household are home produced.
- ! These NFCS data are in raw commodity terms and would need to be converted to an as-eaten basis for use in exposure assessments. Mean net cooking losses averaged over several fruits equals about -90%, meaning that there was a net gain in the weight of the raw commodity due to addition of water or sugar in the cooking of fruits. Since the consumption of the food itself is of concern and not the food product plus added sugar or water, these gains from cooking should probably not be used in exposure assessments. Net preparation losses for fruits equaled about 25%, and cooking losses for fruits equaled about 30%. The net cooking loss for vegetables equaled about 12%.
- ! In general, a per capita consumption rate for a specific food product can be calculated by multiplying a consumers-only consumption rate by the fraction of consumers who consume that food product. For example, the per capita consumption rate for homegrown fruits can be estimated as the product of the consumers-only homegrown consumption rate of 2.68

g/kg/day, derived from the 1987-88 NFCS, and the fraction of household individuals consuming homegrown fruit, 0.078, to arrive at the per capita consumption rate for homegrown fruits of 0.21 g/kg/day. This consumption rate refers to fruits “used” in households. Therefore, it needs to be converted to an “as-eaten” basis. The information above suggests a preparation loss of 25% and a cooking loss of 30%, so that the final as-eaten rate is estimated as 0.11 g/kg/day (0.21 g/kg/day · [1-0.25] · [1-0.30]). A second per capita consumption rate for homegrown fruits can be arrived at by a different pathway: by multiplying the per capita consumption rate for fruits, 3.4 g/kg/day from the 1989-91 CSFII, by the fraction of fruit consumed that is homegrown, 0.04, to arrive at a per capita consumption rate of homegrown fruit of 0.14 g/kg/day. The analogous rates of per capita consumption of homegrown vegetables are calculated as 0.33 g/kg/day and 0.30 g/kg/day. These per capita consumption rates for homegrown fruits and vegetables are not relevant when estimating individual exposures when the individual is assumed to be a home producer. In that case, a risk assessor should apply the 2.68 and 2.08 g/kg/day consumption rates for homegrown fruit and vegetables, respectively. However, if an assessor wishes to calculate population impacts and does not have specific information on home-growing practices (i.e., fraction of individuals in an exposed population who home grow and their consumption rates), it would be appropriate to use the per capita consumption rates for homegrown products.

6.5.4. Calculating Daily Intake from Animal Tissue. Human daily intake due to ingestion of a single contaminated animal tissue group is calculated by:

$$Dla_j = A_j Ca_j \tag{6-33}$$

where:

- Dla_j = daily intake of contaminant from ingestion of j th animal tissue group ($\mu\text{g}/\text{kg}/\text{day}$)
- A_j = concentration of contaminant in j th animal tissue group (μg contaminant/g whole weight)
- Ca_j = daily human consumption of locally produced items of j th animal tissue group (g whole weight/kg body weight/day).

Total human daily intake from consumption of all animal products is calculated by summing the contributions of each specific animal tissue group:

$$Dla = \sum_{j=1}^n Dla_j \quad (6-34)$$

where:

- Dla = total daily intake of contaminant from consumption of animal tissue ($\mu\text{g}/\text{kg}/\text{day}$)
- Dla_j = daily intake of contaminant from consumption of j th animal tissue group ($\mu\text{g}/\text{kg}/\text{day}$).

A_j is the total concentration of the contaminant in the j th animal tissue, calculated according to the equations in Section 6.4. for each animal tissue group.

The *Exposure Factors Handbook* (U.S. EPA, 1996) provides considerable detail on the consumption rates for individual meat and dairy products. Following are some consumption rates and other key information from that reference:

- ! The mean per capita consumption rate from the individual surveys of the 1989-91 CSFII for total meat intake was 2.1 g/kg/day and for total dairy intake was 8.0 g/kg/day. The 95% per capita consumption rates for these two broad groups were 5.1 and 29.7 g/kg/day for meats and dairy, respectively. The *Exposure Factors Handbook* also gives information on the fractions of foods "used" that are home produced (in contrast to fraction of individuals who home produce). The fraction of total meat that is homegrown is 0.024, and the fraction of total dairy is 0.012. Therefore, an estimate of a per capita consumption rate for homegrown meats is 0.05 g/kg/day, and an estimate of a per capita consumption rate for homegrown dairy is 0.10 g/kg/day.

- ! The household component of the 1987-88 NFCS allowed for the generation of consumption rates of home-produced meats, dairy products, and eggs. As noted above, these rates can be directly used for dairy products and eggs, since no preparation or cooking loss is assumed. For meats, mean net cooking losses range from about 25% to 35%, while postcooking losses range from 10% to 35%.

! Table 6-6 summarizes information from the 1987-88 NFCS household survey for home-produced meats, dairy products, and eggs. This information includes percentages of individuals in households reporting home production/consumption of the product, the mean consumption rate, the 50th percentile consumption rate, and the 95th percentile consumption rate. Risk assessors may use these values in site-specific assessments for subsistence behaviors, but it is recommended that assessors rely on the *Exposure Factors Handbook* to understand these rates better and to ascertain if there is more appropriate information available for their site.

| Food Product | Percent Home Production | Mean Consumers-only Consumption Rate | 50th Percentile Consumers-only Consumption Rate | 95th Percentile Consumers-only Consumption Rate |
|--------------|-------------------------|--------------------------------------|---|---|
| All meats | 4.92 | 2.21 | 1.39 | 6.78 |
| Beef | 2.64 | 2.45 | 1.61 | 7.24 |
| Pork | 0.92 | 1.23 | 0.90 | 3.37 |
| Poultry | 0.97 | 1.57 | 1.23 | 3.83 |
| Dairy | 0.75 | 14.0 | 10.2 | 44.0 |
| Eggs | 1.10 | 0.73 | 0.47 | 1.69 |

Source: U.S. EPA, 1996

6.6. ALTERNATIVE MODELING APPROACHES FOR TERRESTRIAL FOOD CHAIN

The food chain algorithms presented in this chapter may not be the best ones for use in all assessments. However, they are, at least, reasonable starting points for site-specific or general assessments, and in fact, most food chain exposure modeling has included screening level approaches similar to those used in this assessment. The

assumptions behind models are described carefully throughout this chapter. If these assumptions do not apply to a particular situation, or where assessors require more spatial or temporal resolution, more-complex models should be considered. Finally, it cannot be overemphasized that measured concentrations are generally more reliable than modeled ones. Assessors should use measured concentrations if available and if such measurements can be considered spatially and temporally representative of the exposed populations.

Relatively simple, screening level models are used to model fate, transport, and transfer of bioaccumulating contaminants in this methodology. Simple assumptions are often made in order to arrive at the desired results, which are long-term average exposure media concentrations. The most important assumption is that the stack emissions remain constant throughout the period of emissions. While the air dispersion models are run using temporally varying meteorological data, in fact, the outputs used from these models are the average air concentrations and depositions which drive all other terrestrial and aquatic models.

The first examples of similar multimedia compartment modeling were probably the "fugacity" models proposed by Mackay (1979) and Mackay and Paterson (1981, 1982). Fugacity modeling is perhaps the single most technically sophisticated approach to multi-media modeling. Fugacity in this context is defined as the tendency for a chemical to escape from one environmental media compartment into another. It is based on the fact that at equilibrium, equal fugacities are established in all compartments of a system. The fugacity of a chemical present in an environmental media compartment is modeled using common fate and transport parameters such as octanol water partition coefficients, Henry's Constants, water solubilities, and so on. Modeling of the transfer of contaminants between compartments using fugacity can also involve more theoretical and less commonly available parameters such as conductances, properties of the environmental medium where the contaminant resides, boundary layer thicknesses, and so on. Examples of fugacity modeling include the transfer of nonionic organic chemicals between the atmosphere and surface water

(Mackay et al., 1986), between the atmosphere and plants (Riederer, 1990; McLachlan et al., 1995), and for food chain modeling (Travis and Hattemer-Frey, 1987). A regional fugacity model being used in regulatory risk assessment forums is the CALTOX (DTSC, 1993) model. Mackay (1991) provides a definitive text on multimedia compartment modeling using the fugacity approach.

A key difference between fugacity modeling and the modeling in this assessment is that for fugacity modeling, movement between compartments is considered for both directions — from compartment A to compartment B and also compartment B to compartment A. The modeling in this assessment is essentially one way — air to leaf, air to soil, vegetation to terrestrial animal, and so forth. By definition, fugacity modeling maintains a mass balance; concentrations of contaminants in adjoining compartments are dependent on each other. The models in this chapter do not explicitly maintain a mass balance as do fugacity models. However, correctly parameterized, the food chain models of this chapter should not violate mass balance principles. Explicit consideration of mass balance is the principal reason fugacity modeling can be considered more technically valid than the models of this chapter.

However, an important drawback for the fugacity approach applied to stack emission impacts is it does not consider spatial variability of concentrations within a compartment. For example, air concentrations vary depending on the distance from the source of air emissions. The fugacity approach would typically treat air as a single compartment with a uniform concentration. This would be a concern for a regional model such as the CALTOX model, which is recommended for use on a regional scale assuming a single regional air concentration. One could apply fugacity models to the air:plant:animal food chain starting with an air concentration predicted to occur at an exposure site using the ISC3 or other air dispersion model.

In addition to fugacity approaches, more sophisticated air:soil:plant modeling systems have been described by Trapp and colleagues in Trapp and McFarlane (1995), Trapp and Matthies (1995), and Trapp et al. (1990). For assessors wishing a more rigorous approach to modeling the concentration of the contaminant within the

animal instead of the simple bioconcentration/biotransfer approach, McLachlan (1994) presents a fugacity model for predicting the concentration of hydrophobic contaminants in the various compartments (milk, blood, different fat compartments) of a lactating cow.

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WATER CONCENTRATION AND EXPOSURE PATHWAYS

7.1. INTRODUCTION

Contaminants associated with particles emitted by combustors are deposited on land and water downwind from the combustor at rates determined by meteorology, terrain, and particle physics. Following deposition, these contaminants may be dissolved, repartitioned, or degraded. They may be transported over the ground in runoff to a surface water body or infiltrate the ground and recharge the ground water.

Contaminants from combustor emissions that have been transported into water can be directly ingested when humans or animals drink water. The total intake concentration of contaminant will be influenced by the source from which that drinking water is taken. Water treatment processes can sometimes remove or alter the contaminants available for ingestion. This alteration is specific to the chemistry of the system of water treatment and to the source water quality.

Individuals frequently are exposed to several sources of drinking water in any given day. On average, however, the drinking water ingested by an individual can be assumed to be either from the residence of that individual or from the drinking water source at the place at which he or she regularly spends time, such as the workplace or school. For the purposes of estimation, under the circumstances that the normal work schedule or school day occupies approximately one-half of the waking time of an individual, the intake of drinking water can probably be assumed to be approximately one-half from the residence and one-half from the workplace or school. In cases where an individual is not known to drink water or beverages made with drinking water from the local source, the assumption that the total intake is from his or her residence can be made, although the true total amount ingested may be smaller.

Contaminant intake from drinking water is proportional to the water concentration of the contaminant and the water ingestion rate from the source under examination. For many adults, this will be from one or two primary sources. The estimation of the

concentration of contaminants that are available for ingestion by an individual is significantly determined by the sampling protocol used to collect such information. Samples that are collected from residences can be either first draw or flushed samples. First draw samples are those from the very first water to leave the tap in the morning or after a long period of inactivity in the water line. These samples represent the amount of contaminant that accumulates as the drinking water is (1) in contact with the faucet or as the water lies stagnant allowing growth or regrowth of microbiological material, (2) in the pipe leading to that specific faucet and the solder joints along the way, and (3) in contact with the service line. Such samples have consistently shown higher concentrations of metals and other contaminants that can be derived from extended periods of time with the water in contact with the plumbing closest to the tap.

Another common sample used to estimate drinking water contamination is the flushed sample. This means the sample that is drawn from water that has not stood in the pipes or faucet but rather has passed through the system for only a short time and therefore has had no contact time to leach contaminants from the system. Such samples contain the contaminants that were in the water from the system or from the system materials, which in most cases will not be many because the contact time usually is not long.

Clearly, these two “typical” samples represent different levels of contaminants and are representative of different patterns of water use and, therefore, different types of exposure. It is valuable to know the type of samples from which the estimates of contaminant concentrations in the exposure are taken.

This chapter focuses on the contaminant concentration found in surface water bodies, collected precipitation and ground water, and the ingestion of contaminants through drinking water.

7.2. WATER CONCENTRATIONS OVERVIEW

7.2.1. The Framework. The following framework for estimating impacts to water bodies from combustor stack emissions estimates water column as well as bed sediment

concentrations. Water column concentrations include dissolved, sorbed to suspended sediments, and total (sorbed plus dissolved, or total contaminant divided by total water volume). This framework also provides three concentrations for the bed sediments: dissolved in pore water, sorbed to bed sediments, and total. The model accounts for four routes of contaminant entry into the water body: (1) sorbed to soils eroding into the water body, (2) dissolved in runoff water, (3) direct deposition of particle-bound contaminants, and (4) direct diffusion of vapor phase contaminants into the water body. The model also accounts for four dissipation processes that remove contaminants from the water column and/or bed sediment reservoirs: (1) decay of total contaminants (sorbed + dissolved) within the water column, (2) decay of total contaminants (sorbed + dissolved) within the bed sediment, (3) volatilization of dissolved phase out of the water column, and (4) removal of total contaminant via "burial" from the surficial bed sediment layer.

This burial rate constant is a function of the deposition of sediments from the water column to the upper bed; it accounts for the fact that much of the soil eroding into a water body annually becomes bottom sediment rather than suspended sediment. The effect on the water body usually is assumed to be uniform. This tends to be more realistic for smaller water bodies than for large water bodies and river systems. Uncertainties having to do with the size and spatial distribution of the water body should be considered by the risk assessor. If a body of water is large, uniform deposition to that water body may not be reasonable. In this case, the water body can be divided into segments for purposes of analysis.

The values of the parameters used for each segment should be obtained or calculated for that segment. This may be difficult to do. In cases where there are no measured values for the segments, the risk assessor will have to determine if using an average value for the entire water body is reasonable. If not, considerations such as distance from source, water movement (direction and speed), water quality, and season can enter into the decision of the portion of the total or variation from average that is reasonable for the segment in question. In addition, there may be other sources of

deposition-contaminated sediments to the various segments that need to be considered, as well as dilution by noncontaminated inflows. This model is therefore not well-suited for use with large water bodies that cannot be treated as a unit. It is also oversimplified for the estuarine environment, and is not easily adapted for use in those systems.

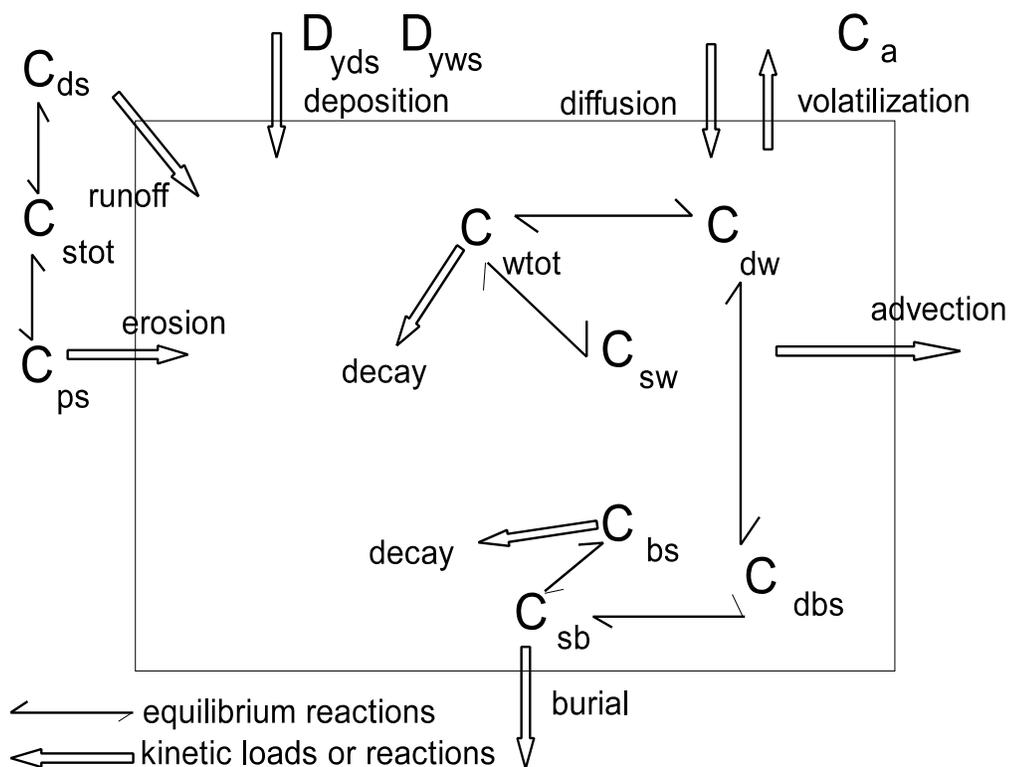
Key assumptions in the surface water impact algorithm are as follows:

- Soil concentrations within a depositional area (which is distinct from a watershed) are assumed to be uniform within the area and can be estimated by the following key parameters representing the area as a whole: dry and wet contaminant deposition rates, a soil dissipation rate, a soil bulk density, and a soil mixing depth. The depositional area is the surface area where contaminants are deposited directly whereas the watershed is often a much larger drainage basin that can carry contaminants from other depositional areas into this one.
- The partitioning of the contaminant within the soil/water matrices — surface soils, suspended solids in the water body, and bed sediments of the water body — can be described by partition coefficients.
- One route of entry into the surface water body is direct deposition. A second route of entry is contaminant dissolved in annual surface runoff. This is estimated as a function of the contaminant dissolved in soil water and annual water runoff. A third route of entry is via soil erosion. A calculated sorbed concentration of contaminant in soil, together with an annual soil erosion estimate, a sediment delivery ratio, and an enrichment ratio, can be used to describe the delivery of contaminant to the water body via soil erosion. A sediment delivery ratio serves to reduce the total potential amount of soil erosion (i.e., the total potential equals a unit erosion rate as in kg/m^2 times a watershed area, in m^2) reaching the water body recognizing that most of the erosion from a watershed during a year is deposited before reaching the water body. The enrichment ratio recognizes the fact that soils that erode tend to be lighter in texture, to be more abundant in surface area, and to have higher organic carbon. All these characteristics lead to concentrations in eroded soils that tend to be higher in concentration than *in situ* soils. A fourth and final route of entry is via diffusion in the gaseous phase. The dissolved concentration of contaminant in a water body is driven toward equilibrium with the vapor phase concentration above the water body. At equilibrium, gaseous diffusion into the water body is matched by volatilization out of the water body. Gaseous diffusion is estimated with a transfer rate (determined internally given user inputs) and a vapor phase air

concentration. This air concentration is specified by the user and is an output of the atmospheric transport model.

- For the steady-state surface water solution algorithm, it is assumed that equilibrium is maintained between contaminants within the water column and contaminants in surficial bed sediments. Equilibrium is established when the dissolved phase concentration in the water column is equal to the dissolved phase concentration within the bed sediments. This condition is imposed by the water body equations. For very large bodies of water, there may be a question about the existence of equilibrium conditions across the entire mass, since such things as currents, inversions, temperature, and local land use may prevent equilibrium conditions from being established across that mass. Here again, the risk assessor should use segments for which the relevant information can be obtained, if indeed they can be obtained or confidently estimated. The key factors in the decision to segment or not to segment the water body are (1) whether the size and shape of the water body and the location of the contaminant source with respect to the water body indicate that variation in deposition onto the surface can be expected to affect the contaminant load within the water body, and (2) whether the conditions affecting equilibrium (mentioned above) will overcome those variations.
- A rate of contaminant burial in bed sediments is estimated as a function of the rate at which sediments from the water column deposit onto the surficial sediment layer. This burial represents a permanent sink; it is recognized that a portion of the soil, and contaminant sorbed to it, erodes into a water body to become bottom sediment whereas the remainder becomes suspended sediment. This solution assumes that there will be a net depositional loss, even though resuspension and redeposition of sediments is ongoing, particularly with moving water bodies. For cases where the net deposition rate is zero, no burial loss is calculated.
- Separate water column and benthic decay rate constants allow for the consideration of decay mechanisms that remove contaminants from the water body. If a transformation yield coefficient is specified, the decay of one chemical is linked to the internal loading of a second chemical.

Figure 7-1 displays the framework for this analysis, with a listing of the 11 concentrations that are part of the solution algorithm. The state equations that link the concentrations follow Figure 7-1.



Definitions

| | | |
|------------|--|--------------------------|
| C_{stot} | total concentration of contaminant on soil | mg/L |
| C_{ds} | concentration dissolved in soil water | mg/L |
| C_{ps} | concentration sorbed to soil | mg/kg |
| D_{yds} | yearly dry deposition to surface water | mg/yr |
| D_{yws} | yearly wet deposition to surface water | mg/yr |
| C_a | concentration in air above water | $\mu\text{g}/\text{m}^3$ |
| C_{wc} | concentration in water column | mg/L |
| C_{wtot} | total concentration, water column and benthic sediment | mg/L |
| C_{dw} | concentration dissolved in water phase | mg/L |
| C_{sw} | concentration sorbed in water phase | mg/kg |
| C_{bs} | total concentration in benthic sediment | mg/L |
| C_{dbs} | concentration dissolved in bed sediment pore water | mg/L |
| C_{sb} | concentration sorbed to bottom sediments | mg/kg |

Figure 7-1

Equilibrium Condition of Water Columns and Bed Sediments

State Equations Corresponding to Figure 7-1

I. Soil

$$C_{stot} = C_S BD \quad (7-1)$$

$$C_{stot} = \theta_{sw} C_{ds} + BDC_{ps} \quad (7-2)$$

$$C_{ps} = C_{ds} Kd \quad (7-3)$$

$$C_{ps} = \frac{C_S Kd BD}{\theta_{sw} + Kd BD} \quad (7-4)$$

$$C_{ds} = \frac{C_S BD}{\theta_{sw} + Kd BD} \quad (7-5)$$

II. Surface Water System

$$C_{wtot} = C_{wc} \cdot d_{wc}/d + C_{bs} \cdot d_{bs}/d \quad (7-6)$$

$$f_{wc} = \frac{(1 + Kd_{sw} \cdot TSS \cdot 10^{-6}) \cdot d_{wc}/d}{((1 + Kd_{sw} \cdot TSS \cdot 10^{-6}) \cdot d_{wc}/d) + (\theta_{bs} + Kd_{bs} \cdot BS) \cdot d_{bs}/d} \quad (7-7)$$

$$f_{bs} = \frac{(\theta_{bs} + Kd_{bs} \cdot BS) \cdot d_{bs}/d}{(1 + Kd_{sw} \cdot TSS \cdot 10^{-6}) \cdot d_{wc}/d + (\theta_{bs} + Kd_{bs} \cdot BS) \cdot d_{bs}/d} \quad (7-8)$$

III. Water Column

$$C_{wc} = f_{wc} \cdot C_{wtot} \cdot d/d_{wc} \quad (7-9)$$

$$C_{dw} = C_{wc} \cdot f_{dwc} = C_{wc} \left[\frac{1}{1 + Kd_{sw} \cdot TSS \cdot 10^{-6}} \right] \quad (7-10)$$

$$C_{sw} = Kd_{sw} \cdot C_{dw} \quad (7-11)$$

IV. Bed Sediment

$$C_{bs} = f_{bs} \cdot C_{wtot} \cdot d/d_{bs} \quad (7-12)$$

$$C_{dbs} = C_{bs} \cdot f_{db}/\theta_{bs} = C_{bs} \left[\frac{1}{\theta_{bs} + Kd_{bs} \cdot BS} \right] \quad (7-13)$$

$$C_{sb} = Kd_{bs} \cdot C_{dbs} \quad (7-14)$$

Note that by substituting the relationship C_{wc} and C_{wtot} into the expression for C_{bs} , we can obtain benthic concentrations as a function of water column concentrations:

$$C_{bs} = C_{wc} \cdot \frac{\theta_{bs} + Kd_{bs} \cdot BS}{1 + Kd_{sw} \cdot TSS \cdot 10^{-6}} \quad (7-15)$$

$$C_{dbs} = C_{dw} \quad (7-16)$$

$$C_{sb} = C_{ps} \cdot Kd_{bs} / Kd_{sw} \quad (7-17)$$

where:

- θ_{sw} = volumetric soil water content (L/L)
- θ_{bs} = bed sediments porosity (L/L)
- Kd = soil/water partition coefficient (mL/g)
- Kd_{sw} = suspended sediment/surface water partition coefficient (mL/g)
- Kd_{bs} = bottom sediment/sediment pore water partition coefficient (mL/g)
- BD = bulk density (g/cm³)(soil)
- BS = bulk density (g/cm³)(sediments)
- C_{stot} = total concentration of contaminant in soil (mg/L)
- TSS = total suspended solids (mg/L)
- C_{dbs} = concentration of dissolved contaminant in benthic sediment (mg/L)
- C_{ds} = concentration of contaminant that is dissolved in soil water (mg/L)
- C_{ps} = concentration of contaminant that is sorbed to soil (mg/kg)
- C_{wtot} = total concentration of contaminant in water body (mg/L)
- C_{dw} = concentration of contaminant that is dissolved in water (mg/L)
- C_{sw} = concentration of sorbed phase contaminant in water (mg/kg)
- C_a = concentration in air above water
- C_{sb} = concentration sorbed to bottom sediments
- C_{bs} = total concentration in benthic sediment (mg/L)
- d_{wc} = depth of water column (m)
- d_{bs} = depth of upper benthic sediment layer (m)
- d = depth of water body, $d_w + d_b$ (m)
- f_{wc} = fraction of total water body contaminant concentration in water column
- f_{bs} = fraction of total water body contaminant concentration in bed sediment

- f_{dwc} = fraction of water column contaminant concentration that is dissolved
- f_{db} = fraction of benthic sediment contaminant concentration that is dissolved

7.2.2. Chemical Mass Balance Equations. If Figure 7-1 is taken as a control volume for the water body, a steady-state mass balance equation can be written that balances chemical loadings with outflow and loss:

$$C_{wtot} = \frac{L_T}{Vf_x f_{wc} + k_{wtot} V_{tot}} \quad (7-18)$$

where:

- C_{wtot} = total water body concentration, water column and benthic sediment (mg/L)
- L_T = total contaminant load to water body (g/yr)
- Vf_x = annual average flow rate through water body (m³/yr)
- f_{wc} = fraction of total water body contaminant concentration in water column
- k_{wtot} = total first-order dissipation rate constant, water column and benthic degradation, volatilization, and burial (yr⁻¹)
- V_{tot} = total volume of water body or water body segment, including water column and benthic sediment (m³)

A mass balance equation can be written for the watershed soils, balancing areal deposition fluxes with chemical loss processes:

$$C_s + \frac{L_{yW}}{k_s Z BD} (1.0 - \exp(-k_s td)) + C_{ps} \quad (7-19)$$

where:

- C_s = soil concentration (µg/g)(average for watershed after deposition)
- L_{yW} = annual average load to watershed — areal basis (g pollutant/m²-yr)

| | | |
|----------|---|---|
| k_s | = | soil loss rate constant resulting from soil leaching (yr^{-1}) |
| t_D | = | total time period over which deposition has occurred (yr) |
| Z | = | watershed mixing depth (to which deposited pollutant incorporates [cm]) |
| BD | = | bulk density (g/cm^3) (representative watershed soil) |
| 100 | = | units conversion factor ($\mu\text{g}\cdot\text{m}^2/\text{g}\cdot\text{cm}^2$) |
| C_{ps} | = | concentration sorbed to soils (naturally) (mg/kg) |

7.2.3. Sediment Mass Balance Equations. Before calculating chemical fate, a mass balance equation for sediments in the water body must be solved, first, for the water column. Referring to Figure 7-2, the soil eroding into the water body, X_w , equals the sum of the amount depositing into the upper bed, X_D , and the advective loss from the water column, X_a . Solving for the suspended solids concentration in the water column:

$$TSS = \frac{X_e A_L SD 10^3}{Vf_x + D_{ss} A_w} \quad (7-20)$$

where:

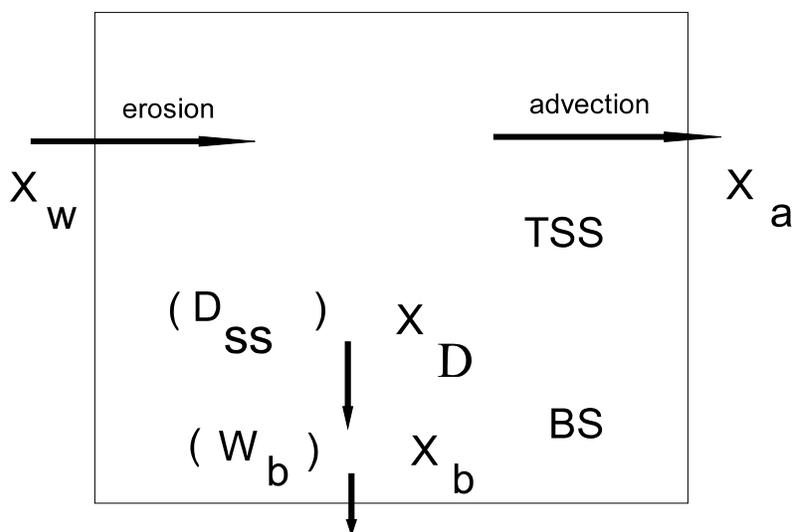
| | | |
|----------|---|--|
| TSS | = | total suspended solids (mg/L) |
| X_e | = | unit soil loss ($\text{kg}/\text{m}^2\text{-yr}$) |
| A_L | = | total watershed surface area (m^2) |
| SD | = | sediment delivery ratio |
| Vf_x | = | average volumetric flow rate through water body (m^3/yr) |
| D_{ss} | = | suspended solids deposition rate (m/yr) |
| A_w | = | water body surface area (m^2) |
| 10^3 | = | units conversion factor |

Often, the user will have data on average suspended solids but not on the deposition rate. In this case, the deposition rate can be calculated as:

$$D_{ss} = \frac{X_e A_L S D 10^3 - V f_x TSS}{A_w TSS} \quad (7-21)$$

where the terms are as defined above.

In the second part of the solids balance, the mass deposited to the bed, X_D , is set equal to the mass buried, X_b . Solving for the burial rate gives:



Definitions

| | | |
|----------|---|----------|
| X_w | soil erosion input from depositional area | g/yr |
| X_a | advective loss from water body | g/yr |
| D_{bs} | deposition onto bottom sediment | g/yr |
| X_b | burial below bottom sediment layer | g/yr |
| TSS | total suspended solids | mg/L |
| BS | bed (bottom) sediments bulk density | g/cm^3 |
| D_{ss} | rate of deposition and suspended solids onto bed sediment | m/yr |
| W_b | rate of burial | m/yr |
| X_D | amount depositing into upper bed | g/yr |

Figure 7-2

STEADY-STATE Representation for Sediments in Water Bodies

In the second part of the solids balance, the mass deposited to the bed, X_D , is set equal to the mass buried, X_b . Solving for the burial rate gives:

$$W_b = D_w \frac{TSS 10^{-6}}{BS} \quad (7-22)$$

where:

- W_b = rate of burial (m/yr)
- D_w = deposition rate (m/yr)
- TSS = total suspended solids (mg/L)
- BS = bed sediments bulk density (g/cm^3)
- 10^{-6} = units conversion factor (kg/mg)

Finally, the benthic porosity, the volume of water per volume of benthic space, is calculated from the benthic solids bulk (i.e., wetted) density concentration and sediment solids density:

$$\theta_{bs} = 1 - BS/\rho_s \quad (7-23)$$

where:

- θ_{bs} = benthic porosity (L/L)
- BS = bed sediments bulk density (g/cm^3)
- ρ_s = solids density, 2.65 kg/L.

For benthic solids bulk densities from 0.5 to 1.5 g/cm^3 , benthic porosity will range between 0.8 and 0.4.

7.2.4. Loads to the Water Body. Total chemical loading to the water body is composed of six inputs:

$$L_T = L_D + L_{ROI} + L_{RO} + L_E + L_{dif} + L_I \quad (7-24)$$

where:

- L_T = total contaminant load to water body (g/yr)

| | | |
|-----------|---|---|
| L_D | = | direct deposition load (mg/yr) |
| L_{ROI} | = | runoff load from impervious surfaces (g/yr) |
| L_{RO} | = | runoff load from pervious surfaces (g/yr) |
| L_E | = | soil erosion load (g/yr) |
| L_{dif} | = | diffusion of vapor phase contaminant (g/yr) |
| L_I | = | internal transformation load (g/yr) |

The runoff and erosion loads require estimating of average contaminant concentration in watershed soils that comprise the depositional area. This is discussed first.

7.2.4.1. Load Owing to Direct Deposition — The load to surface waters via direct deposition is solved as:

$$L_D = (D_{yds} + D_{yws})A_w \quad (7-25)$$

where:

| | | |
|-----------|---|---|
| L_D | = | direct deposition load (mg/yr) |
| D_{yds} | = | yearly average dry deposition rate (g/m ² -yr) (surface water) |
| D_{yws} | = | yearly average wet deposition rate (g/m ² -yr) (surface water) |
| A_w | = | water body surface area (m ²) |

7.2.4.2. Load Owing to Impervious Surface Runoff — A fraction of the chemical wet and dry deposition in the watershed will be to impervious surfaces. Dry deposition may accumulate and be washed off during rain events. If the impervious surface includes gutters, the pollutant load will be transported to surface waters, bypassing the watershed soils. The average load from such impervious surfaces is given by:

$$L_{ROI} = (D_{yww} + D_{ydw})A_I \quad (7-26)$$

where:

| | | |
|-----------|---|--|
| L_{ROI} | = | impervious surface runoff load (g/yr) |
| A_I | = | impervious watershed area receiving pollutant deposition (m ²) |

D_{yww} = yearly average wet deposition (g/m²-yr) (watershed)

D_{ydw} = yearly average dry deposition (g/m²-yr) (watershed)

7.2.4.3. Load Owing to Pervious Surface Runoff — Most of the chemical deposition to a watershed will be to pervious soil surfaces. These loads are accounted for in the soil mass balance equation. During periodic runoff events, dissolved chemical concentrations in the soil are transported to surface waters as given by:

$$L_{RO} = RO(A_L - A_I) \left[\frac{C_s BD}{\theta_{sw} + Kd_s BD} \right] 10^{-2} \quad (7-27)$$

where:

L_{RO} = pervious surface runoff load (g/yr)

RO = average annual runoff (cm/yr)

C_s = soil concentration (µg/g)

BD = bulk density (g/cm³) (soil)

θ_{sw} = volumetric soil water content (cm³/cm³)

Kd_s = soil/water partition coefficient (mL/mg³) [mL = cm²]

A_L = total watershed area receiving pollutant deposition (m²)

A_I = impervious watershed area receiving pollutant deposition (m²)

10^{-2} = units conversion factor (g²/kg-µg)

7.2.4.4. Load Due to Soil Erosion — During periodic erosion events, particulate chemical concentrations in the soil are transported to surface waters as given by:

$$L_E = X_e(A_L - A_I)SDER \left[\frac{C_s Kd_s BD}{\theta_{sw} + Kd_s BD} 10^{-3} \right] \quad (7-28)$$

where:

L_E = soil erosion load (g/yr)

| | | |
|---------------|---|--|
| X_e | = | unit soil loss (kg/m ² -yr) |
| C_s | = | soil concentration (µg/g) |
| BD | = | bulk density (g/cm ³) (soil) |
| θ_{sw} | = | volumetric soil water content (cm ³ /cm ³) |
| Kd_s | = | soil/water partition coefficient (mL/mg) |
| A_L | = | total watershed area receiving pollutant deposition (m ²) |
| A_I | = | impervious watershed area receiving pollutant deposition (m ²) |
| SD | = | sediment delivery ratio |
| ER | = | contaminant enrichment ratio |
| 10^{-3} | = | units conversion factor (g-cm ² /µg-m ²) |

7.2.4.5. Load Owing to Gaseous Diffusion — The change in the total water concentration over time because of volatilization is given by:

$$\frac{\partial C_{wtot}}{\partial t} /_{volat} = \frac{K_v}{d} \left(f_{wc} f_{dwc} C_{wtot} - \frac{C_a 10^{-6}}{H / (RT_{wk})} \right) \quad (7-29)$$

where:

| | | |
|------------|---|---|
| C_{wtot} | = | total water body contaminant concentration (mg/L) |
| K_v | = | overall transfer rate (m/yr) |
| d | = | depth of water body (m) |
| f_{wc} | = | fraction of total water body contaminant concentration in water column |
| f_{dwc} | = | fraction of water column contaminant concentration that is dissolved |
| C_a | = | vapor phase air concentration over water body (µg/m ³) |
| H | = | contaminant Henry's Constant (atm-m ³ /mole) |
| R | = | universal gas constant (8.206×10 ⁻⁵ atm-m ³ /mole-°K) |
| T_{wk} | = | water body temperature (°K) |

$$10^{-6} = \text{units conversion factor}$$

The right-hand side of Equation 7-29 contains two terms. The first term constitutes a first-order loss rate of aqueous contaminant. The second term in Equation 7-29 describes diffusion of gas-phase contaminant from the atmosphere into the water body. Because this term is independent of water body contaminant concentration, it can be treated as an external load. As formulated above, this second term has units of mg/L-yr. It must be converted to loading units by multiplying by the water column volume, V . Noting that V/d is equal to the surface water area A_w , the atmospheric diffusion load is given as:

$$L_{dif} = \frac{K_v C_a A_w 10^{-6}}{H/RT_{wk}} \quad (7-30)$$

where:

- L_{dif} = diffusion of vapor phase contaminant (g/yr)
- K_v = overall transfer rate (m/yr)
- A_w = water body surface area (m²)
- C_a = vapor phase air concentration over water body (μg/m³)
- H = contaminant Henry's Constant (atm-m³/mole)
- R = universal gas constant (8.206×10⁻⁵ atm-m³/mole-°K)
- T_{wk} = water body temperature (°K)
- 10^{-6} = units conversion factor

7.2.4.6. Load Due to Internal Transformation — Chemicals may be transformed chemically or biologically into daughter products, which may be of interest in risk assessment. A transformation yield can be specified for the sequential reaction:



where:

| | | |
|---------|---|---|
| B | = | parent compound |
| C | = | daughter compound (or reaction product) |
| $k(B)$ | = | first-order transformation rate constant (yr^{-1}) |
| $Y(BC)$ | = | reaction yield coefficient (g of C /g of B) |

The internal loading generated by this transformation reaction is given by:

$$L_I = [k_{gwc}(B)C_{wctot}(B)V_{wc} + k_{gb}(B)C_{bt}(B)V_{bs}]Y(BC) \quad (7-32)$$

where:

| | | |
|----------------|---|--|
| L_I | = | internal transformation load to C (g/yr) |
| $k_{gwc}(B)$ | = | water column transformation rate constant—from B to C (yr^{-1}) |
| $k_{gb}(B)$ | = | benthic transformation rate constant — from B to C (yr^{-1}) |
| $C_{wctot}(B)$ | = | total water column concentration of B (mg/L) |
| $C_{bt}(B)$ | = | total benthic concentration of B (mg/L) |
| V_{wc} | = | water column volume (m^3) |
| V_{bs} | = | benthic sediment volume (m^3) |
| $Y(BC)$ | = | reaction yield coefficient (g of C /g of B) |

This loading is added to chemical C . If the yield coefficient is set to zero, then the compounds are treated as independent.

7.2.5. Advective Flow from the Water Body. The first term in the denominator of Equation 7-18 accounts for advective flow from the water body. It is the product of the annual average volumetric flow rate, Vf_x , and the fraction of the chemical in the water body that is present in the water column, f_{wc} . An affected water body derives its annual flow from its watershed or effective drainage area. Flow and watershed area, then, are related, and compatible values should be specified by the user. Given the area of drainage, one way to estimate annual flow volume is to multiply total drainage area by a unit surface water runoff. The Water Atlas of the United States (Geraghty et al., 1973) provides maps with isolines of

annual average surface water runoff, which is defined as all flow contributions to surface water bodies, including direct runoff, shallow interflow, and ground water recharge. The values ranged from 5 to 40 in/yr in various parts of the United States.

7.2.6. Chemical Dissipation Within the Water Body. The second term in the denominator of Equation 7-18 accounts for dissipation within the water body. It is the product of the water body volume, V_{tot} , and the total first order dissipation rate constant, k_{wtot} . The water body volume, in units of m^3 , together with the annual flow rate, in m^3/yr , determines the average residence time of a pollutant traveling through the water body. The residence time for Lake Erie is about 10 years, for example, whereas for the larger Lake Superior, it is estimated to be 200 years. For a swiftly moving river, on the other hand, the residence time can be on the order of hours (1 hour = 0.00011 yr). Larger volumes and residence times allow the internal dissipation processes to have a greater effect on pollutant concentration; smaller volumes and residence times lessen the effect. The user should take care to specify reasonable volumes for the type of surface water body being represented. In addition, the user should specify compatible values for related water body parameters, such as surface area, A_w . The water body volume divided by the surface area gives the average depth, which can vary from a fraction of a meter for small streams to a few meters for shallow reservoirs to tens of meters for deep lakes.

The total dissipation rate constant, k_{wtot} , applies to the total water body concentration, C_{wtot} , and includes processes affecting any of the chemical phases— dissolved or sorbed in the water column or benthic sediments. Volatilization, water column and benthic degradation, and burial are considered:

$$k_{wtot} = f_{dwc} k_{gwc} + f_{bs} k_{gb} + f_{dwc} k_{vwc} + f_{bs} k_b \quad (7-33)$$

where:

- k_{wtot} = overall total water body dissipation rate constant (yr^{-1})
- k_{gwc} = water column degradation or transformation rate constant (yr^{-1})
- k_{gb} = benthic degradation or transformation rate constant (yr^{-1})
- k_{vwc} = water column volatilization loss rate constant (yr^{-1})

| | | |
|-----------|---|---|
| k_b | = | benthic burial rate constant (yr^{-1}) |
| f_{dwc} | = | fraction of total water body contaminant concentration in water column |
| f_{bs} | = | fraction of total water body contaminant concentration in benthic sediment. |

7.2.6.1. Chemical/Biological Degradation — Contaminants can be degraded by a number of processes in the water column or in the benthic sediment. The major chemical and biological processes include hydrolysis, photolysis, oxidation, and biodegradation. Each of these processes has been studied and is incorporated in a mechanistic way in advanced water quality models. In this methodology, the overall first-order water column and benthic degradation rate constants are user input variables and should be based on knowledge about the contaminant behavior in similar surface water systems.

7.2.6.2. Volatilization — Volatile chemicals can move between the water column and the overlying air. Diffusion into the water from the atmosphere is treated as an external load. The quantity $f_{dwc} f_{dw} C_{wtot}$, which is equal to the water column dissolved phase concentration, C_{dw} , is subject to volatilization loss. The rate constant for volatilization from the water column, k_{vwc} , is given as:

$$k_{vwc} = \frac{K_v f_{dwc}}{d} \quad (7-34)$$

where:

| | | |
|-----------|---|---|
| k_{vwc} | = | water column volatilization loss rate constant (yr^{-1}) |
| K_v | = | overall transfer rate (m/yr) |
| f_{dwc} | = | fraction of contaminant in the water column that is dissolved |
| d | = | depth of water body (m) |

The overall transfer rate, K_v or conductivity, is determined by the two-layer resistance model. The two-resistance method assumes that two “stagnant films” are bounded on either

side by well-mixed compartments. Concentration differences serve as the driving force for the water layer diffusion. Pressure differences drive the diffusion for the air layer. From balance considerations, it is obvious that the same mass must pass through both films, thus the two resistances combine in series, so that the conductivity is the reciprocal of the total resistance:

$$K_v = (R_L + R_G)^{-1} = (K_L^{-1} + (K_G \frac{H}{RT_{wk}})^{-1})^{-1} \quad (7-35)$$

where:

| | | |
|----------|---|--|
| K_v | = | overall transfer rate (m/yr) |
| R_L | = | liquid phase resistance (yr/m) |
| R_G | = | gas phase resistance (yr/m) |
| K_L | = | liquid phase transfer coefficient (m/yr) |
| K_G | = | gas phase transfer coefficient (m/yr) |
| H | = | Henry's law constant for the pollutant (atm-m ³ /mole) |
| R | = | universal gas constant (8.206× 10 ⁻⁵ atm-m ³ /mole-°K) |
| T_{wk} | = | water body temperature (°K) |

The value of K_v , the conductivity, depends on the intensity of turbulence in a water body and in the overlying atmosphere. As the Henry's Law coefficient increases, the conductivity tends to be increasingly influenced by the intensity of turbulence in water. As the Henry's Law coefficient decreases, the value of the conductivity tends to be increasingly influenced by the intensity of atmospheric turbulence.

Because Henry's Law coefficient generally increases with increasing vapor pressure of a compound and generally decreases with increasing solubility of a compound, highly volatile low-solubility compounds are most likely to exhibit mass transfer limitations in water, and relatively nonvolatile high-solubility compounds are more likely to exhibit mass transfer

limitations in the air. Volatilization is usually of relatively lower magnitude in lakes and reservoirs than in rivers and streams.

The estimated volatilization rate constant is for a nominal temperature of 20°C. It is adjusted for the actual water temperature using the equation:

$$K_{v,T} = K_{20}\theta^{(T-20)} \quad (7-36)$$

where:

- θ = temperature correction factor, set to 1.026
- T = water body temperature (note that because the temperature in the model is in °K, the water body temperature will have to be converted to Kelvin—conversion factor 0°K = -273.16 °C.

A variety of methods have been proposed to compute the liquid phase (K_L) and gas phase (K_G) transfer coefficients. The particular method that is recommended here is the O'Connor method, as described below in Section 7.2.6.4.

The liquid and gas film transfer coefficients computed under this option vary with the type of water body. The type of water body is specified as one of the surface water constants and can either be a flowing stream, river, or estuary, or a stagnant pond or a lake. The primary difference is that in a flowing water body, the turbulence is primarily a function of the stream velocity, whereas for stagnant water bodies, wind shear may dominate. The formulations used to compute the transfer coefficients vary with the water body type, as shown below.

7.2.6.3. Flowing Stream or River — For a flowing system (type 0), the transfer coefficients are controlled by flow-induced turbulence. For these systems, the liquid film transfer coefficient (K_L) is computed using the O'Connor and Dobbins (1956) formula:

$$K_L = \left(\frac{10^{-4} D_w u}{d} \right)^{1/2} (3.15 \times 10^7) \quad (7-37)$$

where:

- K_L = liquid phase transfer coefficient (m/yr)

| | | |
|--------------------|---|---|
| u | = | current velocity (m/s) |
| D_w | = | diffusivity of the chemical in water (cm ² /sec) |
| d | = | depth of water body (m) |
| 10^{-4} | = | units conversion factor |
| 3.15×10^7 | = | units conversion factor |

The gas phase transfer coefficient (K_G) is assumed constant at 36,500 m/yr for flowing systems.

7.2.6.4. Quiescent Lake or Pond — For a stagnant system (type 1), the transfer coefficients are controlled by wind-induced turbulence, and the liquid film transfer coefficient (K_L) is computed using the O'Connor et al. (1983) equations where:

$$K_L = u^* \left(\frac{\rho_a}{\rho_w} \right)^{0.5} \left(\frac{k^{0.33}}{\lambda_2} \right) Sc_{Cw}^{-0.67} (3.15 \times 10^7) \quad (7-38)$$

$$K_G = u^* \left(\frac{k^{0.33}}{\lambda_2} \right) Sc_a^{-0.67} (3.15 \times 10^7) \quad (7-39)$$

$$u^* = C_d^{0.5} W_{10} \quad (7-40)$$

$$Sc_a = \frac{\mu_a}{\rho_a D_a} = \frac{V_a}{D_a} \quad (7-41)$$

$$D_a = \frac{1.9}{MW^{2/3}} \quad (7-42)$$

$$V_a = (1.32 + 0.009 T) \times 10^5 \quad (7-43)$$

and where :

K_L = liquid phase transfer coefficient (m/yr)

$$Sc_w = \frac{\mu_w}{\rho_w D_w} \quad (7-44)$$

$$D_w = \frac{22 \times 10^{-5}}{MW^{2/3}} \quad (7-45)$$

$$\rho_w = 1 - 8.8 \times 10^{-5} T_{wc} \quad (7-46)$$

$$\log(\mu_w) = \left[\frac{1301}{998.333 + 8.1855(T_{wc} - 20) + 0.00585(T_{wc} - 20)^2} \right] - 3.0233 \quad (7-47)$$

| | | |
|-------------|---|--|
| K_G | = | gas phase transfer coefficient (m/yr) |
| u^* | = | shear velocity (m/s) |
| C_d | = | drag coefficient (= 0.0011) |
| W_{10} | = | wind velocity, 10 m above water surface (m/s) |
| ρ_a | = | density of air corresponding to water temperature (g/cm ³) |
| ρ_w | = | density of water corresponding to water temperature (g/cm ³) |
| k | = | von Karman's constant (= 0.4) |
| λ_2 | = | dimensionless viscous sublayer thickness (= 4) |
| Sc_a | = | air Schmidt number (dimensionless) |
| Sc_w | = | water Schmidt number (dimensionless) |
| D_a | = | diffusivity of chemical in air (cm ² /sec) |
| D_w | = | diffusivity of chemical in water (cm ² /sec) |
| μ_a | = | viscosity of air corresponding to air temperature (g/cm-s) |
| μ_w | = | viscosity of water corresponding to water temperature (g/cm-s) |
| V_a | = | dynamic viscosity of air (cm ² /sec) |
| MW | = | molecular weight |
| T | = | air temperature (note that because the temperature in the model is in °K; the result of this will have to be converted to Kelvin—conversion factor 0°K = -273.16°C) |
| T_{wc} | = | water temperature (note that because the temperature in the model is in °K; the result of this will have to be converted to Kelvin—conversion factor 0° K = -273.16°C) |

$$3.15 \times 10^7 = \text{units conversion factor}$$

7.2.6.5. Deposition and Burial — The rate of burial, W_b , in the benthic situation is determined as a function of user input variables as part of the sediment balance (see Section 7.2.3.). This burial rate is used to determine the mass loss of contaminant from below the surficial benthic sediment layer. As seen in Figure 7-1, the burial loss rate is applied to the total benthic contaminant concentration, C_{bt} . The water body contaminant burial loss rate is solved by equating the mass loss rate of total water body chemical with mass loss rate of benthic chemical:

$$C_{wtot} V_{tot} k_b = C_{bt} V_{bs} \frac{W_b}{d_{bs}} \quad (7-48)$$

where:

- C_{wtot} = total water body contaminant concentration, including water column and benthic sediment (mg/L)
- V_{tot} = total volume of water body or water body segment, including water column and benthic sediment (m^3)
- k_b = first-order burial rate constant for total chemical (yr^{-1})
- C_{bt} = total benthic contaminant concentration (mg/L)
- V_{bs} = volume of upper benthic sediment layer (m^3)
- d_{bs} = depth of upper benthic sediment layer (m)
- W_b = rate of burial (m/yr)

The state equations given after Figure 7-1 indicate that the total benthic contaminant concentration, C_{bt} , can be expressed as a function of the total water body concentration, C_{wtot} . Solving for the total chemical burial rate gives:

$$k_b = f_{bs} \frac{W_b}{d_{bs}} \quad (7-49)$$

where:

- f_{bs} = fraction of total water body contaminant concentration in bed sediment
- W_b = rate of burial (m/yr)
- d_{bs} = depth of upper benthic sediment layer (m)
- k_b = benthic burial rate (yr^{-1})

7.2.6.6. Peak Storm Event Concentrations — The previous equations together describe the long-term average water body concentrations of sediment and chemical. Short-term peak concentrations also may be of interest in assessing risk from some chemicals. The basic mass balance equations for determining peak storm event concentrations of sediment and chemical are:

$$TSS_{storm} = \frac{X_{storm}}{V_{storm}} 10^3 \quad (7-50)$$

$$C_{storm} = \frac{L_{storm}}{V_{storm}} \quad (7-51)$$

where:

- TSS_{storm} = total suspended solids during peak storm event (mg/L)
- C_{storm} = peak chemical concentration during storm event (mg/L)
- V_{storm} = peak water body volume during storm event (m^3)
- X_{storm} = total load of sediment from watershed during storm (kg)
- L_{storm} = total load of chemical from watershed during storm, runoff and erosion (g)
- 10^3 = g/kg

The water body volume during the storm is first calculated; the assumption is that the storm runoff volume is added to the average streamflow volume:

$$V_{storm} = \frac{Vf_x t_{storm}}{365 \times 24} + Q_{ROstorm} \quad (7-52)$$

where:

- V_{storm} = peak water body volume during storm event (m^3)
- Vf_x = annual average stream flow (m^3/yr)
- t_{storm} = duration of storm event (hr)
- $Q_{ROstorm}$ = total storm runoff volume (m^3)
- 365 = days/yr
- 24 = hr/day

The total storm runoff volume, $Q_{ROstorm}$, is the sum of runoff from pervious and impervious areas of the watershed:

$$Q_{ROstorm} = (A_L - A_I) d_{RO} 10^{-2} + A_I M_{tot} 10^{-2} \quad (7-53)$$

where:

- $Q_{ROstorm}$ = total storm runoff volume (m^3)
- A_L = total watershed surface area (m^2)
- A_I = impervious surface area on watershed (m^2)
- M_{tot} = depth of total rainfall for storm event (cm)
- d_{RO} = depth of runoff from pervious areas of watershed (cm)
- 10^{-2} = m/cm

The runoff depth, d_{RO} , is estimated by the following equation:

$$d_{RO} = \frac{(RO + M_{tot} - 0.2S)^2}{RO + M_{storm} + 0.8S} \quad (7-54)$$

where:

- d_{RO} = depth of runoff from pervious areas of watershed (cm)
- RO = runoff (cm/yr)

- M_{tot} = depth of total rainfall for storm event (cm)
 M_{storm} = depth of snowmelt during storm event (cm)
 S = watershed retention parameter (cm)

The watershed retention parameter, S , is calculated from the Soil Conservation Service runoff curve (number input by the user) according to the following equation:

$$S = 2.54[(1000 / CN) - 10] \quad (7-55)$$

where:

- S = watershed retention parameter (cm)
 CN = runoff curve number

Next, the mass of sediment eroded from the watershed to the receiving water during a storm event can be estimated with the Modified Universal Soil Loss Equation (MUSCLE):

$$X_{storm} = 2.04 \times 10^6 (Q_{ps} q_p)^{0.56} K L S C P S D \quad (7-56)$$

where:

- X_{storm} = total load of sediment from watershed during storm (kg)
 Q_{ps} = volume of runoff from pervious area (km²-cm)
 q_p = peak runoff from pervious area (m³/sec)
 K = erodibility factor (tons/acre)
 LS = topographic or slope length factor (unitless)
 C = cover management factor (unitless)
 P = supporting practice factor (unitless)
 SD = sediment delivery ratio

This equation is an empirical relationship, and the units must be consistent with those shown above. Selection of K , LS , C , P , and SD is discussed in Wischmeier and Smith (1978) and U.S. EPA (1985).

The storm runoff volume from pervious areas is calculated from the runoff depth according to:

$$Q_{ps} = (A_L - A_I)d_{RO} 10^{-6} \quad (7-57)$$

where:

- Q_{ps} = volume of runoff from pervious area (km²-cm)
- A_L = total watershed surface area (m²)
- A_I = impervious surface area on watershed (m²)
- d_{RO} = depth of runoff from pervious areas of watershed (cm)
- 10^{-6} = km²/m²

A trapezoidal hydrograph is assumed so that the peak runoff rate can be calculated as:

$$q_p = \frac{(A_L - A_I)d_{RO}}{t_{storm}} \left[\frac{RO + M_{tot}}{RO + M_{storm} - 0.2S} \right] \frac{10^{-2}}{3600} \quad (7-58)$$

where:

- q_p = peak runoff from pervious area (m³/sec)
- A_L = total watershed surface area (m²)
- A_I = impervious surface area on watershed (m²)
- d_{RO} = depth of runoff from pervious areas of watershed (cm)
- M_{tot} = depth of total rainfall for storm event (cm)
- M_{storm} = depth of snowmelt during storm event (cm)
- RO = runoff (cm/yr)
- S = watershed retention parameter (cm)
- t_{storm} = duration of storm event (hr)
- 10^{-2} = m/cm
- 3600 = sec/hr

Finally, the mass of chemical load to the receiving water during the storm event is calculated:

$$L_{storm} = L_{ROIstorm} + L_{ROstorm} + L_{sE} \quad (7-59)$$

where:

- L_{storm} = total load of chemical from watershed during storm, runoff and erosion (g)
- $L_{ROIstorm}$ = storm runoff load from impervious surfaces (g)
- $L_{ROstorm}$ = storm runoff load from pervious surfaces (g)
- L_{sE} = storm erosion load from pervious surfaces (g)

Runoff from impervious surfaces includes dryfall accumulated since the previous rainfall event and wetfall during the present rainfall event:

$$L_{ROIstorm} = \left(\frac{D_{ydw} t_{acc}}{365} + \frac{D_{yww} t_{event}}{24 \times 365} \right) A_I \quad (7-60)$$

where:

- $L_{ROIstorm}$ = storm runoff load from impervious surfaces (g)
- D_{ydw} = yearly average dry deposition (g/m^2 -yr)
- D_{yww} = yearly average wet deposition (g/m^2 -yr)
- A_I = impervious surface area on watershed (m^2)
- t_{acc} = time since previous storm event (days)
- t_{event} = duration of rainfall event (hr)
- 24 = hrs/day
- 365 = days/yr

Runoff from pervious soil surfaces transports dissolved chemical concentrations in the soil to the water body:

$$L_{ROstorm} = (A_L - A_I) d_{RO} C_{ds} 10^{-2} \quad (7-61)$$

where:

- $L_{ROstorm}$ = storm runoff load from pervious surfaces (g)
- C_{ds} = dissolved chemical concentration in soil (mg/L)
- A_L = total watershed surface area (m²)
- A_I = impervious surface area on watershed (m²)
- d_{RO} = depth of runoff from pervious areas of watershed (cm)
- 10^{-2} = units conversion factor (m/cm)

The mass of chemical eroded from the watershed to the receiving water during a storm event can be calculated from the sediment loss and the particulate soil concentration:

$$L_{sEstorm} = X_{storm} SD ER C_{ps} 10^{-3} \quad (7-62)$$

where:

- $L_{sEstorm}$ = erosion load of chemical from watershed during storm (g)
- X_{storm} = total load of sediment from watershed during storm (kg)
- C_{ps} = chemical concentration sorbed to soil (mg/kg)
- SD = sediment delivery rate
- ER = soil enrichment ratio
- 10^{-3} = g/mg

For risk assessment purposes, the dissolved chemical concentration can be of interest. It may be assumed, for example, that the sorbed chemical fraction is removed in a water treatment plant, and that the dissolved fraction is passed through to the user. The dissolved concentration in the river during the storm event is calculated by:

$$C_{dstorm} = C_{storm} \left[\frac{1}{1 + Kd_{sw} TSS_{storm} 10^{-6}} \right] \quad (7-63)$$

where:

- C_{dstorm} = dissolved concentration of chemical during storm event (mg/L)

- C_{storm} = peak chemical concentration during storm event (mg/L)
- TSS_{storm} = total suspended solids (during peak storm event) (mg/L)
- Kd_{sw} = suspended sediment/surface water partition coefficient (L/kg)
- 10^{-6} = kg/mg

7.2.7. Parameter Guidance. The following text is offered as abbreviated guidance for all user input and internally solved terms for the water equations.

- D_{ydw} , D_{yww} , C_a : Based on output from the atmospheric transport model, the user must specify the long-term watershed average values for three loading parameters: dry and wet deposition of contaminants sorbed to particulates and the vapor phase air concentration. In addition, the user must specify the duration of the atmospheric loading. Together, these parameters drive the watershed soil and water body contamination. The deposition fluxes are in units of g/m²-yr, the air concentration is in units of µg/m³, and the time of concentration is in yr.
- ksg , Y_{pi} , C_{sb} : The overall chemical degradation/transformation rate constant, yield coefficient, and background concentration must be specified for the soil. The soil degradation rate constant, ksg , is specific to the contaminant and to environmental conditions, such as climate, soil type, and soil moisture. In EPA's indirect exposure document (U.S. EPA, 1990a), cadmium was assumed not to undergo soil degradation, and ksg was given a value of 0. The degradation rate constant for benzo(a)pyrene was set at 0.803 yr⁻¹. If chemical C is created by a transformation reaction of chemical B in soils, the yield coefficient, Y_{pi} , must be specified. One example is the methylation of inorganic mercury, represented as chemical B , into methyl mercury, represented as chemical C , with a yield coefficient of 1.0. If the yield coefficient is left at 0, no transformation will be calculated. The background concentration is the concentration of the

contaminant sorbed to the soil or the natural concentration in the soil prior to contaminant deposition. This value will be 0.0 for most organic contaminants. Nonzero values for the naturally occurring metals, however, generally should be specified.

- k_{gwc} , k_{gb} , Y : Chemical degradation/transformation rate constants and a yield coefficient must be specified for the water column and benthic sediment. The degradation rate constants are specific to the contaminant and to environmental conditions, such as pH, bacterial levels, or light. If chemical C is created by a transformation reaction of chemical B in the water column or benthic sediment, the yield coefficient Y must be specified. If the yield coefficient is left at 0, no transformation will be calculated.
- H , T_w , T_a , u , W : Henry's Constant, H , water temperature, T_w , air temperature, T_a , water velocity, u , and wind speed, W , are required for estimating volatile losses and diffusive loads of contaminant into soils and water bodies. Henry's constants are known for many contaminants of interest. They are expressed here in units of atm-m³/mole. Average water and air temperatures should be specified by the user. Values generally range between 10 and 20°C and are converted internally to Kelvin units. Water velocity can vary from essentially 0 for stagnant ponds or lakes to 1.5 m/sec for fast-moving streams. Sustained average wind speeds may vary from close to 1 to 10 m/sec. Data may be obtained from local weather stations.
- M , I , RO , EV : These are yearly water balance quantities. Precipitation, M , is available from common meteorologic references. Irrigation, I , is a site-specific parameter and should not be zero if the watershed is composed of irrigated farm lands. Runoff, RO , can be estimated using the *Water Atlas of the United*

States (Geraghty et al., 1973). This reference provides maps with isolines of annual average surface-water runoff, which is defined as all flow contributions to surface-water bodies, including direct runoff, shallow interflow, and ground-water recharge. The range of values shown includes 5-15 in/yr throughout the Midwest corn belt, 15-30 in/yr in the South and Northeast, 1-5 in/yr in the desert Southwest, and a wide range of 10-40 in/yr in the far West. Since these values are total contributions and not surface runoff, they need to be reduced to estimate surface runoff. A reduction by 50% should suffice if using the *Water Atlas* for the *R* term. Evapotranspiration, *EV*, can be estimated from pan evaporation data. A "potential evapotranspiration," *PEV*, can be estimated by an annual pan evaporation times 0.70 (or thereabouts) and is defined as the evapotranspiration that occurs when soil water is not limiting. "Actual" evapotranspiration, or *EV*, is about one-half of *PEV*. Site-specific values for these terms should be obtained if possible.

- *Z*: The user must specify the mixing depth into which contaminant is incorporated for average watershed soils. If the watershed is dominated by soils that are not tilled, a value of 1 cm is recommended. This is a value commonly used for nontilled situations, such as undeveloped land, pasture land, or residential properties. If the watershed is dominated by tilled agricultural land, then a value of 20 cm is recommended. This is a value commonly used for tilled soils, including tilled agricultural fields and home gardens.
- *BD*, θ_s : These soil properties include the bulk density, *BD*, and the surface soil water content, θ_s . *BD* has a relatively narrow range of about 0.93-1.84 g/cm³ depending on the soil type (Hoffman and Baes, 1979). A value of 1.50 g/cm³ should suffice for most uses unless site-specific information is available. Volumetric water content, θ , can be estimated as the midpoint

between a soil's field capacity and wilting point, if a representative watershed soil can be ascertained for the combustor being evaluated. A reasonable range for θ is 0.10 (for very sandy soils) to 0.30 (for heavy loam/clay soils).

- BS, TSS, D_w : These water body properties are analogous to the bulk density for soils noted above. The benthic sediment bulk density, BS , should range between 0.5 and 1.5 kg/L. A value of 1.0 kg/L should be reasonable for most applications. D_w is the depth of the water column.

As described in the beginning of Section 7.2.3., either the TSS or D_w must be known; one can be estimated from the other (and other parameters).

Total suspended solids (TSS) is one of the most variable of all water quality parameters. Annual average TSS may range among rivers from <1 to $>10^4$ mg/L, and may vary by 3 orders of magnitude within a given river (Thomas and Meybeck, 1996). Given similar soil erosion loads, values will be lower for standing water bodies such as ponds or lakes will be lower than that for rivers and streams. The more turbulent flow in rivers will reduce the effective deposition rate and suspend sediments to a greater degree than will the flow in a relatively calm lake. The accurate specification of average annual TSS in the model is important because the mass of soil entering the water body in excess of the amount that can remain suspended (as determined by the TSS value) is assumed by the model to be deposited as bed sediment and subsequently buried. Therefore, site specific data should be used for TSS wherever possible. If measurements are not immediately available, users should refer to available Federal or local governmental water quality monitoring databases to find nearby monitoring values for the same system. Alternatively, values should be used for nearby systems that are similar in terms of soils, land use and discharge.

Federal water quality databases include the *STOrage* and *RETrieval* System for Water and Biological Monitoring Data (STORET, <http://www.epa.gov/OWOW/STORET/>) maintained by the U.S. EPA Office of Water, and the U.S. Geological Survey National Stream Water-Quality Monitoring Networks (WQN, <http://wwwrvares.er.usgs.gov/wqn96/>).

Net solids deposition is a complex process and depends on the size of the particle and the shear stress near the bed. Deposition will be a fraction of the Stokes settling velocity, which varies from 117 m/yr for fine silt (2 micron diameter) to 3000 m/yr for medium silt (10 microns) to 73,000 m/yr for fine sand (50 microns).

- A_L, A_I : These are the watershed surface areas for determining loading to the water body. A_L is the total watershed surface area affected by deposition that drains to the body of water. A_I is the impervious watershed area affected by deposition that is guttered and that drains to the water body.

Properly assigning values to A_L and A_I is nontrivial. The areas can be quite extensive, as the dispersion and deposition model may predict only gradual declines in deposition as a function of distance from the stack. What is also important to consider is the watershed hydrology in the absence of any deposition considerations. Total sediments in a water body may have originated from watershed soils that have been (or have the potential to be) affected by combustor deposition as well as by soils unaffected by such depositions. If the combustor is depositing principally on a land area that feeds a tributary of a larger river system, then what might be termed an “effective drainage area” should be considered. An effective drainage area will almost always be less than the total area of a watershed. A watershed includes all the

land area that contributes water to a river system. For large river systems, this area is in the order of thousands of square miles and includes several tributaries and smaller streams feeding into the main branch of the river. Each stream and tributary has its own drainage area. If the deposition area can be ascertained to lie within that drainage area, then it would be appropriate to assign WA_L and WA_L' based on the drainage area size.

Another consideration for determining A_L and A_I is the location of the area affected by deposition fallout with respect to the point where water is extracted for drinking and fish are caught for consumption. If these points are significantly upstream in the river system in relation to the deposition area, there is no reason to conclude that sediments or water near where the water is extracted are affected by the combustor. If these withdrawal points are downgradient from the deposition area, then there is reason to believe that sediments and water are affected. However, if they are downgradient from the deposition area but not at the bottom of the watershed, then sediment and water quality further downgradient from the withdrawal points is not of concern, and land draining into these downgradient portions would not be part of the effective drainage area. When determining the size of the effective drainage area, another possible consideration is how far upgradient in the watershed to go. Although sediments introduced at the farthest points may eventually work their way down to the mouth of the watershed, this may take geologic time and not recent historic time. Therefore, sediment quality near a deposition area need not consider these far reaches.

For a standing water body such as a lake or a pond substantially fed by groundwater recharge, an assumption is made using the simple framework of this assessment, that all sediments within the lake/pond are completely mixed.

Therefore, A_L should equal all the area around the lake/pond contributing sediment and (as in the above discussion on river systems) a part of the land area contributing sediments to streams or rivers that may feed the standing water body.

- $A_w, V_{tot}, d_{bs}, Vf_x$: This set of parameters defines and characterizes the water body or reach. A_w is the water body surface area in m^2 . The volume of the water column, V_{tot} in m^3 , and the average flow volume, Vf_x in m^3/yr , determine the average residence time of a pollutant in the water body. The time can vary from hours in streams to years in lakes. Average flows can be obtained from gaging stations or from calculations with the use of watershed area and average runoff coefficients, as summarized elsewhere in this section. Flows may vary from 10^5 m^3/yr in small streams or ponds draining less than a square kilometer to 10^9 m^3/yr in large rivers the size of the Potomac. Volumes for a lake or pond can be calculated as the product of surface area and average depth. Volumes for a stream reach can be calculated as the product of reach length, average width, and average depth. The upper benthic sediment depth, d_{bs} , representing the portion of the bed in equilibrium with the water column, cannot be precisely specified. Values from 0.01 to 0.05 m would be appropriate.
- R, K, LS, My, C, SD, ER : These factors describe the erosion of soil and contaminant from the watershed to the water body. The first five terms are multiplied together to give the long-term average soil loss, X_e , in $kg/m^2\text{-yr}$. These are the terms for the Universal Soil Loss Equation (USLE) and are also described in Section 7.2.3. of the indirect exposure document (U.S. EPA, 1990a). Following are brief notes on the five terms needed for the USLE.

RO: Runoff expressed here as rainfall/erosivity index. The *RO* term represents the influence of precipitation on erosion and is derived from data on the frequency and intensity of storms. This value is typically derived on a storm-by-storm basis, but it has been compiled regionally for the development of average annual values (Wischmeier and Smith, 1978). Annual values range from <50 for the arid western United States to >300 for the Southeast. The value used in the indirect exposure document (U.S. EPA, 1990a) was 400.

K: Soil erodibility. The soil erodibility factor reflects the influence of soil properties on erosion, with values ranging from <0.05 for nonerodible sandy soils to >0.50 for highly erodible silty soils. The value used in the indirect exposure document (U.S. EPA, 1990a) is 0.21.

LS: Length-slope factor. The topographic factor reflects the influence of slope steepness and length of the field in the direction of the erosion. Steeper slopes and longer lengths lead to higher *LS* values, with a range of 0.1 for slopes <1.0% and lengths <100 ft to >2.0 for slopes generally >10%. The two key considerations for its assignment, therefore, are the size of the field for which erosion estimates are being made and the slope of that field. The indirect exposure document (U.S. EPA, 1990a) uses the USLE to estimate erosion losses off the edge of a unit area within a watershed, which might be an acre or a hectare, for example. The *LS* assigned in the indirect exposure document is 0.179, implying flat terrain and a small unit field. For example, a combination of slope length of 200 m and slope of 2%, gives an *LS* value of 0.20.

P: Support practice factor. The support practice factor reflects the use of surface conditioning, dikes, or other methods to control runoff/erosion. *P* can be no greater than 1.0. However, values less than 1.0 should be assigned only

when specific practices are employed that are designed to reduce erosion. P is assigned a value of 1.0 in the indirect exposure document (U.S. EPA, 1990a).

C : Management practice factor. The final term in the USLE is the cover and management practice factor, C , which primarily reflects how vegetative cover and cropping practices, such as planting across slope rather than up and down slope, influences erosion. C values can be no greater than 1.0, with this value appropriate for bare soils. A C value of 1.0 is an appropriate choice for active landfills or sites of high soil contamination (like Superfund sites) mostly devoid of vegetation. For an inactive landfill with grass cover or any area with dense vegetative cover such as grass, a value of 0.1 or less is appropriate. Values greater than 0.1 but less than 0.7 are appropriate for agricultural row crops, which offer more protection than bare soil but not as much protection as dense vegetation. The indirect exposure document (U.S. EPA, 1990a) assigns a value of 0.5 for C .

SD : Sediment delivery ratio. The sediment delivery ratio for a large land area (a watershed or part of a watershed) can be calculated based on the area of the watershed using an approach proposed by Vanoni (1978) and shown here:

$$SD = a(A_L)^{-b} \quad (7-64)$$

where:

- SD = sediment delivery ratio
- A_L = watershed area receiving pollutant deposition (m^2)
- b = empirical slope coefficient (= -0.125)
- a = empirical intercept coefficient (see below)

Based on various studies of sediment yields from watersheds, it was concluded that the sediment delivery ratios vary approximately with the $-(1/8)$ power of the

drainage area. Inspection of the data suggests that the “*a*” parameter in the above equation varies with the size of the watershed. Although the EPA is currently evaluating methods for estimating sediment yields, the equation along with the following values for “*a*” are recommended in the interim:

| <u>Watershed area (sq mi)</u> | <u>“<i>a</i>” coefficient(-)</u> |
|-------------------------------|----------------------------------|
| ≤ 0.1 | 2.1 |
| 1 | 1.9 |
| 10 | 1.4 |
| 100 | 1.2 |
| 1000 | 0.6 |

Note: 1 square mile is equivalent to $2.59 \times 10^6 \text{ m}^2$.

For example, with A_L given in the indirect exposure document (U.S. EPA, 1990a) as $1.5 \times 10^7 \text{ m}^2$, SD is estimated as 0.18.

ER: Enrichment ratio. Enrichment refers to the fact that erosion favors the lighter soil particles, which have higher surface area to volume ratios and are higher in organic matter content. Therefore, concentrations of organic contaminants, which are a function of organic carbon content of sorbing media, would be expected to be higher in eroded soil as compared with *in situ* soil. Although enrichment is best ascertained with sampling or site-specific expertise, generally *ER* has been assigned values in the range of 1 to 5 for organic matter, phosphorous, and other soil-bound constituents of concern. The enrichment ratio would be expected to be higher in sandy soils than in silty or loamy soils because the finer silt particles that erode from a soil generally characterized as sandy are more a deviation from the norm than are the silt particles that erode from a soil generally characterized as silty or loamy. A value of 3 for organic contaminants would be a reasonable first estimate.

- Kd_s, Kd_{sw}, Kd_{bs} : These three adsorption partition coefficients describe the partitioning of a contaminant between sorbing material, in this case, soil, surface water suspended solids and bed sediments, and water in a sorbing material/water mixture. For organic contaminants, this partition coefficient has been estimated as a function of the organic carbon partition coefficient and the fraction of organic carbon in the partitioning media:

$$Kd_i = Koc fOC_i \quad (7-65)$$

where:

- Kd_i = partition coefficient for pollutant j associated with sorbing material characterized by organic carbon content, OC_i (L/kg or cm^3/g)
- Koc = organic carbon partition coefficient for contaminant j (L/kg)
- fOC_i = fraction organic carbon content of sorbing material (dimensionless)

In the absence of measured values, the Koc can be estimated from a chemical's octanol water partition coefficient, Kow . Empirical equations relating Kow to Koc are listed in Lyman et al. (1982). Of six different equations listed in that reference, the following derived by Karickhoff et al. (1979) is recommended for use for chemicals with high Kow (highly sorbed, hydrophobic contaminants such as PCBs, dioxins):

$$\log Koc = \log Kow - 0.21 \quad (7-66)$$

where:

- Koc = organic carbon partition coefficient (L/kg)
- Kow = octanol-water partition coefficient (dimensionless)

This equation was empirically developed from a limited number of hydrophobic contaminants ($n=10$, $R^2= 1.00$). It implies that K_{oc} is very similar to K_{ow} for strongly sorbed compounds such as the dioxin-like compounds.

To assign Kd_s to organic contaminants, the organic carbon contents of solids and sediments of water bodies are needed. Solids of water bodies are generally higher than organic carbon contents of the surrounding lands. Furthermore, organic carbon contents of suspended organic materials and solids are typically greater than those of bottom sediments. A significant sink for strongly hydrophobic contaminants such as dioxin-like compounds is thought to be suspended, or nonsettling, organic material. In modeling 2,3,7,8-TCDD in Lake Ontario (U.S. EPA, 1990b) with the use of the WASP4 model, a compartment separate from suspended solids, termed "nonsettling organic matter," served as a permanent sink. For the framework offered above, a single reservoir of suspended materials is modeled onto which incoming contaminants sorb.

Foth (1978) lists the organic nitrogen content of several soil types ranging from sand and sandy loam to clay. The range from that list is 0.0002 to 0.0024 on a fractional basis. When a carbon to nitrogen ratio of 10 (Brady and Selle, 1984, who notes that C:N ratios vary from 8 to 15, with the typical range of 10 to 12) is assumed, organic carbon contents of soil generally might range from 0.002 to 0.024. The organic carbon content of bottom sediments will be higher given arguments that erosion favors lighter textured soils with higher organic carbon contents and also that bottom sediments are partially composed of detritus materials. A range of 0.03 to 0.05, given surface soil content at 0.01, might be reasonable. The organic carbon content of suspended materials can approach

0.20, but a range between 0.05 and 0.10 might be more reasonable given that previous assignments were 0.01 and 0.03 to 0.05.

The Kd_s supplied in the indirect exposure document (U.S. EPA, 1990a) for benzo(a)pyrene and cadmium are 1.2×10^5 L/kg and 500 L/kg, respectively.

7.3. PRECIPITATION

The procedure to estimate contaminant concentration in water of precipitation collection systems may lead to overestimates. The procedure divides the total deposition rate by the precipitation rate. Some of the contaminant in dry deposition may have low solubilities and settle out of suspension. For the purposes of estimating concentrations of contaminants from stack emissions in precipitation, it is suggested that the frequency of precipitation events be compared with the frequency of stack emission episodes for the period of time of interest. When it can be reasonably assumed that stack emissions occurred regularly during precipitation events, it is also reasonable to assume that the total contaminant load was deposited on the surface of the water bodies, plants, and soil near the emission point in the same manner as described for wet deposition. When it is not reasonable to assume that the precipitation and emission events occurred simultaneously, the emissions from the source are already accounted for in previous sections of this chapter.

If the collection system causes turbulent mixing of the water, particulates could be suspended and the current approach would be appropriate. If such mixing does not occur, the current procedure is acceptable for bounding estimates. If, however, more realistic estimates are desired, the risk assessor should limit the concentrations of all contaminants to their solubility limit. For organics, further refinement may be possible through the use of equilibrium partitioning.

7.4. GROUNDWATER

Combustors may have different conditions that would exacerbate the effects of groundwater and invalidate the conclusion that groundwaters are not affected by combustor's emissions. Combustors that deposit contaminants from their emissions onto surfaces where groundwaters are considered to be under the influence of surface waters should consider that the soluble portion of the contaminants that reach those surface waters can reach the groundwater. This portion of the contaminant should be handled in the same way the soluble portion of the contaminant was handled in previous sections of this chapter.

Site-specific conditions may be encountered where the effects of groundwater may be greater. In contrast to the original examples, conditions that might enhance the effects of groundwater include emission deposition rates that are several times greater than the average, the existence of more soluble compounds in the emissions, and higher recharge rates that would occur in areas with very permeable soil and bedrock near the surface. In these circumstances, site-specific groundwater modeling may be required before this pathway can be eliminated from consideration.

7.5. DAILY INTAKE FROM WATER (*DI*)

This methodology assesses only the risk associated with increased exposure from combustor emissions; the background concentration of contaminants is not included in the quantitation of *DI*. This may be a difficult distinction to make unless the maximum amount of possible contaminants has been calculated. Then the maximum possible total is the upper limit of the value used for *DI*. *DI* is calculated as follows:

$$DI = \frac{C_w CR_w}{BW} \quad (7-67)$$

where:

- DI* = daily intake of contaminant from water ingestion (mg/kg-day)
- C_w* = concentration of contaminant in water (mg/L)
- CR_w* = consumption rate of water (L/day)
- BW* = body weight (kg)

To determine if the contaminant adversely affects human health, the *DI* is compared with the reference dose for chronic oral exposure to systemic toxicants or the dose used to determine excess risk for carcinogens. This is discussed in Chapter 10.

7.5.1. Water Contaminant Concentration (C_w). The model in this chapter calculates the dissolved phase concentration (along with the total concentration and sorbed phase concentration) of contaminants in affected surface water bodies (mg/L). For drinking water taken from systems that use filtration, use of the dissolved phase concentration, termed C_{dw} , is most appropriate as the input for determining human exposure from water ingestion. The basis for this recommendation is that water treatment systems filter out particulates; what remains is the dissolved phase of the contaminant.

For systems that do not use filtration as part of their treatment process, it is necessary to include the particulate component of the contaminant as well. The assumption can be made that contaminants remain in the system if filtration is not used. Alterations in the contaminants as a result of the type of treatment used are system specific, and the analysis of finished water that is delivered to the drinking water system is probably the best source of such information. This may be an oversimplification of the chemistry of the system, especially in complex drinking water systems where a water may remain in the system for some extended period, but it would be impossible to factor all of these changes into the evaluation.

In rural areas individuals primarily, but not exclusively, use groundwater as their water supply. The exposure to contaminants from an emission source are less likely in groundwater systems. Those groundwaters that are under the influence of surface water may, however, have contaminants from that surface water dissolved in them or, to a lesser extent, carried in particulate form in them. In some rural areas, large-diameter shallow wells are still the main water source for humans, animals, and crops. These large-diameter shallow wells are frequently not as protected by covers and are more likely to receive chemicals from contaminated emissions than are the standard small-diameter wells or wells finished in material deeper than 50 feet, which are frequently closed at the ground surface.

Some individuals use cisterns and catchment basins to collect water for drinking and home use. These cisterns and catchments are often metal or lined with metal. Some of these are completely open to the air and should be considered in the same way as are surface waters. The water that is collected in these containers is from precipitation and runoff from roofs and gutters. The concentration of contaminants in such water can reasonably be considered equal to that in the precipitation. There are some circumstances where this concentration could change. If the pH of the water is low, contaminants could be leached from the container materials or from residues that build up in such containers, increasing the total concentration. If the water in the container is turbid or if the container is not covered or screened in some way, particulate matter could be deposited directly into the water. This matter could remove some contaminant from the dissolved phase of the water, precipitating it into bottom sludge or leaving it in suspended matter, yet unavailable for ingestion in dissolved form. The mechanisms described in this chapter for dealing with concentrations in water are applicable to this kind of water.

7.5.2. Water Consumption Rate (C_{rw}). The U.S. EPA has traditionally used a value of 2 L/day to represent the average daily water consumption of adults and 1 L/day to represent the average daily water consumption of children with body weights of ≤ 10 kg. However, the Exposure Factors Handbook (U.S. EPA, 1995) presents data that suggest these values may overestimate actual water consumption rates. These data, generated in several consumption surveys, show that a value of 1.4 L/day may be a more accurate average of water consumption for adults. A value of 2 L/day most likely represents a 90th percentile value. The data also show that average tapwater consumption by young children is lower than suggested by the 1 L/day value typically applied. U.S. EPA (1995) recommendations regarding average- and upper-percentile tapwater consumption rates for adults and children of various ages, based on analysis of the results of available surveys, are listed in Table 7-1. Consult the Exposure Factors Handbook (U.S. EPA, 1997) for more detailed information regarding human water consumption rates.

| TABLE 7-1 Tapwater Consumption Rates Recommended by U.S. EPA (1995) | | |
|--|--------------------|----------------------------|
| Age Group (yr) | Average (L/day) | 90th percentile (L/day) |
| <1 | 0.3* | 0.7* |
| 1-10 | 0.7 | 1.3 |
| 11-19 | 1.0 | 1.7 |
| 20+ | 1.4 | 2.0 |

*These values are for water-based beverages but may not include water used to prepare powdered infant formula.

7.6. DERMAL EXPOSURE FROM WATER

Once contaminants in combustor emissions reach water sources, humans may be exposed by absorbing them through the skin while swimming or bathing. Dermal absorption can be a significant source of exposure from contaminated water when compared with ingestion. For example, Brown et al. (1984) showed that the dermal route may be a significant contributor to total exposure to volatile organic contaminants in tap water. They noted that under some circumstances, the tap water could be, but not always is, a major source of contaminants. The model presented in this chapter estimates human exposure resulting from skin contact with contaminants in water.

7.6.1. Daily Dermal Intake from Water. The daily dermal intake from water represents the increase above background in daily human dermal intake due to combustor emissions. Exposure resulting from dermal absorption from water is influenced by the contaminant concentration in water, the nature of the contaminant, and the extent of contact. The nature of the contaminant determines how well it permeates the skin. The extent of contact is affected by duration and frequency of exposure, as well as the condition of the skin and surface area available for contact.

The daily dermal intake of a compound in an aqueous medium is estimated using the following equation:

$$DDI_w = \frac{D_{event} EV EF A_s}{BW 365} \quad (7-68)$$

where:

| | | |
|-------------|---|--|
| DDI_w | = | daily dermal intake of contaminant from water (mg/kg-day) |
| D_{event} | = | dermally absorbed dose per event (mg/cm ² -event) |
| A_s | = | skin surface area available for contact (cm ²) |
| EV | = | event frequency (events/day) |
| EF | = | exposure frequency (day/yr) |
| BW | = | body weight (kg) |
| 365 | = | adjustment to calculate average daily dose (day/yr) |

A decision matrix that appears in Section 9 of the dermal exposure assessment document (U.S. EPA, 1992) can be used to determine whether absorption is significant enough to require further assessment.

7.6.2. Estimating the Dermally Absorbed Dose per Event (D_{event}). Current agency methodology includes a nonsteady-state approach for estimating the dermally absorbed dose from water for organic chemicals (U.S. EPA, 1992). This approach appears to offer significant advantages over the traditional steady-state approach for risk assessment application. First, the nonsteady-state method more accurately reflects normal human exposure conditions since the short contact times associated with bathing and swimming generally mean that steady state will not occur. Second, the method accounts for the dose that can occur after the actual exposure event as the result of absorbing contaminants stored in skin lipids. For these reasons, U.S. EPA recommends the non-steady state approach.

The following procedures are recommended for estimating D_{event} . This term, as used in this context, represents the absorbed dose per cm² of exposed skin occurring during a single water contact event such as bathing or swimming.

Un-ionized Organic Chemicals

Calculate D_{event} (mg/cm²-event) using the nonsteady-state approach, as follows:

$$\text{If } t_{event} < t^*, \text{ then: } D_{event} = \frac{2Kp C_w \sqrt{\frac{6T t_{event}}{\pi}}}{1000} \quad (7-69)$$

$$\text{If } t_{event} > t^*, \text{ then: } D_{event} = \frac{Kp C_w \left[\frac{t_{event}}{1+B} + 2T \left(\frac{1+3B}{1+B} \right) \right]}{1000} \quad (7-70)$$

where:

| | | |
|-------------|---|--|
| D_{event} | = | dose absorbed per unit area per event (mg/cm ² -event) |
| Kp | = | permeability coefficient from water for contaminant (cm/hr) |
| C_w | = | concentration of contaminant in water (mg/L) |
| t_{event} | = | duration of event (hr/event) |
| T | = | lag time (hr) |
| t^* | = | time to reach steady-state (hr) |
| B | = | parameter to describe relative contribution of permeability coefficients in stratum corneum and viable epidermis (dimensionless) |
| 1000 | = | unit adjustment factor (cm ³ /L) |

Values for Kp , t^* , T , and B for many common organic pollutants are presented in Table 5-8 of the dermal absorption assessment document (U.S. EPA, 1992). For other chemicals, these quantities can be estimated as described below.

Inorganic Chemicals and Ionized Organic Chemicals

Most inorganic chemicals and ionized organic chemicals do not have measurable octanol-water partition coefficients (or if measurable, the coefficients are very small). Consistent with this observation, the skin usually has a low storage capacity for these

chemicals, thus reaching steady-state conditions soon after the initial exposure. Therefore, it is appropriate to assume that t^* , lag time and B are all nearly zero.

Consequently, Equations 7-69 and 7-70 simplify the traditional steady-state approach. Calculate D_{event} for inorganic chemicals or ionized organic chemicals by using the steady-state approach:

$$D_{event} = \frac{2KpC_w t_{event}}{1000} \quad (7-71)$$

where:

| | | |
|-------------|---|---|
| D_{event} | = | dose absorbed per unit area per event (mg/cm ² -event) |
| Kp | = | permeability coefficient from water for contaminant (cm/hr) |
| C_w | = | concentration of contaminant in water (mg/L) |
| t_{event} | = | duration of event (hr/event) |
| 1000 | = | unit adjustment factor (cm ³ /L) |

Partially Ionized Organic Chemicals

For organic chemicals that are present as both ionized and un-ionized species at the conditions of the aqueous solution, calculate D_{event} as the sum of the D_{event} for the un-ionized species (by using Equations 7-69 and 7-70 and the concentration of the un-ionized species) and the D_{event} for the ionized species (by using Equation 7-71 and the concentration of the ionized form of the chemical).

7.6.2.1. Water Concentration (C_w) Ionized or Un-ionized — This chapter provides a model that calculates both dissolved phase and total water column concentrations of contaminants in impacted surface water bodies (mg/L). Dermal exposure to contaminants in water can occur while bathing or swimming. For exposure while bathing or swimming in a pool, employing the dissolved phase concentration (C_{wd}) would be most appropriate because water treatment systems filter out particulates and what remain are the dissolved phase residues of the contaminant. For exposure while swimming in a lake or stream, particulate-bound contaminant may be present, but use of the dissolved phase

concentration (C_{wd}) is still recommended because this represents the concentration that is freely available to enter the body (the total water column concentration includes particulate-bound contaminant that is not readily bioavailable).

The concentration of ionized forms of organic acids and bases are estimated as follow. For organic acids with one dominant acid-base reaction.

$$C_{WI} = \frac{C_{wd}}{1 + 10^{(pH - pK_a)}} \quad (7-72)$$

For organic bases with one dominant acid-base reaction,

$$C_{WI} = \frac{C_{wd}}{1 + 10^{(pK_a - pH)}} \quad (7-73)$$

7.6.2.2. Event Duration (t_{event}) — Event duration (hr/event) is the time over which a single contact event occurs. The two events associated with dermal contact to water are swimming and bathing. Showers were reported to be the primary means of bathing for 75% of American men and 50% of American women (Tarshis, 1981). U.S. EPA (1995a) presented a cumulative frequency distribution of shower times based on a study conducted in Australia (James and Knuiman, 1987). Examination of records from 2500 Australian households showed that shower times ranged from 1 to 20 minutes with a median of 7 minutes, a 75th percentile of 9 minutes, and a 90th percentile of 12 minutes. Bath duration is likely to be somewhat longer than shower duration; Brown and Hattis (1989) assumed a 20-minute bath time to estimate the dermal absorption from hypothetical bathtub scenarios. Adding a few minutes to the observed shower times for water residues to dry and to account for presumably longer bath times, a default range of 10 (median) to 15 (90th percentile) minutes is recommended.

Much less information is available on the time of swimming. The SEAM (U.S. EPA, 1988) suggested that a national average value based on the U.S. Department of the Interior (DOI) Bureau of Outdoor Recreation survey (U.S. DOI, 1973) be applied. According to this survey, the average duration of a swimming event is 2.6 hours. However, further investigation of this survey revealed that the exposure time value represented more than

actual time in water. Accordingly, no reliable data on swimming time could be found, and it is recommended that risk assessors make judgments of their own on a site-specific basis. Consideration should be given to geographic factors, such as proximity or availability of surface waters for recreation, and seasonal factors. Furthermore, certain subpopulations (e.g., competitive swimmers) will encounter a greater mean exposure time. Based on judgment, a reasonable average value for a recreational swimmer may be 0.5 hr/event and a reasonable upper percentile value for a person who swims regularly for exercise or competition may be 1 hr/event.

7.6.2.3. Permeability Coefficient from Water (K_p) — The permeability coefficient from water, K_p , for a contaminant is a flux value, normalized for concentration, that represents the rate at which the contaminant permeates the skin from an aqueous solution (cm/hr). Permeability coefficients are chemical and vehicle dependent. Permeability coefficients from aqueous solution have been experimentally determined for many chemicals. These permeability coefficients were derived from experiments that used different protocols and skins from animals as well as from humans, and these coefficients presented some significant uncertainty regarding their use for representing *in vivo* permeability of human skin. Experimentally derived K_p values for potential environmental contaminants are presented in U.S. EPA (1992). K_p values can also be estimated by a number of methods, as described in U.S. EPA (1992). Recommended means of obtaining K_p values for inorganic and organic chemicals are described below.

Inorganic Chemicals and Ionized Chemicals

For inorganic chemicals, the experimentally derived K_p values presented in U.S. EPA (1992) are recommended. It is indicated that most inorganic chemicals have K_p values near 10^{-3} cm/hr, and a few are lower. Accordingly, a default assumption of 10^{-3} cm/hr is recommended for inorganic chemicals not listed. Based on a recent review of the literature, K_p values of metals are generally lower than 10^{-3} cm/hr (Hostynek et al., 1997).

Organic Chemicals

For organic chemicals, K_p values estimated according to the following equation derived by Potts and Guy (1992) are recommended:

$$\log K_p = -2.72 + 0.71 \log K_{ow_i} - 0.0061 MW \quad (7-74)$$

where:

- K_p = permeability coefficient from water for contaminant (cm/hr)
 K_{ow_i} = octanol-water partition coefficient for contaminant
 MW = molecular weight of contaminant

The uncertainty in the predicted K_p values is judged to be within plus or minus one order of magnitude from the best-fit value.

The Potts and Guy (1992) equation was derived empirically from a database assembled by Flynn (1990) containing permeability coefficients for more than 90 structurally diverse chemicals with molecular weights ranging from 18 to >750 and $\log K_{ow_i}$ values ranging from -3 to +6. The equation is, therefore, most appropriate for use with chemicals that meet these criteria. However, based on physical reasons and experimental data, in the absence of skin metabolism, K_p should not exceed a value of about 0.3 cm/hr (Kasting and Robinson, 1993). In the absence of any suitable alternative, the use of Equation 7-81 with superlipophilic chemicals (e.g., dioxins) is not unreasonable provided the calculated value for K_p is not allowed to exceed a limiting maximum. As a conservative estimate, K_p of 1 cm/hr should be used if the value calculated from Equation 7-81 is larger than 1 cm/hr.

The recommendation to use estimated K_p values for organic chemicals follows as a consequence of the use of the nonsteady-state model to calculate the daily dermal event (DD_{event}) for these chemicals. The nonsteady-state model requires input parameters that are difficult to measure, such as the stratum corneum diffusion coefficient (D_{sc} , used to calculate T as shown below). Thus, these chemical-specific factors must generally be estimated. Cleek and Bunge (1993) derived a procedure to estimate D_{sc} by using the Potts and Guy (1992) correlation for estimating K_p values. Therefore, for purposes of internal consistency, the K_p value used in the nonsteady-state model should also be the K_p derived from the Potts

and Guy (1992) correlation. This leads to the somewhat unexpected recommendation that for organics, K_p values predicted by the correlation should be used instead of the measured values derived from experiments. This being the case, it is notable that the K_p values predicted from the correlation agree reasonably well with the experimentally derived K_p values for most chemicals.

7.6.2.4. Relative Contribution of Permeability Coefficients (B) — This dimensionless parameter is used in the nonsteady-state method of DD_{event} calculation to describe the relative contribution of permeability coefficients in the stratum corneum and the viable epidermis. It is employed only in the nonsteady-state methodology and applies only to organic chemicals. It is calculated from the K_{ow} as follows:

$$\text{For organics: } B = \frac{K_{ow_i}}{10^4} \quad (7-75)$$

7.6.2.5. Lag Time (T) — In the nonsteady-state methodology recommended here to calculate DD_{event} for organic contaminants, the nonsteady-state period is a function of the lag time, T (hr). The following equation can be used to calculate T :

$$T = \frac{l_{sc}^2}{6D_{sc}} \quad (7-76)$$

It is assumed that l_{sc} , the apparent thickness of the stratum corneum, is equal to the thickness of the stratum corneum, which is estimated to be roughly 10-20 μm over most of the body (Kalia et al., 1996).

D_{sc} (cm^2/hr), the diffusion coefficient of the chemical in the stratum corneum, is calculated from the following equation, assuming that $l_{sc} = 10 \mu\text{m} = 10^{-3} \text{ cm}$:

$$\text{Log} \frac{D_{sc}}{l_{sc}} = -2.72 - 0.0061MW \quad (7-77)$$

Values of T are calculated by also assuming that $l_{sc} = 10 \mu\text{m} = 10^{-3} \text{ cm}$.

7.6.2.6. Time to Reach Steady-State (t^*) — The t^* , the time to reach steady-state (hr) in the nonsteady-state methodology recommended for use with organic contaminants, can be calculated from B and T as follows:

$$\text{If } B \leq 0.1, \text{ then } t^* = 2.4T \quad (7-78)$$

$$\text{If } 0.1 \leq B \leq 1.17, \text{ then } t^* = (8.4 + 6 \log B)T \quad (7-79)$$

$$\text{If } B \geq 1.17, \text{ then } t^* = 6(b - \sqrt{b^2 - c^2})T \quad (7-80)$$

$$b = \frac{2}{\pi}(1 + B)^2 - c \quad (7-81)$$

$$c = \frac{1 + 3B}{3} \quad (7-82)$$

7.6.2.7. Event (EV) and Exposure Frequency (EF) — Event and exposure frequency are two of the variables necessary for calculation of daily dermal intake (DDI) by Equation 7-77. Event frequency (i.e., events/day) and exposure frequency (i.e., days/yr) refer to how often the contact event occurs. The following discussion summarizes the values for these parameters for dermal exposure to contaminants in water by bathing and swimming.

Approximately 90% of the American population bathes every day, and 5% average more than one bath a day (Tarshis, 1981). Since the range of likely values is so narrow, a single default value of 1 event/day, 350 days/yr is recommended for bathing frequency. The upper default of 350 days/yr was selected over 365 days/yr to reflect the probability that most people spend some time away from their residence, using water from a different source.

Much less information is available on the frequency of swimming. The SEAM (U.S. EPA, 1988) suggests that a national average value based on the U.S. DOI Bureau of Outdoor Recreation survey (U.S. DOI, 1973) be applied. This survey reported an average swimming frequency of 7 days/yr. The reliability of this frequency estimate appears questionable, however. Accordingly, it is recommended that risk assessors make judgments of their own on a site-specific basis. Consideration should be given to

geographic factors, such as proximity or availability of surface waters for recreation, and seasonal factors. Furthermore, certain subpopulations (e.g., competitive swimmers) will encounter a greater mean exposure frequency. Based on judgment, a reasonable average value for a recreational swimmer may be 5 days/yr, 1 event/day, and a reasonable upper value for a person who swims regularly for exercise or competition may be 150 days/yr, 1 event/day.

7.6.3. Skin Surface Area (A). Dermal intake of a contaminant is proportional to the exposed surface area (cm^2). For exposure via swimming and bathing, the exposed surface area is assumed to be the total body surface area. Data regarding total body surface area of human adults and children was reviewed by U.S. EPA (1992, 1995), and median and upper 95th percentile values are presented in Table 4-5 (Chapter 4). U.S. EPA (1992, 1995) recommended using values of 20,000 cm^2 and 23,000 cm^2 to represent central tendency and upper percentile adult total body surface areas, respectively. For children, U.S. EPA (1992, 1995) recommended using the median and 95th percentile values from Table 4-5 for the appropriate age group. Consult U.S. EPA (1992, 1995) for more detailed discussion of dermal surface area of adults and children.

7.7. UNCERTAINTY IN THE AQUEOUS DERMAL EXPOSURE MODEL

Exposure risk assessors are cautioned that the procedure recommended for deriving DD_{event} for organic chemicals is based on a recently developed model that currently is being reviewed by the scientific community. On a conceptual basis, it has advantages over the traditional approach involving direct application of Fick's first law. One, it accounts for the unsteady-state conditions that characterize the relatively short exposure periods associated with bathing. Two, it accounts for the dose that can occur after the actual exposure incident because of absorption of contaminants stored in the skin lipids. Actual calculations performed by EPA have shown that this approach provides a more conservative total absorbed dose over the traditional steady-state equation for organic compounds. Preliminary testing showed that this new approach indicates that the dermal dose resulting from 10-minute showers exceeds the dose associated with drinking 2 L/day for a number of

the pollutants. For the fastest penetrating chemicals, the dermal dose was predicted to exceed the ingested dose by about two orders of magnitude. This seems counterintuitive and raises concerns that the model may be overly conservative. Lack of data makes validation of the model very difficult.

One “reality check” that risk assessors should make for bathing scenarios is to compare the total amount of contaminant in the bathing water with the dose. The amount of contaminant in the water is easily computed by multiplying the contaminant concentration by the volume of water used (modern water-saving showers typically use 2.5 gal/min, while older showers use 5-15 gal/min). Obviously, the dose cannot exceed the amount of contaminant in the water. In fact, it seems unlikely that a high percentage of the contaminant in the water could be dermally absorbed. As a preliminary guide, if the dermal dose estimate exceeds 50% of the contaminant in the water, the risk assessor should question the validity of the dose estimate.

Volatile compounds have been shown to volatilize significantly during showering. Andelman (1988) found that about 90% of TCE volatilized during showering. This would suggest that the effective concentration of the contaminant in water and resulting dermal dose may be reduced. So, for volatile compounds, risk assessors may want to assume a reduced contaminant concentration in water contacting the skin.

The dermal permeability estimates are probably the most uncertain of the parameters in the dermal dose equation, with an uncertainty of as much as plus or minus two orders of magnitude, although most chemicals are probably within an order of magnitude. The measured values probably have an uncertainty of plus or minus a half order of magnitude. Systematic deviations may occur for some classes of chemicals, such as the halogenated organic chemicals, for which the K_p is probably consistently underestimated by Equation 7-74. Accordingly, the final dose and risk estimates must be considered highly uncertain. Some idea of the range of possible values can be obtained by first using average or typical values for each parameter to get a typical dose estimate, and then setting two or three of the

most variable parameters to their upper values and the others to their average values to get some idea of the possible upper-dose estimate.

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Chapter 7

Water Concentration and Exposure Pathways

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DETERMINING EXPOSURE FROM INTAKE OF AQUATIC ORGANISMS

8.1. INTRODUCTION

Once contaminants from combustor emissions are transported to surface water bodies, they may be incorporated into the aquatic food chain. Humans and fish-eating wildlife are then exposed to contaminants when they eat fish collected from contaminated bodies of water. The model presented in this chapter estimates exposure resulting from consumption of fish taken from water sources in the vicinity of a combustor.

In the 1990 U.S. EPA document *Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions*, a bioconcentration factor was used to predict the concentrations of pollutants in fish attributable to receiving water bodies. Bioconcentration is defined as the net accumulation of a substance by an aquatic organism as a result of uptake directly from the ambient water; this occurs through gill membranes or other external body surfaces. The term bioconcentration factor (BCF) is defined as the equilibrium concentration of a chemical in a biological medium divided by the equilibrium concentration of a chemical in the environmental medium through which the exposure directly occurs. In this document a bioaccumulation factor (BAF) is used. Bioaccumulation is the accumulation of a substance by an organism as a result of all environmental sources. The BAF is roughly defined as the equilibrium concentration of a chemical in a biological medium divided by the equilibrium concentration of a chemical in an environmental medium (in this case ambient water) where both the organism and its food were exposed. Both BCFs and BAFs are proportionality constants that relate concentrations of a substance in aquatic organisms to concentrations of the substance in water. Although similar to a BCF, a BAF not only predicts the uptake and retention of chemicals that result from direct contact with an environmental medium, but also accounts for uptake and retention from the food chain that may connect the environmental medium to the biological medium of interest.

8.2. CALCULATING DAILY HUMAN INTAKE FROM FISH

Human daily intake of contaminant from fish (DI_f) is proportional to the concentration of contaminant in the water, the contaminant's bioaccumulation factor, and the rate of ingestion of contaminated fish. DI_f is calculated as follows:

$$DI_f = \sum \left(\frac{Wc \ BAF_i \ DI_{fi}}{BW} \right) \quad (8-1a)$$

where:

- DI_f = human daily intake of contaminant from fish (mg/kg-day)
- Wc = contaminant concentration in water (mg/L)
- BAF_i = bioaccumulation factor for fish of trophic level i (L/kg)
- DI_{fi} = daily human consumption of locally-caught fish of trophic level i (kg/day)
- BW = body weight (kg)

Aquatic organisms may be categorized by their role in the flow of energy through the biological community. Energy is transferred as autotrophic species are consumed by heterotrophic species; autotroph-consuming heterotrophs may in turn be consumed by other heterotrophs, and the transfers continue to the apex predators. This series of transfers is conceptualized as a food chain or food web. The categories are defined by the diets of the species that comprise the web; each category is called a trophic level. Aquatic communities typically have three or more trophic levels: (1) primary producers, such as phytoplankton; (2) primary consumers, such as zooplankton; and (3) secondary consumers, such as small fish. Other trophic levels that may occur include (4) tertiary consumers such as larger fish and quaternary consumers such as higher chordates (e.g., fish-eating reptiles, birds, and mammals, including humans). Benthic invertebrates (5) may accumulate and retain pollutants via uptake from interstitial water of sediment, uptake from water column, ingestion of chemical bound to particulate and consumption of contaminated detritus and phytoplankton.

These models assume chemical equilibrium between organisms of all trophic levels and the environment in which they reside. This simplification does not examine the dynamic and temporal nature of pollutant accumulation. For example, if pollutant load to a water body is dramatically increased or decreased, the system will not be in equilibrium. Since the models presented here assume chemical equilibrium, it is best to not apply them to systems in disequilibrium.

For this methodology, it is recommended that the BAF and DI_{fi} be determined separately for aquatic species of different trophic levels. The total daily intake of contaminant from fish, then, is the sum of the intake attributed to fish from each trophic level. This accounts for different levels of accumulation for members of different trophic levels.

The biota sediment accumulation factor (BSAF) for fish of trophic level i can be substituted for the bioaccumulation factor (BAF_i) in Equation 8-1a. In this equation the contaminant concentration in water (C_w) is replaced by the concentration of the pollutant in the benthic sediment (C_{bs}). Please see Equation 8-6 and the discussion that follows.

$$\frac{BSAF_i DI_{fi}}{BW} \quad (8-1b)$$

where:

- DI_f = human daily intake of contaminant from fish (mg/kg-day)
- C_{bs} = contaminant concentration in benthic sediment (mg/g)
- $BSAF_i$ = biota-sediment accumulation factor for trophic level i
- DI_{fi} = daily human consumption of locally-caught fish of trophic level i (g/day)
- BW = body weight (kg)

8.2.1. Total Water Column Contaminant Concentration (C_{wctot}) and Benthic Sediment Concentration (C_{bs}). To be compatible with the BAF as derived above, the total water column concentration of contaminant (C_{wctot} , discussed in Chapter 7) should

be used to calculate human daily intake from consumption of contaminated fish in Equation 8-1a. To be compatible with the BSAF in Equation 8-1b, the benthic sediment concentration should be used.

8.2.2. Bioaccumulation Factor (BAF). Bioaccumulation refers to the net accumulation of a substance by an organism as a result of uptake and retention from all environmental sources. The degree to which a chemical accumulates above ambient concentrations in an aquatic organism is indicated by the magnitude of the BAF, which is the result of pollutant uptake and retention. Specifically, the BAF is defined as the ratio of the contaminant concentration in all or a specific part (e.g., muscle tissue) of an aquatic organism ($\mu\text{g/g}$ fresh weight) to the contaminant concentration in the water body where the organism was exposed ($\mu\text{g/L}$), in situations where both the organism and its food were exposed. The BAF, therefore, has units of $(\mu\text{g contaminant/g fresh tissue})/(\mu\text{g contaminant/L water})$ or L/g . Defined in this way, the BAF considers the absorption of a pollutant by an organism from the ambient water, as well as consumption of contaminated food and, in theory, is directly applicable to situations found in the environment. The BAF also accounts for retention of a contaminant in the body of an organism and thereby accounts for metabolism of the pollutant.

Direct uptake of a contaminant in the water by the organism occurs by simple diffusion across external surfaces, including those used for respiration. Uptake rates are often related to respiration rates, which in turn are a function of daily kilocalorie expenditure and body size (Schmidt-Nielsen, 1970). A dietary contaminant enters through the gut of the aquatic organism and must pass through the intestinal lining to accumulate. Once the chemical is in the bloodstream, subsequent accumulation depends upon the metabolic capabilities of the organism as well as factors such as lipid content that determine chemical affinity for the organism relative to that of the water. With continuous exposure to a compound, the rate of excretion eventually equals the rate of uptake. At this point, a steady-state equilibrium is attained between the concentration of contaminant in the tissues of the organism, in its prey, and in the ambient water. (For extremely hydrophobic compounds that are not expected to

achieve steady-state equilibrium, the use of a BSAF is recommended [see discussion of BSAF].) Measured BAFs also account for metabolic transformations that may occur in organic contaminants. Metabolism may have a significant impact on the ultimate contaminant concentration in an organism and as a result will affect the BAF.

Bioaccumulation factors are chemical specific and, to some degree, specific to the existing aquatic food web and the body of water in which they are measured. The compounds with the greatest tendency to bioaccumulate are those that are lipophilic, resistant to biological degradation, or readily transferred from the gut of aquatic organisms and subsequently accumulated in the affected tissues. Because bioaccumulation is influenced by the metabolic capabilities of the organism and, for many pollutants, the lipid content of the organism's tissues, a measured BAF is specific to the species and tissue in which it is evaluated. Bioaccumulation is also influenced by the bioavailability of the chemical of concern in the water. Bioavailability is affected by properties of the chemical, but also by properties of the water being tested (e.g., dissolved organic carbon content, particulate organic carbon content). The differences between the water body in which the BAF was measured and the water body of study and the anticipated impacts of these differences should be described in the risk characterization.

For inorganic chemicals, in many cases the BCF and BAF are assumed to be equal. Chemical concentrations in water in laboratory tests should be greater than normal background concentrations in water bodies. If the chemical is an essential micronutrient, the concentrations should be greater than the concentrations required for normal nutrition. Additionally, the concentrations used should be below those that adversely affect the study organisms.

For lipophilic nonpolar organic chemicals, several adjustments can be made in order to make a BAF measured in a particular tissue of a particular species in a particular water body more generally applicable across tissues/species and test waters (U.S. EPA, 1995b). One adjustment is to calculate the lipid-normalized concentration

of the chemical in the tissue. The lipid-normalized tissue concentration, C_l , is defined according to the following equation:

$$C_l = \frac{C_B}{f_l} \quad (8-2)$$

where:

- C_l = lipid-normalized tissue concentration of organic contaminant ($\mu\text{g/g}$ lipid)
- C_B = concentration of organic contaminant in tissue of aquatic biota (either whole organism or specified tissue) ($\mu\text{g/g}$ fresh tissue)
- f_l = fraction of the tissue that is lipid

This adjustment is predicated on the assumption that lipophilic nonpolar organic contaminants will partition into the tissue lipids. It implies that BAFs for organic contaminants can be extrapolated from one tissue to another and from one aquatic species to another on the basis of percent lipid within a trophic level. The lipid-normalized concentration (C_l) is defined as the total concentration of a contaminant in a tissue or a whole organism divided by the lipid fraction of the tissue or the whole organism (Mackay, 1982).

While lipid normalization is thought to be a reasonable basis for extrapolating across species for organisms that are generally similar to one another (e.g., in terms of metabolism), it is not meant to imply here that lipid normalization will account for all of the variability in bioaccumulation potential across species; there are limits as to the extent of cross-species extrapolation that can reasonably be made based on lipid content alone. For example, invertebrates are sufficiently different from vertebrates in terms of metabolism, growth rate, and other considerations that it is generally not recommended to extrapolate results between invertebrate and vertebrate species. It is also not generally recommended to extrapolate results across trophic levels because of food chain biomagnification effects.

The percent lipid fraction used when calculating the BAF for the trophic levels of fish consumed should be weighted by the human consumption rate of the species for the population being considered (e.g., recreational anglers). To derive a consumption-weighted average fish lipid concentration, the risk assessor needs to determine the types and quantities of aquatic organisms consumed by humans as well as the percent lipid content of these organisms. These data sets should ideally be collected from the site of interest.

A second adjustment is to express the BAF in terms of the bioavailable concentration (BC) of the contaminant in the water. It is assumed that the BC corresponds to the concentration that is freely dissolved in the water. Contaminant sorbed to dissolved organic carbon (DOC) or particulate organic carbon (POC) in the water is not considered to be bioavailable. The freely dissolved concentration of the organic chemical in the water, C_w^{fd} , is defined by the following equation:

$$C_w^{fd} = (f_{fd})(C_w^t) \tag{8-3}$$

where:

C_w^{fd} = freely dissolved concentration of the organic contaminant in the ambient water (mg/L)

C_w^t = total concentration of the organic contaminant in the ambient water (mg/L)

f_{fd} = fraction of total organic contaminant in the ambient water that is freely dissolved

The fraction of total organic chemical freely dissolved in the study water, f_{fd} , can be estimated from DOC and POC of the water body and K_{ow} of the organic contaminant as follows:

$$f_{fd} = \frac{1}{1 + \frac{(DOC)(K_{ow})}{10} + (POC)(K_{ow})}$$

(8-4)

where:

f_{fd} = fraction of organic contaminant freely dissolved in ambient water

DOC = concentration of dissolved organic carbon in test water (kg/L)

POC = concentration of particulate organic carbon in test water (kg/L)

K_{ow} = octanol-water partition coefficient for the organic contaminant

Using these adjustments a measured BAF (designated BAF_T^t , because it is based on total contaminant concentration in tissue and water) for an organic chemical can be used to derive a normalized BAF, designated BAF_d^f , because it is based on the freely dissolved concentration of contaminant in water and lipid-normalized tissue concentration of the contaminant. The BAF_d^f is a general baseline BAF for an organic contaminant that can subsequently be used to predict the BAF_T^t applicable to a specific exposure scenario by taking into account the bioavailability of the contaminant in the specific water body of concern and the lipid content of the specific fish species and tissues consumed. It is this predicted BAF_T^t that is used to calculate human intake of the contaminant due to fish consumption in Equation 8-1.

8.2.2.1. Derivation of Baseline BAF Values — It was noted previously that normalization based on lipid content is a reasonable basis for species-to-species extrapolation for organic chemicals, but only for species that are fundamentally similar to one another (in terms of metabolism, growth rate, trophic level, etc.). For inorganic chemicals, as well, it seems reasonable to limit extrapolation to species that are fundamentally similar to one another. It is, therefore, recommended that baseline BAF values be determined separately for fish, and shellfish if they are included in the assessment. Fish should always be included, because the vast majority of aquatic species locally caught and consumed in freshwater and estuarine environments (the aquatic environments most likely to be affected by a combustor) are fish. Shellfish may be included if there is significant human consumption of shellfish from water bodies in the vicinity of the specific combustor being modeled. It is further recommended that separate baseline BAF values be determined for fish that eat zooplankton (trophic level 3) and piscivorous fish (trophic level 4) because position in the food chain affects bioaccumulation and because humans may consume fish from either trophic level (although piscivorous fish predominate in the human diet).

U.S. EPA (1995b) discusses four methods that can be used to derive baseline BAF values for a chemical. In order of decreasing preference these are: (1) adapt BAF values from field studies of acceptable quality, (2) predict baseline BAF values from field-measured BSAF values of acceptable quality, (3) predict baseline BAF values from BCF values measured in laboratory studies of acceptable quality, and (4) predict baseline BAF values from K_{ow} values of acceptable quality. Each of these options is described in more detail below. The selection of approach may be driven by the available data.

Adapt BAF values from field studies. An adequately conducted field study is the most desirable source of a BAF value for either an inorganic or organic chemical. An adequate study would need to have shown that contaminant concentrations over the range of territory inhabited by the study organism (fish, or if applicable to the combustor site, shellfish) remained relatively constant for a sufficiently long period of time for steady state to have been reached, and that conditions at the site of the study were not so unique that the results cannot be extrapolated to other sites. In addition, for organic chemicals, the study should have included data regarding percent lipid of the tissue used to determine the BAF, and concentrations of DOC and POC in the study water.

For an inorganic chemical, an adequate field-measured BAF based on wet weight of an edible tissue (e.g., muscle) can simply be adopted as a baseline BAF. For an organic chemical, a field-measured BAF from an adequate study can be converted to a baseline BAF using the following equation (BAF_i^{fd} is adopted as the baseline BAF):

$$BAF_i^{fd} = \left(\frac{\text{Measured } BAF_T^t}{f_{fd}} - 1 \right) \left(\frac{1}{f_l} \right) \quad (8-5)$$

where:

- BAF_i^{fd} = BAF for organic contaminant normalized for lipid content of tissue/organism tested and bioavailability in test water (L/g lipid)
- BAF_T^t = field-measured BAF based on total concentration of contaminant in fish tissue and test water (L/g fresh tissue)

- f_l = fraction of the tested tissue composed of lipid
- f_{fd} = fraction of total organic contaminant freely dissolved in the test water

Adequate field-measured BAF values are not widely available in the literature. EPA Ambient Water Quality Criteria Documents and the Aquatic Toxicity Information Retrieval (AQUIRE) database may be useful sources for field-measured BAF values.

If more than one baseline BAF derived from a field study is available for a given chemical in a particular species, then the geometric mean should be calculated to produce the species mean baseline BAF. If a baseline BAF derived from a field study is available for more than one species in a trophic level, then the geometric mean of the species mean baseline BAF values should be calculated to produce the baseline BAF for that trophic level. If a baseline BAF based on a field study can be calculated directly only for fish from one trophic level (trophic level 3 or 4), then a baseline BAF for fish from the other trophic level can be estimated using the ratio of the FCMs (food chain multipliers) for the chemical (see Table 8-1).

As is the case with many other measures of media transfer coefficients, BAF values are generally developed as a measure of bioaccumulation rather than as a predictor of bioaccumulation. The application of this method results in their use as predictors.

Calculate BAF values based on BSAF values. For organic chemicals, BAF values may be estimated using field-measured BSAF values from adequate studies (U.S. EPA, 1994a). This method generally does not apply to inorganic chemicals. The BSAF is the ratio of a substance's lipid-normalized concentration in tissue of an aquatic organism to its organic carbon-normalized concentration in surface sediment. This assumes that the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism. Use of the BSAF to estimate bioaccumulation is most suitable for highly hydrophobic chemicals such as dioxin and biphenyls, which are detectable in fish tissues and bottom sediments but difficult to measure in the water

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TABLE 8-1
 Food Chain Multipliers for Trophic Levels 3 and 4^a

| Log K _{ow} | Trophic Level 3 ^b | Trophic Level 4 ^c |
|---------------------|------------------------------|------------------------------|
| 2.0 | 1.005 | 1.000 |
| 2.5 | 1.010 | 1.002 |
| 3.0 | 1.028 | 1.007 |
| 3.1 | 1.034 | 1.007 |
| 3.2 | 1.042 | 1.009 |
| 3.3 | 1.053 | 1.012 |
| 3.4 | 1.067 | 1.014 |
| 3.5 | 1.083 | 1.019 |
| 3.6 | 1.103 | 1.023 |
| 3.7 | 1.128 | 1.033 |
| 3.8 | 1.161 | 1.042 |
| 3.9 | 1.202 | 1.054 |
| 4.0 | 1.253 | 1.072 |
| 4.1 | 1.315 | 1.096 |
| 4.2 | 1.380 | 1.130 |
| 4.3 | 1.491 | 1.178 |
| 4.4 | 1.614 | 1.242 |
| 4.5 | 1.766 | 1.334 |
| 4.6 | 1.950 | 1.459 |
| 4.7 | 2.175 | 1.633 |
| 4.8 | 2.452 | 1.871 |
| 4.9 | 2.780 | 2.193 |
| 5.0 | 3.181 | 2.612 |
| 5.1 | 3.643 | 3.162 |
| 5.2 | 4.188 | 3.873 |
| 5.3 | 4.803 | 4.742 |
| 5.4 | 5.502 | 5.821 |
| 5.5 | 6.266 | 7.079 |
| 5.6 | 7.096 | 8.551 |
| 5.7 | 7.962 | 10.209 |
| 5.8 | 8.841 | 12.050 |
| 5.9 | 9.716 | 13.964 |
| 6.0 | 10.556 | 15.996 |

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TABLE 8-1 cont.

| Log K _{ow} | Trophic Level 3 ^b | Trophic Level 4 ^c |
|---------------------|------------------------------|------------------------------|
| 6.1 | 11.337 | 17.783 |
| 6.2 | 12.064 | 19.907 |
| 6.3 | 12.691 | 21.677 |
| 6.4 | 13.228 | 23.281 |
| 6.5 | 13.662 | 24.604 |
| 6.6 | 13.980 | 25.645 |
| 6.7 | 14.223 | 26.363 |
| 6.8 | 14.355 | 26.669 |
| 6.9 | 14.388 | 26.669 |
| 7.0 | 14.305 | 26.242 |
| 7.1 | 14.142 | 25.468 |
| 7.2 | 13.852 | 24.322 |
| 7.3 | 13.474 | 22.856 |
| 7.4 | 12.987 | 21.038 |
| 7.5 | 12.517 | 18.967 |
| 7.6 | 11.708 | 16.749 |
| 7.7 | 10.914 | 14.388 |
| 7.8 | 10.069 | 12.050 |
| 7.9 | 9.162 | 9.840 |
| 8.0 | 8.222 | 7.798 |
| 8.1 | 7.278 | 6.012 |
| 8.2 | 6.361 | 4.519 |
| 8.3 | 5.489 | 3.311 |
| 8.4 | 4.683 | 2.371 |
| 8.5 | 3.949 | 1.663 |
| 8.6 | 3.296 | 1.146 |
| 8.7 | 2.732 | 0.778 |
| 8.8 | 2.246 | 0.521 |
| 8.9 | 1.837 | 0.345 |
| 9.0 | 1.493 | 0.226 |

^a Source: U.S. EPA (1995b)

^b Fish that feed on zooplankton. FCM values for trophic level 3 are the geometric mean of FCM values for sculpin and alewife.

^c Piscivorous fish

column. It should be noted that the BSAF, like the BAF, is a simplification of the complex processes by which pollutants are transferred from aquatic ecosystems to aquatic organisms. Since BSAF are measured values and include effects of metabolism and bioaccumulation among others, they are appropriate predictors of accumulation. It should also be noted that the values are generally developed as a measure of bioaccumulation rather than as a predictor of bioaccumulation, which is the manner in which they are used here.

Criteria for an adequate study are: use of fish or (if appropriate to the combustor site) shellfish; determination of percent lipid in the tissue used to derive the BSAF; use of surface-bottom sediment samples (0-1 cm) from a location where there is net deposition of fine sediments that is representative of average surface sediment in the vicinity of the organism and is not so unique that the results cannot be extrapolated to other areas; and determination of the organic carbon content of the sediment. For organisms that are highly mobile, average bottom sediment concentrations from a larger area (e.g., lakewide sediment concentration data) may be needed. Special consideration may need to be given if a larger body of water is included in the assessment or if the species of concern feed in a specific area of the water body. In these cases as well as in other related cases, the source of the environmental pollutant concentration should be justified. An assessment of the chemical concentration in the aquatic system is also important. If chemical inputs are decreasing or increasing, the system may not be in equilibrium. This may result in an increase or a decrease in the exposure of fish through the water column or bottom sediments. Like BAF, the BSAF should be measured in systems at equilibrium.

The BSAF from an adequate study is calculated as follows:

$$BSAF = \frac{C_i}{C_{SOC}}$$

(8-6)

where:

BSAF = biota-sediment accumulation factor

C_l = lipid-normalized concentration of the organic contaminant in tissue
($\mu\text{g/g}$ lipid)

C_{SOC} = organic carbon-normalized concentration of the organic contaminant in
sediment ($\mu\text{g/g}$ organic carbon)

The lipid-normalized contaminant concentration, C_l , is calculated from the tissue fresh weight concentration and the lipid fraction of the tissue, as shown in Equation 8-2.

The organic carbon-normalized concentration of the contaminant in sediment, C_{SOC} , is calculated using the following equation:

$$C_{\text{SOC}} = \frac{C_{\text{bs}}}{f_{\text{OC}}} \quad (8-7)$$

where:

C_{SOC} = organic carbon-normalized concentration of organic contaminant in
sediment ($\mu\text{g/g}$ organic carbon)

C_{bs} = concentration of organic contaminant in sediment ($\mu\text{g/g}$ sediment)

f_{OC} = fraction of the sediment that is organic carbon

BSAF values of acceptable quality can be used to estimate BAF values based on the expected proportionality between the two quantities. The method depends on having not only an adequate BSAF for the chemical in question, but also adequate BAF and BSAF values for a reference chemical that can be used as a basis of comparison. That is, predicting a BAF from a BSAF requires data from a steady-state (or near steady-state) condition between sediment and ambient water for both a reference organic chemical r with a BAF_i^{fd} (baseline BAF) derived from a field study and the organic chemical i for which the BAF is to be determined. The method is shown in the following equation:

$$(BAF_{baseline})_i = (BAF_{baseline})_r \frac{(BSAF)_i (K_{ow})_i}{(BSAF)_r (K_{ow})_r} \quad (8-8)$$

where:

- $(BAF_{baseline})_i$ = BAF for organic contaminant *i*
- $(BAF_{baseline})_r$ = BAF for reference organic contaminant *r*
- $(BSAF)_i$ = BSAF for organic contaminant *i*
- $(BSAF)_r$ = BSAF for reference organic contaminant *r*
- $(K_{ow})_i$ = octanol-water partition coefficient for organic contaminant *i*
- $(K_{ow})_r$ = octanol-water partition coefficient for reference organic contaminant *r*

Adequate field-measured BSAF and BAF values are not widely available in the literature. EPA Ambient Water Quality Criteria Documents and the Aquatic Toxicity Information Retrieval (AQUIRE) database may be useful sources for BSAF and BAF values. U.S. EPA (1993b, 1994a) discusses BSAF values for dioxin-like compounds and PCBs. Based on the approach delineated above and the aforementioned BSAF values, U.S. EPA (1995b) determined bioaccumulation equivalency factors (BEFs) for the dioxin-like congeners. These BEFs show the propensity for each congener to bioaccumulate, relative to TCDD; they are presented in Table 8-2.

If more than one baseline BAF is predicted from BSAFs in a particular species, then the geometric mean should be calculated to produce the species mean baseline BAF. If a baseline BAF predicted from the BSAF is available for more than one species in a trophic level, then the geometric mean of the species mean baseline BAF values should be calculated to produce the baseline BAF for that trophic level. If a baseline BAF based on BSAF can be calculated directly only for fish from one trophic level (trophic level 3 or 4), then a baseline BAF for fish from the other trophic level can be estimated using the ratio of the FCMs for the chemical (see Table 8-1).

If these data are not available, the BSAF term can replace the BAF term used to predict fish concentrations. Note that sediment concentrations should be employed.

Estimated BAF values based on BCF values. The BCF (bioconcentration factor) is defined as the ratio (in L/g) of a substance's concentration in the tissue of an aquatic organism to its concentration in the ambient water, in situations where the organism is

| TABLE 8-2 | |
|---|------|
| Bioaccumulation Equivalency Factors for Dioxin-like Compounds | |
| Congener | BEF |
| 2,3,7,8-TCDD | 1.0 |
| 1,2,3,7,8-PeCDD | 0.9 |
| 1,2,3,4,7,8-HxCDD | 0.3 |
| 1,2,3,6,7,8-HxCDD | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.05 |
| OCDD | 0.01 |
| 2,3,7,8-TCDF | 0.8 |
| 1,2,3,7,8-PeCDF | 0.2 |
| 2,3,4,7,8-PeCDF | 1.6 |
| 1,2,3,4,7,8-HxCDF | 0.08 |
| 1,2,3,6,7,8-HxCDF | 0.2 |
| 2,3,4,6,7,8-HxCDF | 0.7 |
| 1,2,3,7,8,9-HxCDF | 0.6 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.4 |
| OCDF | 0.02 |

Source: U.S. EPA (1995b)

exposed through the water only and the ratio does not change substantially with time. The BCF is, therefore, similar to the BAF but does not take into account accumulation via the food chain (i.e., the organism's prey are not exposed). BCF values are generally derived from laboratory studies. An adequate study is generally a flow-through or renewal test conducted long enough for steady state to be achieved, using a measured water concentration that does not adversely affect the test organisms (fish, or if applicable to the combustor site, shellfish). Results should be expressed in terms of wet weight, and for organic chemicals, the tissue lipid content and POC and DOC of the test solution should be reported.

An acceptable laboratory-derived BCF, based on total water and tissue contaminant concentrations (designated by BCF_T^t), can be used to estimate a baseline BCF. For an inorganic chemical, the baseline BCF can be estimated by adopting an acceptable BCF_T^t calculated on the basis of wet weight of an edible tissue. For an organic chemical, the baseline BCF can be estimated as the lipid and bioavailability-normalized BCF_I^{fd} derived from an acceptable BCF_T^t using the following equation:

$$BCF_I^{fd} = \left[\frac{\text{Measured } BCF_T^t}{f_{fd}} - 1 \right] \left[\frac{1}{f_l} \right] \quad (8-9)$$

where:

- BCF_I^{fd} = BCF for organic contaminant normalized for lipid content of tissue/organism tested and bioavailability in test water (L/g lipid)
- BCF_T^t = BCF based on total concentration of organic contaminant in tissue and water (L/g)
- f_l = fraction of the tissue composed of lipid
- f_{fd} = fraction of the total organic contaminant freely dissolved in the test water

Laboratory-measured BCF values for many chemicals are available in the published literature and in EPA reports. EPA Ambient Water Quality Criteria Documents and the AQUIRE database are useful sources of measured BCF values.

For both inorganic and organic contaminants, the baseline BCF can be used to estimate the baseline BAF. The relationship is shown in the following equation:

$$BAF_{baseline} = (FCM)(BCF_{baseline}) \quad (8-10)$$

where:

- $BAF_{baseline}$ = baseline BAF for an organic or inorganic contaminant
- $BCF_{baseline}$ = baseline BCF for an organic or inorganic contaminant
- FCM = food chain multiplier

The FCM is a function of the trophic level of the organism tested and the lipophilicity of the test compound. For inorganic chemicals, the FCM is assumed to be 1 unless chemical-specific data suggest that a FCM other than 1 be used (e.g., some metals, such as mercury, have organometallic forms that may biomagnify). For organic chemicals, the FCM appropriate for use with fish of trophic levels 3 and 4 can be obtained or estimated by linear interpolation from Table 8-1. If shellfish, which feed primarily on detritus and plant material, are included in the assessment, it would be appropriate to use a FCM of 1 for organic chemicals.

If more than one baseline BAF predicted from a BCF is available for a particular species, then the geometric mean should be calculated to produce the species mean baseline BAF. If a baseline BAF predicted from a BCF is available for more than one species in a trophic level, then the geometric mean of the species mean baseline BAF values should be calculated to produce the baseline BAF for that trophic level. If a baseline BAF predicted from a BCF can be calculated directly only for fish from one trophic level (level 3 or 4), then a baseline BAF for fish from the other trophic level can

be estimated by applying the FCM from the other trophic level to the available baseline BCF.

Estimated BAF values based on K_{ow} . The octanol-water partition coefficient, K_{ow} , can be used to estimate BAF values for an organic chemical. n-Octanol/water partition coefficient (K_{ow}) is defined as the ratio of the concentration of a substance in the octanol phase to its concentration in the aqueous phase in an equilibrated two-phase octanol-water system. The log of the octanol-water partition coefficient is a base 10 logarithm. Theory predicts that the baseline BCF, i.e., $BCF_{baseline}^{fd}$, for a slowly metabolized, lipophilic nonpolar organic chemical with $\log K_{ow} > 3$ will be approximately equal to the K_{ow} (U.S. EPA, 1995b, 1994b). Therefore, for such chemicals, a baseline BAF can be calculated according to the following relationship:

$$BAF_{baseline} = (FCM)(predicted\ BCF_{baseline}) \approx (FCM)(K_{ow}) \quad (8-11)$$

where:

- $BAF_{baseline}$ = baseline BAF for an organic contaminant
- FCM = food chain multiplier
- K_{ow} = octanol-water partition coefficient

FCM values to calculate baseline BAF values for fish of trophic levels 3 and 4 can be obtained from Table 8-1. If shellfish are included in the assessment, a FCM of 1 should be assumed for these species.

8.2.2.2. Application of Baseline BAF Values — The methodology described above leads to derivation of two baseline BAF values for each contaminant: one applicable to fish that eat zooplankton (trophic level 3) and one applicable to piscivorous fish (trophic level 4). In some cases, a third baseline BAF applicable to shellfish may have been calculated as well. In order to use bioaccumulation information to calculate human daily intake due to fish consumption at the combustor site, it is necessary to

convert these baseline BAF values to predicted BAF values applicable to the specific site.

For inorganic contaminants, the baseline BAF for a trophic level is adopted as the predicted BAF for that trophic level. For organic contaminants, baseline BAF values are tissue lipid- and bioavailability-normalized values (BAF^{fd}_i) that must be converted, using data that describe conditions at the specific site in question, to values based on total contaminant concentration in water and tissue in order to derive predicted BAF values (BAF^t_T) for the site. The following equation shows how a baseline BAF (BAF^{fd}_i) for an organic contaminant may be converted to the corresponding BAF^t_T predicted to apply to the site in question:

$$Predicted\ BAF^t_T = [(BAF_{baseline}) (F_l) + 1] (F_{fd}) \quad (8-12)$$

where:

- BAF^t_T = BAF for an organic contaminant predicted to apply to combustor site (will convert total water concentration to total tissue concentration in Equation 8-1) — applies to a specific trophic level
- $BAF_{baseline}$ = baseline BAF (BAF^{fd}_i) for an organic contaminant — applies to a specific trophic level
- F_l = lipid content of species caught at combustor site — applies to a specific trophic level
- F_{fd} = freely dissolved concentration of organic contaminant at combustor site

The freely dissolved water fraction at the local site of interest, F_{fd} , can be calculated as the ratio of dissolved water column concentration (C_{dw} from Chapter 7) to total water column concentration (C_{wt} from Chapter 7).

Tissue lipid content, F_l , should be representative of species caught and consumed locally in the vicinity of the combustor. A separate F_l would apply to each trophic level included in the assessment. Ideally, F_l for each trophic level would be calculated as the average of lipid content of meat from species of that trophic level

caught in the water body of interest, weighted according to consumption. U.S. EPA (1995a) and USDA (1979-1984) present data regarding lipid content for many species of fish and shellfish. However, in the absence of data regarding the specific species taken locally and/or the lipid content of the meat consumed from these species, default values may be applied. U.S. EPA (1980) reported that the average lipid fraction of freshwater and estuarine species, the species potentially affected by combustor emissions, weighted by average daily consumption, was 0.03 (3%). U.S. EPA (1995b) calculated average lipid fractions of 0.0182 (1.82%) and 0.0310 (3.10%) for freshwater fish of trophic levels 3 and 4, respectively, in the Great Lakes water system. These values may be applicable to other freshwater systems as well.

8.2.2.3. Benthic Invertebrates — If BAF_i or $BSAF_i$ measures are not available for a benthic species of concern or if the assessor is concerned about the applicability of a reference BAF or BSAF, pollutant concentrations in benthic invertebrates can be estimated through alternative models such as a model presented in Thomann et al. (1992). In this model benthic organisms may accumulate pollutant in sediment, sediment interstitial waters, and the water column as well as contaminated phytoplankton. The Thomann et al. model also accounts for growth of the organism and excretion.

The value or the distribution of the bioaccumulation factor utilized in an assessment should be justified in the parameter description of the assessment. The strengths as well as weaknesses of the data from which the BAF or the BAF distribution was derived should be characterized. The description of the BAF should describe the nature of the variability in the data and the uncertainty in the data.

If pollutant concentrations are simulated for larger water bodies and there is predicted to be spatial variability in pollutant concentration, the dissolved water concentration or sediment concentration utilized in the estimation of pollutant levels in aquatic species should be carefully selected and justified, particularly for species that are non-migratory or that are known to feed in a specific area.

8.2.3. Fish Ingestion (DI_f). Consumption of fish is highly variable across the U.S. population, unlike consumption of other dietary components, which may be more widespread. Inclusion of this source of protein in the diet varies with geographic location, season of the year, and ethnicity, as well as personal food preferences. Analysis of dietary survey data (Crochetti and Guthrie, 1982) showed fish to be among the most infrequently consumed food groups.

For the purposes of estimating human intake of fish potentially contaminated by emissions from a nearby combustor, the most pertinent subpopulations are those that consume fish from these waters; studies of consumption rates of local fish typically identify a distribution of consumption rates across the subpopulation. This distribution of consumption rates may include two classes of anglers, the recreational anglers and subsistence anglers who fish these waters. Other members of the local population that receive and consume local fish, such as family members of fishers, friends, etc., should also be considered as part of the exposed population. Subsistence fish consumers are generally defined as obtaining their daily protein requirements or their daily energy requirements from fish. Commercially caught fish are usually distributed widely so that predictions of exposure from a single combustor are difficult.

Generally freshwater exposure scenarios are conducted for combustors' risk assessments; however, combustor emissions could also affect estuarine species if the combustor is located in a coastal area. Except possibly for anadromous species such as salmon, marine life that has been contaminated from a single combustion source is not expected to pose a significant health risk to humans. Ingestion of marine fish and shellfish is not generally considered in indirect exposure estimates of single emission sources (although marine species could be included if the risk assessor deems an assessment warranted).

Aquatic species consumed by humans vary by locale and are based, in part, on local availability of an organism as well as the cultural background of the consumer. Finfish, shellfish, and other benthic-dwelling organisms may be included in a local diet. Consumption rates of these species may or may not include a survey of fish

consumption rates. The risk assessor should identify the types of local aquatic organisms consumed by the subpopulation of concern and compare this with the information collected in the survey of fish consumption rates.

Data on fish consumption rates are typically calculated as either “per capita” or “per user.” The former term is obtained by dividing the supply of fish across an entire population to establish a per capita consumption rate. The latter term divides the supply of fish across only the portion of the population that consumes fish, providing per user rates of consumption. Because many people in a population may not eat any fish, and even fewer may eat locally-caught fish, per capita consumption estimates might significantly underestimate the actual consumption rates for fish consumers, such as recreational fishers and subsistence fish consumers. Therefore, per user estimates based on consumption in these groups provide more relevant estimates of central tendency and upper percentile exposure than per capita estimates.

Recent fish consumption surveys of anglers who fish at the potentially affected water bodies in the region around the combustor are the best source of fish consumption data and estimates of the size of the local fish-consuming population. However, in the absence of adequate local data, the results of surveys from other regions can be used as surrogates to estimate both the size of the local fish-consuming population and the distribution of fish consumption rates within that population. When surrogate fish-consuming populations are used, significant differences between the surrogate and the site being evaluated should be described. For example, the fish consumption rates or the size of the fish-consuming population may vary between two sites because of the weather, the aesthetic quality of the site, access to the site, the existence of posted health advisories, or the types of fish typically caught. The fish consumption rates or the size of the population may also vary between sites because of differences in ethnic composition or the distribution of income levels. Finally, humans typically do not consume the entire fish; however, the body parts of fish that are consumed may vary among some populations. (For example, Toy et al. 1995 noted that members of the Tulalip and Squaxin Island tribes consume some fish with skin-on

and that some members consumed head, bones, and eggs.) These differences should be noted in the assessment.

The available data on human consumption of freshwater fish has been reviewed and evaluated in U.S. EPA's 1997 Exposure Factors Handbook (Volume II-Food Ingestion Factors, Chapter 10). As a surrogate for a local survey of freshwater fish consumption rates, U.S. EPA (1997) identified three relevant freshwater recreational angler studies as follows: Fiore et al. (1989), Connelly et al. (1990), and Hudson River Sloop Clearwater, Inc. (1993). U.S. EPA (1997) used the data in these studies of recreational anglers to identify mean and 95th percentile intake consumption rates of 8 and 25 grams of fish per day, respectively.

U.S. EPA (1997) also evaluated freshwater fish consumption rates among Native American Tribesmen that consume fish at subsistence quantities (i.e., fish is either the primary source of dietary protein or the primary source of energy in the diet). As a surrogate for subsistence consumers, U.S. EPA (1997) identifies four Native-American subsistence freshwater subsistence angler studies as follows: Wolfe and Walker (1987), AIHC (1994), Columbia River Inter-Tribal Fish Commission (CRITFC, 1994), and Peterson et al. (1994). U.S. EPA (1997) used the data in these studies of Native American subsistence anglers to identify mean and 95th percentile intake consumption rates of 70 and 170 grams of fish per day, respectively. If subsistence fishers are evaluated in an assessment, the parts of the fish consumed should be identified. For example, Toy et al. (1995) examined fish consumption among members of the Tulalip and Squaxin Island tribes of Puget Sound (Washington, USA). Toy and collaborators reported that approximately 10% of the population surveyed indicated that they consumed parts of the fish other than the muscle (e.g., head, bones, eggs).

Specific Native American Tribes are not the only subpopulation within the United States that consume fish and shellfish at subsistence levels. Other ethnic groups such as Asians (for example, individuals of Vietnamese, Laotian, Cambodian, and Hmong descent) and Pacific-Islanders may consume large quantities of fish. Other individuals

in the population may also consume subsistence levels of locally caught fish as a dietary preference.

8.2.4. Body Weight. Dose estimates are normalized over body weight to express them in a manner that is consistent with dose-response relationships. A weight of 70 kg has traditionally been used by U.S. EPA to represent average adult body weight. Data reviewed by U.S. EPA (1997) support continued use of this value for hypothetical adults (see Table 7-11; Chapter 7 of U.S. EPA, 1997). In fact, U.S. EPA (1997) reports that the mean body weight for all adults both sexes is 71.8 kg. For children, average body weight for the entire population by age are presented for both genders in Table 7-3 of U.S. EPA (1997). Consult U.S. EPA (1997) for more detailed information regarding human body weight.

8.3. OTHER AQUATIC MODELS

For some situations more complicated models are required that may require more site and chemical data. More expertise may also be needed to run these models and accurately interpret the predicted results. These other models may also be used to corroborate estimates from the simpler models presented in this methodology.

For example, EPA has developed models that estimate the concentrations of pollutants in fish. FGETS (Food and Gill Exchange of Toxic Substances) is a FORTRAN simulation model that predicts temporal dynamics of whole-fish body concentration ($\mu\text{g chemical}/[\text{g live weight fish}]$) of nonionic, nonmetabolized, organic chemicals that are bioaccumulated from either: (a) water only, which is the predominant route of exchange during acute exposures, or (b) water and food jointly, which is more characteristic of chronic exposures. By assuming that a chemical elicits its pharmacological response through a narcotic mode of action, FGETS estimates the time needed to reach the chemical's lethal activity.

FGETS considers both the biological attributes of the fish and the physicochemical properties of the chemical that determine diffusive exchange across gill membranes and intestinal mucosa. Important biological characteristics addressed by the model are the fish's gill and intestinal morphometry, the body weight of the fish,

and the fractional aqueous, lipid, and structural organic composition. Relevant physicochemical properties are the chemical's aqueous diffusivity, molar volume, and the n-octanol/water partition coefficient that is used as a surrogate to quantify chemical partitioning to the fish's lipid and structural organic fractions. The chemical's log K_{ow} is used in calculating the fish's bioconcentration factor. Its molecular volume is used to estimate the chemical's aqueous diffusivity, and its melting point is used in conjunction with log P to calculate the chemical's activity within the fish.

FGETS is parameterized for a particular fish species by means of two morphological/physiological databases that delineate the fish's gill morphometry, feeding and metabolic demands, and body composition. Presently, joint water and food exposure is parameterized for salmonids, centrarchids, cyprinids, percids, and ictalurids.

FGETS is a model developed by Center for Exposure Assessment Modeling (CEAM). For information about obtaining this or one of the other CEAM models, contact:

U.S. Environmental Protection Agency (U.S. EPA)
Office of Research and Development (ORD)
National Exposure Research Laboratory - Ecosystems Research Division
960 College Station Road
Athens, Georgia (GA) 30605-2700 USA
e-mail: ceam@epamail.epa.gov

Thomann and his collaborators have developed a series of steady-state and dynamic models of pollutant accumulation in the aquatic food web. These multicompartment models have been developed to predict concentrations of (primarily) organic molecules in the tissues of aquatic species based on concentrations in environmental compartments (e.g., dissolved chemical concentrations in the water column). The modeled biologic compartments include benthic invertebrates, phytoplankton, zooplankton, forage fish, and piscivorous fish. Some of the presented models (e.g., Thomann, 1992; Thomann et al., 1992) base the predicted pollutant concentration in fish tissues on food web transfers and, in part, on other factors such as fish age (thereby accounting for changes in the fish diet as the size of the fish

increases). Organism/pollutant interactions included in Thomann's simulations include diffusive exchange across membranes, consumption of contaminated prey, growth and depuration. Uptake may result from bioconcentration and bioaccumulation. Growth results in a dilution of accumulated pollutant. Depuration rates reduce predicted pollutant concentrations in fish.

Examples of the aquatic organisms considered in the modeling efforts include the following:

- ! The marine bivalves *Crassostrea virginica* and *Mytilus edulis* (Thomann et al., 1995)
- ! Striped Bass and White Perch (Thomann et al., 1991)
- ! Alewife and Lake Trout (Thomann, 1992)
- ! Rainbow Trout (Thomann et al., 1997)

8.4. SPECIAL CONSIDERATIONS FOR FARM-RAISED FISH

In the United States an increasing number of individuals obtain freshwater fish from fish farms; on these farms the fish are fed a special diet and there is little exposure through the food chain. If there is a fish farm in the area around the combustion source of concern, then the application of a BAF may be inappropriate, as it may overestimate the amount of pollutant that accumulates in the bodies of the fish. This overestimate is the result of including a contribution to the fish body burden from the aquatic food chain. Since these fish are typically fed premixed feeds from other sources, there would be no multiplication through the aquatic food chain. As a result, it may be more appropriate to apply a water-column-to-fish bioconcentration factor approach to these stocks. This assumes, of course, that the feed is not more contaminated than the normal prey. The risk assessor should also consider benthic sediments in the ponds, which may contain pollutant concentrations from runoff and erosion.

8.5. FISH PREPARATION FACTOR

The effect of preparation and cooking on chemical levels in fish tissue is a complex issue. Various preparation and cooking procedures may decrease, concentrate, or degrade pollutants in edible fish tissues. Several studies have indicated that the trimming and removal of fish adipose tissue reduces the concentrations of fat- soluble contaminants in the consumed portion of the fish (Sander and Haynes, 1988; Armbruster et al., 1989; Skea et al., 1979; Voiland et al., 1990); various cooking procedures have also been shown to reduce the concentrations of fat- soluble contaminants in the consumed portions of some fish (Skea et al., 1979; Armbruster et al., 1989). Contaminants that are not fat soluble appear to act differently. For example, Morgan et al. (1997) reported that, while the total amount of mercury in fish remained constant, mercury concentrations in fillets were higher after preparation, presumably because of water loss.

The use of fish preparation factors may be appropriate for some exposure assessments; for example, for exposures in commercially prepared fish. Given the wide range of preparation techniques, types of pollutants, and types of fish in the United States, and also in consideration of the uncertainties associated with such factors, preparation factors are not employed in this methodology.

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BREAST MILK PATHWAY

9.1. INTRODUCTION

Numerous chemicals, both environmental and contaminants, have been identified in human breast milk (Abadin et al., 1997; Adamovic et al., 1978; Atkinson, 1979; Byczkowski et al., 1994; Cerutti et al., 1976; Jensen, 1983, 1991; Jensen and Slorach, 1991; U.S. EPA, 1980, 1983, 1994; WHO, 1985, 1989). Residues of organohalogen, organometallic and inorganic contaminants, many of which are found in emissions from combustion sources, have been detected in human milk. The major route of human exposure to these occurs through ingestion of fresh-water fish, seafood, plants, and other food contaminated by many sources including the fallout of air pollutants (Smith, 1987; Siebert et al., 1991; Stevens, 1991; Sullivan et al., 1991). This document focuses on contaminants that are likely to be emitted from stationary combustion sources, but these must be considered within the context of existing burdens from all sources.

Exposures predicted by the infant exposure model presented in this Chapter should always be considered in the context of the benefits of breast feeding (see Text Box 9-1). In addition, the application of the model is somewhat limited because of the current lack of infant dose-response data. Predicted infant exposures, however, can still be used to estimate incremental lifetime cancer risk and for comparison to the Reference Dose (RfD) for noncancer effects for screening purposes.

9.2. CHEMICAL CONTAMINANTS IN BREAST MILK ARISING FROM COMBUSTION

The chemical contaminants in breast milk can be generally considered in three major categories:

- 1) Persistent highly-lipophilic organic contaminants, such as polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans PCDFs, and polychlorinated dibenzo-p-dioxins (PCDDs), are by far the most documented group. These, by virtue of their lipophilicity, are found almost

Text Box 9-1 Breast-Feeding: Benefits vs. Risk

Potential risk to the infant from exposure to contaminants in breast milk must be balanced against the well-documented benefits of breast feeding. In particular, infant exposure models should be relatively free of bias, particularly towards over prediction of risk. Breast feeding has a number of universally accepted benefits for the infant as well as for the mother. A discussion on physical and psychological benefits obtained by the nursing mother, as well as by the developing infant from breast feeding can be found in Mukerjee (1998). Several studies show the beneficial effects of breast feeding despite the presence of contaminants associated with developmental (pre- and post-natal) neurological effects. PCB and PCDD/PCDF exposures through breast milk resulted in subtle neurological and developmental deficits, but many effects were more than compensated for by the developmental benefits of breast feeding vs bottle feeding (Huisman et al., 1995; Koopman-Esseboom et al., 1996). Neurological effects in children were associated with (presumably) high levels of methylmercury in breast milk (Amin-Zaki et al., 1981). In another study, however, infants exposed to lower levels of MeHg in breast milk reached developmental milestones more quickly than infants not breast fed (Grandjean, et al., 1995b). As toxicity is dose related, at some level of the contaminant in breast milk, the benefits of breast feeding would be neutralized. One study of PCB exposure to breast-fed human infants suggests adverse effects associated with milk concentrations greater than 780 ng/ml, but not below (Jacobson and Jacobson, 1990). Data addressing infant dose response from contaminants in breast milk are generally lacking, so interpretation of exposure levels with respect to toxicity to the infant is problematic.

entirely in the milk fat. Lipophilic metabolites such as PCB methyl sulfones and hexachlorobenzene (HCB) methyl sulfones have also been found in the lipid phase of breast milk. Polyaromatic hydrocarbons (PAHs) occur in breast milk, but they are not as persistent as the halogenated aromatics and metabolites are more laborious to analyze.

- 2) Combustion-source compounds with relatively low octanol:water partition coefficients such as phenol, benzene, halobenzenes, halophenols, some aldehydes and the more polar metabolites of PCBs, PAHs and pesticides may occur in both the aqueous and lipid phases of breast milk. However,

there is sparse information available, as the aqueous fraction is often ignored.

- 3) Inorganic compounds, metals, and some organo-metallics, including the heavy metals arsenic, lead, cadmium, and mercury, have been found in breast milk. Trace nutrients such as copper, iron and zinc may be present at elevated levels if maternal contamination is high. These inorganics are generally found in the aqueous phase and most are bound to proteins, small polypeptides, and free amino acids. Some organo-metallics and metalloids (such as As and Se) may also be found in the lipid phase to some degree. Table 9-1 presents some examples of organic contaminants in human milk, with their respective water solubilities and $\text{Log } K_{ow}$ (\log_{10} octanol-water partition coefficient) values to help assess relative solubility in the aqueous or fat phase of breast milk.

9.2.1. Residues of Highly Lipophilic Organic Contaminants in Human Milk.

9.2.1.1. PCDDs and PCDFs — Several reports have been published on the presence of PCDDs, PCDFs, PCBs, and polybrominated biphenyls (PBBs) in human milk (Jensen and Slorach, 1991; Jensen, 1987; Dewailly et al., 1991; Rogan and Ragan, 1994; Hong et al., 1994; Dahl et al., 1995). 2,3,7,8-Tetra-CDD (TCDD), the most toxic PCDD, is found at a very low level compared to other PCDDs. More than 50% of the total PCDD content consists of Octa-CDD, perhaps the least toxic PCDD congener. Average TCDD levels in human milk fat samples from West Germany (Rappe, 1980), northern Sweden (Rappe et al., 1985), Netherlands (Fürst et al., 1986), and Yugoslavia (Fürst et al., 1986) were reported to be 1-3 ppt, 0.6 ppt, 9.7 ppt, and <0.1 ppt respectively. The average level of TCDD in human milk fat in industrial countries is around or below 2 ppt (ng/kg) (Jensen, 1987).

One of the PCDDs which is not found in any commercial products as a contaminant but always found in the emissions from the waste incinerators is 1,2,3,7,8-Penta-CDD (PeCDD). Detection of residues of 1,2,3,7,8-PeCDD with other

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Breast Milk Pathway

TABLE 9-1

Ranges of water solubilities and octanol:water partition coefficients for representative chemical emissions which may occur in breast milk (Adapted from ATSDR, 1994a,b, 1995, 1997a,b,c and Mackay et al., 1992)

| Chemical | Chlorine Substitution | Mol. Weight | Water Solubility (mg/L) | Log K _{ow} |
|----------------|----------------------------|-------------|-------------------------|---------------------|
| Phenol | | 94.1 | 86600 | 1.5 |
| Chlorophenol | 2,4 | 163 | 6194 | 3.1 |
| Chlorophenol | 2,3,4,5,6 | 266.4 | 14 | 5 |
| Benzene | | 78.1 | 1780 | 2.1 |
| Toluene | | 92.1 | 515 | 2.7 |
| Xylene | para-CH ₃ (1,4) | 106.2 | 215 | 3.2 |
| Chlorobenzene | 1 | 112.6 | 484 | 2.8 |
| Chlorobenzene | 1,2,3 | 181.4 | 21 | 4.1 |
| Chlorobenzene | 1,2,4 | 181.4 | 40 | 4.1 |
| Chlorobenzene | 1,2,3,4,5 | 250.3 | 0.65 | 5 |
| Chlorobenzene | 1,2,3,4,5,6 | 284.8 | 0.005 | 5.5 |
| Benzo(a)pyrene | | 252.3 | 0.0038 | 6.1 |
| Biphenyl | | 154.2 | 7 | 3.9 |
| PCB 4 | 2,2' | 223.1 | 1 | 4.9 |
| PCB 15 | 4,4' | 223.1 | 0.008 | 5.3 |
| PCB 47 | 2,2',4,4' | 292 | 0.09 | 5.9 |
| PCB 52 | 2,2',5,5' | 292 | 0.03 | 6.1 |
| PCB 77 | 3,3',4,4' | 292 | 0.001 | 6.5 |
| PCB 95 | 2,2',3,5',6 | 326.4 | 0.034 | 6.1 |
| PCB 99 | 2,2',4,4',5 | 326.4 | 0.018 | 6.5 |
| PCB 101 | 2,2',4,5,5' | 326.4 | 0.01 | 6.4 |
| PCB 128 | 2,2',3,3',4,4' | 360.9 | 0.0006 | 7 |
| PCB 138 | 2,2',3,4,4',5' | 360.9 | 0.0017 | 6.8 |
| PCB 153 | 2,2',4,4',5,5' | 360.9 | 0.001 | 6.9 |
| PCB 209 | 23456-2'3'4'5'6' | 498.7 | 0.000001 | 8.3 |
| PCDF 83 | 2,3,7,8 | 306 | 0.00042 | 5.7 |
| PCDF 114 | 2,3,4,7,8 | 340.4 | 0.00024 | 6.9 |
| PCDF 131 | 1,2,3,4,6,7,8 | 409.3 | 0.000014 | 7.9 |
| PCDD 48 | 2,3,7,8 | 322 | 0.000019 | 6.7 |

PCDDs/PCDFs in human milk indicates that the major source of exposure to this congener of PCDD is occurring from waste incinerator emissions (Rappe et al., 1984; Buser and Rappe, 1984; Mukerjee and Cleverly, 1987).

Around 70% of the total Hexa-CDDs (HxCDDs) is 1,2,3,6,7,8-HxCDD, and the remainder is mainly 1,2,3,4,7,8-HxCDD and 1,2,3,7,8,9-HxCDD. Of the Hepta-CDDs(HpCDDs) only 1,2,3,4,6,7,8-HpCDD residues have been reported in human milk.

Residue levels of PCDFs in human milk tend to be lower than those of PCDDs (Dewailley et al., 1991), even though PCDFs dominate in combustion residues and are more dominant in the atmospheres over these residues (Hansen and O'Keefe, 1996). HxCDDs/HxCDFs and HpCDDs/HpCDFs are prevalent in pentachlorophenol. Incineration of wood and other products impregnated with pentachlorophenol results in the further formation and emission of hexa- and hepta-CDDs/CDFs. Both 1,2,3,7,8- and 2,3,4,7,8-PeCDFs have been detected in human milk, but 90% of the PeCDFs is generally 2,3,4,7,8-PeCDF (Fürst et al., 1989). 1,2,3,4,7,8- , 1,2,3,6,7,8- , and 2,3,4,6,7,8-HxCDFs; and 1,2,3,4,6,7,8-HpCDF are also prevalent.

PCDDs, PCDFs, coplanar PCBs and other coplanar compounds with lateral chlorines have one common mechanism of action through the aryl hydrocarbon receptor (AhR) (Poland and Knutson, 1982; Safe, 1986; Blankenship et al., 1994). Similar predictable responses to these compounds make it possible to compare potencies by measuring select endpoints. TCDD is the most potent of the AhR agonists and is assigned a "Toxic Equivalency Factor" (TEF)¹ of 1 for AhR mediated effects only. If the composition of a mixture is known, the TCDD Equivalency (TEQ) can be derived by summing TEF normalized concentrations.

Women from industrial countries have more PCDDs/PCDFs in their milk than developing countries. Human milk fat dioxin TEQs of PCDDs and PCDFs from United States, Japan, Canada and Germany have been reported to be 20, 27, 26, and 27 ppt

¹ TEFs, in this case, can be considered to be TCDD equivalency factors.

respectively, while those from Thailand, Cambodia, and Siberia were found to be 3, 3, and 12 ppt respectively (Schechter, 1991).

9.2.1.2. PCBs and Related Compounds — Although a downward trend of PCB levels has been observed in industrial countries from 1960 to 1990 (Jensen, 1991; Johansen et al., 1994; Mes et al., 1993), exposures directly or indirectly related to combustion sources still occur (Hansen, 1998; Siebert et al., 1991; Stevens, 1991). The levels of PCBs in human milk are still much higher than the total concentrations of PCDDs and PCDFs (Jensen, 1987; Koopman-Esseboom et al., 1994). Ortho-substituted PCBs are found to a greater extent in human milk than coplanar PCBs (Norén et al., 1990; Norén and Lundén 1990; Brevik and Bjerk, 1978; Hansen, 1998). Coplanar PCBs 77, 126 and 169 are found at much lower concentrations, but mono-ortho congeners with TCDD-like activity may contribute TEQs equal to or greater than those from PCDDs and PCDFs (Dewailley et al., 1991; Grandjean et al., 1995a; Johansen et al., 1994; Koopman-Esseboom et al., 1994; Jensen, 1987; Hansen, 1998). Fish intake has long been considered to be the major source of PCBs. Human milk samples in the United States contain high levels of PCBs (Bush et al., 1985; Safe et al., 1985). The average level of total PCBs in human milk fat from industrial countries has been estimated to be between 0.5 and 4 ppm (Jensen, 1987). PCBs have been detected in the sera (Schantz et al., 1994), adipose tissues (Niessen et al., 1992; Teufel et al., 1990) and bone marrow (Scheele et al., 1995) of breast-fed children.

As with the PCDDs and PCDFs, the PCB congeners reported in breast milk are more closely linked to the analytes selected rather than the actual compounds present (Hansen, 1998). Earlier studies did not report the coplanar PCBs because of analytical limitations and low levels; more recent studies focus on coplanar ("non-ortho") and mono-ortho congeners because of their similarity to TCDD. Due to technical difficulties and the lack of many standards, early chromatographic studies may have mis-assigned peaks, which may carry over to more recent documents.

The ortho-substituted nonplanar PCB congeners 138, 153 and 180 have been reported as the most frequent congeners found in human milk, followed by PCBs 70,

99, 118 and 170 (Fürst et al., 1994; Koopman-Esseboom et al., 1994; Schechter et al., 1994). The three most frequently found congeners (138, 153 and 180) were reported at breast milk concentrations of 2.1, 3.2 and 1.2 ng/g, respectively (Bush et al., 1985), with PCB-153 comprising 30% of the total PCBs measured (Abraham et al., 1995). The prevalence of ortho-substituted PCBs is more likely a result of greater amounts of ortho-congeners than coplanar congeners in the environment (Lake et al., 1995; McFarland and Clarke, 1989). Furthermore, congener distribution patterns in contaminated fish and human milk are very similar suggesting that one of the primary sources of human exposure to PCBs is ingestion of contaminated fish (Jensen, 1987).

Identification of many PCB congeners is complicated by co-elution in the fractionation process. As an example, PCB-70 has been reported at concentrations of 1.7 ng/g, but it is equally likely to be PCB-74, which nearly co-elutes with PCB-70 and has been found to be prevalent in human samples. Considering co-elution phenomena, whole milk concentrations and milk:blood ratios for the major PCB congeners (52% of total PCBs, Bush et al., 1985) are probably best represented by Table 9-2.

| PCB Congener | Mean \pm SE (ng/g Whole milk) | Whole Milk:Maternal Blood |
|---------------|---------------------------------|---------------------------|
| 153 | 3.2 \pm 0.4 | 10 |
| 118 (not 179) | 2.5 \pm 0.3 | 9.2 |
| 138 | 2.1 \pm 0.4 | 3.5 |
| 70 or 74 | 1.7 \pm 0.2 | >500 |
| 180 | 1.2 \pm 0.1 | 9.4 |
| 99 | 1.1 \pm 0.1 | 8.9 |
| 156 | 1.0 \pm 0.1 | 125 |
| 105 | 1.0 \pm 0.2 | 3.8 |

The largest milk: blood concentration ratios in Table 9-2 (>100) are probably a result of anomalously low maternal serum levels, so it is reasonable to suggest that whole milk/blood ratios for PCBs will be in the range of 4 to 10. Serum PCB levels, however, are not useful as reliable predictors of breast milk PCB concentrations. Mes et al. (1984) found no statistically significant correlation between total PCB in maternal blood and milk, mainly due to the accumulation of lower chlorinated congeners in milk fat but clearance of these congeners from blood. There was some correlation between PCBs 118, 138, 153 and 180 in maternal plasma and total PCBs in human milk, but the variability in the relationship was too great to be of predictive use (Koopman-Esseboom et al., 1994).

9.2.2. Compounds Partitioning into both Lipid and Aqueous Phases. Human breast milk is generally 2-4% fat and 0.8-1% protein. As most proteins are solubilized in the aqueous phase, compounds binding to proteins will be considered together with water-soluble compounds in the aqueous phase. Although nonpolar compounds partition to some degree into the aqueous compartment, the most commonly analyzed organic contaminants are highly concentrated in the lipid phase; the concentrations of most halogenated aromatics in breast milk are not significantly underestimated by ignoring the aqueous phase. On the other hand, compounds with greater water solubilities and lower K_{ow} may be present at significant levels in the aqueous phase. In practice, these more polar compounds are often extracted by the solvents used to extract the lipids and are discarded if not specifically targeted as analytes (e.g. Hong et al., 1992; Noren et al., 1990, 1996). In some methods, the aqueous fraction is discarded without extraction (Davies and Mes, 1987). Thus, the most common methods for milk analysis tend to underestimate whole milk concentrations of “semi-polar” organics, such as the less chlorinated benzenes and biphenyls (see Table 9-1).

In addition to chloro-naphthalenes and chlorobenzenes, large amounts of chlorofulvenes and chlorofulvalenes are produced by the incomplete incineration of plastic and trichloroethylene containing wastes (Blankenship et al., 1994; Villalobos et al., 1996). These structural isomers of benzene and naphthalene would be expected to

have similar physical and chemical properties. Over 250 compounds were indicated in these extracts with only pentachlorobenzene and HCB being common breast milk analytes. Whether these would be in the aqueous or lipid phase would depend on specific properties and metabolism, but it is unlikely that many would be target analytes.

Some metabolites have been target analytes. Methyl sulfonyl metabolites of chlorinated aromatics are produced through a series of hepatic/gut flora/hepatic reactions and retain many of the lipophilic and enzyme induction properties of the parent compounds. Methyl sulfonyl PCBs were found at 5% total PCBs in the breast milk of an occupationally exposed Japanese mother (Yoshida and Nakamura, 1979). In less contaminated subjects, breast milk methyl sulfones averaged 0.6% total PCB in Canadian women (Newsome and Davies, 1996) and 0.4-0.9% in Swedish women (Noren et al., 1996). In both studies, the 4,4'-DDE-3-methylsulfone was a consistent 0.2% total DDE. The presence of PCBs and DDE in human milk could be factored up by about 1% to account for these metabolites, but this would still be well within the range of analytical and individual uncertainty; therefore, it would make little difference in the risk assessment unless particularly potent metabolites are described.

The more polar hydroxylated metabolites of lower chlorinated PCBs are more potent estrogens than are the parent compounds (reviewed in Hansen, 1998); however, these are generally conjugated or otherwise bound in the mother. The higher chlorinated hydroxy PCBs may be antiestrogens and are more persistent. A highly chlorinated 4-hydroxy PCB metabolite has been identified in milk from Canadian donors at about 2 ppt (pg/g) or 0.02 % of the total PCB (Newsome and Davies, 1996). The hydroxy metabolites would be assumed to be at higher levels (relative to parent) in the aqueous phase of milk, but the small contribution to total intake should have little impact on the infant.

There are very limited data on the relative distribution of more water soluble chemicals between phases in human milk. The presence of dichloro- and trichloro-benzenes (80-400 and 5-64 ppb, respectively) in the lipid fraction (Davies and Mes,

1987) indicates that these less lipophilic chemicals contribute to the total milk burden, but the total contribution cannot be known without a determination of the aqueous phase concentrations.

There is a need for additional data on aqueous phase contaminants of human milk, many of which may have been overlooked because:

- 1) They were not target analytes;
- 2) The aqueous phase may have been discarded; or
- 3) The total milk extract was partitioned to concentrate the more lipophilic contaminants.

The complex nature of emissions from combustion sources makes it desirable to characterize the transfer and milk-phase distribution of model compounds such as benzene, chlorobenzenes, naphthalene, naphthols, methyl benzenes, phenols or cresols to make further modeling possible.

9.2.3. Residues of Inorganic and Organometallic Contaminants in Human Milk.

Residues of various nonnutrient elements including aluminum, arsenic, lead, cadmium, mercury and silicon are common in human milk. Inorganic and organic compounds of metals are found in human breast milk, but are not associated with milk fat (Jensen, 1991). Trace nutrients including copper, fluorine, iodine, iron, manganese, selenium and zinc may be deficient or reach toxic levels in human milk (Casey et al., 1995; Grandjean et al., 1992; Sternowsky and Wessolowski, 1985; Pavlovic and Jokic, 1994). Great care must be taken when analyzing the trace elements; sample contamination is common and the risk assessor must be certain appropriate blanks and quality control procedures were used before applying the data.

Mercury, particularly in its methylated form, is a compound of concern because of its bioaccumulation in fish and potential for developmental toxicity (see U.S. EPA, 1997a for a comprehensive review). Elevated levels of methylmercury have been reported in breast milk for human populations consuming large amounts of pilot whale meat and fish (Grandjean et al., 1995a), or fish alone (Oskarsson et al., 1996). The

hair mercury concentrations in children nursed by mothers whose milk contained methylmercury are also increased (Grandjean et al., 1995a).

Lead is also of concern because of developmental toxicity. The mean lead concentration in milk collected during week 1 to 4 of lactation from 12 women living in urban districts was 49 µg/L (range 25-95 µg/L). Three samples of colostrum contained 136-151 µg/L of lead. One of these three women was subsequently followed. The lead concentration was 137 µg/L in colostrum, and 43, 57 and 47 µg/L in milk samples during week 1, 3 and 4 post partum (Amore et al., 1983). Average levels of lead, cadmium and zinc in milk samples from women living in a very polluted region of Yugoslavia were found to be 43, 11 and 295 µg/L, respectively. Ninety percent of these milk samples were positive for lead, while 60 and 100% of the samples were positive for cadmium and zinc respectively (Pavlovic and Jokic, 1994). Although all human milk contains zinc as a nutrient, this level was nearly 100 times normal values.

Ingestion of certain fish and crustacea which have arsenic, mainly arsenobetaine, can result in the presence of arsenic in human milk (Dang et al., 1983; Grimanis et al., 1979; Byrne et al., 1983). In spite of food chain accumulation of cadmium from combustion and other sources (ATSDR, 1993; Hattemer-Frey and Travis, 1991; Hansen and Schaeffer, 1995), cadmium levels are generally low in breast milk and have been shown to increase the most with maternal cigarette smoking (Casey et al., 1995). Concentrations of lead, cadmium, mercury and arsenic in human milk from Taiwan ranged up to 56, 6, 5 and 3,002 µg/L, respectively (Hwia-Cheng et al., 1993). In human milk, collected 2-6 days post partum, the levels of lead and cadmium respectively were found to range from <4 to 421.5 µg/L and 0.024 to 20 µg/L, with corresponding means of 29.9 and 18.0 µg/L (Riolfatti and Modenese, 1990).

Concentrations of iron, zinc and copper are generally maintained within narrow ranges in human milk, being highest in the colostrum. Minor variations may occur with geographical area and maternal nutritional status. Zinc deficiency is more likely than zinc excess (Casey et al., 1995). Cadmium interacts with the status of these nutrients as well as calcium (see Hansen and Schaeffer, 1995; Kross et al., 1995), and may

influence nutrient levels in milk through maternal exposure. Manganese, like iron, is mostly bound to lactoferrin in human milk, which makes the low levels (relative to manganese in milk of other species) more bioavailable to the human infant (Casey et al., 1995). Selenium, iodine and fluorine concentrations in human milk are more affected by intake than the other trace nutrients, with large geographical variations (Casey et al., 1995).

9.2.4. Factors Influencing Transfer of Contaminants into Human Milk. Lifestyle factors, such as cigarette smoking, may increase contaminant concentrations. For example, increased cadmium (Radisch et al., 1987; Hallen et al., 1995) and PCB (Hong et al., 1994) levels have been found in the breast milk of smokers. Alcohol consumption has also been found to increase the levels of PCBs in human milk (Dewailly et al., 1996; Kreiss et al., 1981; Wolff et al., 1982). Alcohol may increase the absorption through the gastrointestinal tract of the organohalogenes by enhancing their solubility (Dewailly et al., 1996). More likely is the direct effect of ethanol on oxytocin release; this decreases milk production and increases the lipid content which would favor higher concentrations of lipophilic compounds (Neville and Walsh, 1995).

Metal concentrations have been reported to be lower in breast milk than in plasma (Hallen et al., 1995), apparently due to binding of the metals to metallothionein and protein in the mammary gland (Radisch et al., 1987). On the other hand, during pregnancy and lactation, lead in bone is mobilized, increasing plasma lead which may then be available for transport into breast milk.

Maternal age, parity, length of lactation, and body weight influence the concentration of PCB, PBB and PCDD/PCDF in breast milk (Drijver et al., 1988; Pluim et al., 1993; Hong et al., 1994; Beck et al., 1994; Jacobsen et al., 1989; Jensen, 1987; Jensen, 1995; Fürst et al., 1987, 1992). The extent to which these variables influence the transfer of metals to milk is not well-characterized.

9.3. AVERAGE DAILY DOSE OF CONTAMINANT TO THE NURSING INFANT

The average daily dose to the infant ingesting breast milk can be estimated from the levels of contaminant concentrations in the milk, which in turn can be estimated on

the basis of the contaminant intake by the mother. Linear pharmacokinetic models have been developed by Smith (1987), Sullivan et al. (1991) and Travis et al. (1988), and are also presented in *Estimating Exposure to Dioxin-Like Compounds* (U.S. EPA, 1994). These models are theoretical constructs, based on first order kinetics (linear), that were developed for persistent lipophilic organic chemicals, such as chlorinated pesticides, PCBs, and dioxins/dibenzofurans, for which fat serves as a significant reservoir. With slight modifications these approaches can, however, be extended to include nonlipophilic compounds. Equation 9-1 is a modification of the model of Smith (1987) to include a term for nonlipophilic compounds. The average daily dose (intake) for the infant can be estimated as follows:

$$DI_{INF} = \frac{[C_{milkfat} f_{mbm} + C_{aqueous} (1 - f_{mbm})] CR_{milk} f_{ai} ED}{BW_{INF} f_{am} AT} \quad (9-1)$$

where:

- DI_{INF} = average daily contaminant intake for the infant (mg/kg-d)
- $C_{milkfat}$ = concentration of contaminant in maternal milk fat (mg/kg)
- $C_{aqueous}$ = concentration of contaminant in aqueous phase of maternal milk(mg/kg)
- f_{mbm} = fraction of fat in breast milk (dimensionless)
- CR_{milk} = ingestion rate of breast milk (kg/day)
- f_{ai} = fraction of ingested contaminant that is absorbed by the infant (dimensionless)
- ED = exposure duration (yr)
- BW_{INF} = body weight of infant (kg)
- f_{am} = fraction of ingested contaminant that is absorbed by the mother (dimensionless)
- AT = averaging time (yr)

DI_{INF} is an estimate of the ingested intake (external dose) for the infant adjusted for the difference in oral absorption between infants and adults; this allows for incorporation of data on differential absorption when the difference is significant. For most compounds, either $C_{milkfat}$ or $C_{aqueous}$ will be negligible. So, for example, as in the practical application of Equation 9-1, the aqueous pathway can be ignored for highly lipophilic compounds, such as PCDD/PCDFs, and the milk fat pathway can be ignored for water soluble compounds, such as salts of metals or other polar compounds.

9.3.1. Contaminant Concentration in Breast Milk Fat ($C_{milkfat}$): First Order Kinetics

Approach. Two approaches are presented here for determining contaminant concentration in breast milk fat. Both approaches predict levels of contaminants on the basis of the estimated contaminant intake by the mother. One approach uses estimates of the contaminant concentration (or body burden) in the fat compartment of the mother and assumes either steady-state (Smith, 1987) or changing (Sullivan et al., 1991) contaminant concentrations with time. Both variations assume first order kinetics for contaminant elimination from the body. The kinetic models are the preferred methods for determining contaminant concentrations in breast milk. The other approach, by Travis et al. (1988), uses a biotransfer factor (BTF) based on the octanol-water partition coefficient in conjunction with maternal intake to estimate contaminant concentration. The BTF approach requires less data than the kinetic models, but should be considered more of a screening model than a predictive one. The BTF approach is presented in Section 9.3.2.

The approaches utilized in this methodology are linear, in which the predicted contaminant concentrations in breast milk are directly proportional to the inputs, or, in the case where steady state is not assumed, linear in the kinetic parameters. Another approach, multi-compartment physiologically-based pharmacokinetic (PBPK) modeling, explicitly accounts for the distribution and transfer of compounds among many body compartments. The output of PBPK models is dynamic over time and nonlinear by nature. PBPK modeling is designed to be a more realistic representation of the behavior of xenobiotic compounds in living systems, but is usually compound specific.

Text Box 9-2 discusses some of the issues involved in the choice of models for breast milk exposure.

The steady-state model presented by Smith (1987) assumes that the concentration in the maternal fat compartment has reached steady state and that the concentration in breast milk fat is the same as in maternal body fat. The contaminant concentration in breast milk fat can then be estimated as:

$$C_{milkfat} = \frac{DAI_{MAT} f_f}{k_{elim} f_{fm}}$$

(9-2)

Text Box 9-2

Choice of Model: Linear vs. PBPK

There are a number of true physiologically based pharmacokinetic (PBPK) models in the open peer-reviewed literature for describing the whole process of exposure and disposition (absorption, distribution, metabolism and excretion), as well as lactational transfer of both lipophilic and nonlipophilic compounds. These models can handle both maternal and infant's pharmacokinetics (Shelley et al., 1988), multiple routes of administration and different exposure scenarios, and can accommodate changes in physiology and metabolism over time (Andersen and Greenlee, 1991). PBPK models are non-linear and have a power of predicting (and extrapolating) chemical disposition beyond the experimental range, in contrast to the classical one- or two-compartment linear models (Medinsky and Klaassen, 1997). PBPK models were developed, for example, for several dioxin and PCB derivatives (Andersen et al., 1993; Kedderis et al., 1993; Leung et al., 1990a,b; Santostefano et al., 1998). These models, however, are not directly applicable to estimating infant exposure through consumption of breast milk from mothers indirectly exposed to combustion emissions. Either the models lack a breast milk compartment or they are designed specifically for inhalation exposure. Also, these models require data for a large number of parameters, much of which is unavailable. The adequacy of linear algebraic models for predicting human breast milk concentrations of highly lipophilic compounds is unknown. Although, in laboratory animal studies, the pharmacokinetics of TCDD and related compounds is highly non-linear and dose-dependent (at acutely toxic doses), linear behavior was observed at lower, environmentally relevant doses (Roth et al., 1994). A better approximation with linear models may be obtained, however, for pharmacokinetics of nonlipophilic compounds, although bone-seeking compounds may be an exception. The kinetics of compartmentalization of lead in bone is complex and nonlinear and may not be well-represented by 1st order kinetics (Dalley et al., 1990; O'Flaherty, 1991).

On the linear side, a two-compartment model for lipophilic compounds has also been published (Hoover et al., 1991). While a multi-compartment model would be somewhat more physiologically realistic than the one-compartment model used for the MPE breast milk model (Equations 2, 3 and 4), the model parameters in Hoover et al. (1991) are essentially identical to those in Equation 2. It is unlikely that predictions from the two models would differ significantly.

where:

C_{milkfat} = concentration in maternal milk fat (mg/kg [ppm] of milk fat)

DAI_{MAT} = daily maternal absorbed intake of contaminant (mg/kg of body weight/day)

f_f = fraction of contaminant that is stored in maternal fat (dimensionless)

k_{elim} = biological elimination constant for contaminant in adult women (days⁻¹)

f_{fm} = fraction of mother's weight that is fat (kg maternal fat/kg total body weight)

The assumption that contaminant concentration in milk fat will be the same as in general body fat appears reasonable for highly lipophilic compounds (e.g., PCDDs, PCDFs, PCBs, HCBs). Beck et al. (1994) showed similar breast milk and adipose tissue concentrations for PCDDs/PCDFs. Ignoring the time required to reach near-steady-state concentrations, however, results in an overprediction of $C_{milkfat}$. Overpredictions of 10-fold, or greater, can occur when the half-life is large and the exposure duration is small (see Section 9.3.). Equation 9-2 is a reasonable simplification for scenarios in which the biological half-life of the compound is fairly small relative to the duration of exposure. Otherwise, the time required for the fat concentration to reach a relatively constant level should be considered, as in Equation 9-3.

$$C_{milkfat} = \frac{DAI_{MAT} f_f}{k_{elim} f_{fm}} (1 - e^{-k_{elim} t_{pn}}) \quad (9-3)$$

where:

$C_{milkfat}$ = concentration in maternal milk fat (mg/kg [ppm] of milk fat)

DAI_{MAT} = daily maternal absorbed intake of contaminant (mg/kg of body weight/day)

f_f = fraction of contaminant that is stored in maternal fat (dimensionless)

k_{elim} = biological elimination constant for contaminant in adult women (day^{-1})

f_{fm} = fraction of mother's weight that is fat (kg maternal fat/kg total body weight)

t_{pn} = duration of mother's exposure prior to nursing (days)

In both equations, maternal body burden of the chemical is estimated assuming a constant intake and first-order elimination. The kinetic term $(1 - e^{-k_{elim} t_{pn}})$ in Equation 9-3 accounts for the time required to reach a (pseudo) steady-state fat concentration.

Over predictions of breast milk concentrations will also result if maternal contaminant losses from breast feeding are not considered. As an example, PCDDs and PCDFs tend to be excreted in breast milk at the highest levels within the first few weeks after delivery; after 1 year of breast feeding, milk concentrations appear to approach steady state and are about 30-50% of the initial levels (Fürst et al., 1989). The over prediction of milk concentration from ignoring breast-feeding losses, in contrast to the steady-state over prediction, is greater for longer maternal exposure durations (and for longer nursing periods), but of lower magnitude (10-90% over prediction; see Section 9.3.). Both Smith (1987) and Sullivan et al. (1991) present models that incorporate breast feeding losses. The Smith (1987) model retains the steady-state assumption for pre-nursing exposures, which will still overestimate breast milk concentrations. The Sullivan et al. (1991) model includes a term for initial concentration of contaminant in infant fat, which complicates estimation of infant dose from breast feeding alone. Equation 9-4 is a modification of the Smith (1987) model that includes pre-nursing kinetics and gives the average contaminant concentration in breast milk over the entire period of breast feeding. This model is also essentially the same as Sullivan et al. (1991) without the initial infant body burden term. A detailed derivation of Equation 9-4 is presented in Appendix C.

$$C_{milkfat} = \frac{DAI_{MAT} f_f}{k_{elim} f_{fm}} \left[\frac{k_{elim}}{k_{elac}} + \frac{1}{k_{elac} t_{bf}} (1 - e^{-k_{elim} t_{pn}} - \frac{k_{elim}}{k_{elac}}) (1 - \right. \\ \left. (9-4)$$

where:

$C_{milkfat}$ = average concentration of contaminant in maternal milk fat over duration of breast feeding (mg/kg [ppm] of milk fat)

- DAI_{MAT} = daily maternal absorbed intake of contaminant (mg/kg of body weight/day)
- f_f = fraction of contaminant that is stored in maternal fat (dimensionless)
- f_{fm} = fraction of mother's weight that is fat (kg maternal fat/kg total body weight)
- k_{elim} = biological elimination constant for contaminant in adult women (days^{-1})
- k_{elac} = biological elimination constant for contaminant in lactating women (days^{-1})
- t_{pn} = duration of mother's exposure prior to nursing (days)
- t_{bf} = duration of breast feeding (days)

Each of these inputs is described in more detail in Sections 9.3.1.1-9.3.1.7. Note that Equation 9-4 relates the average whole-body concentration over the breast-feeding period to the maximum theoretical steady-state concentration predicted by Equation 9-2 by a fraction that is dependent on the two rate constants, duration of exposure, and duration of breast feeding. Although not immediately evident by inspection, this fraction is always less than one.

9.3.1.1. Biological Elimination Constant for Contaminant in Nonlactating Women (k_{elim}) — The biological elimination constant is a first-order rate constant for elimination of the contaminant from the body and is related to the half-life (in days) of any given substance in the human body by the formula given in Equation 9-5.

$$k_{elim} = \frac{\ln 2}{t_{\frac{1}{2} b}} \quad (9-5)$$

where:

- $t_{\frac{1}{2} b}$ = biological half-life of contaminant in lactating women (days)
- $\ln 2$ = natural logarithm of 2 (0.693)

The half-life in the human body is chemical specific and is empirically derived. Lipophilic chemicals partition into body fat compartments and, in general, tend to have relatively long half-lives (i.e., slow rate of elimination). These chemicals accumulate with age, and the chemical concentration in fat increases over time. Lipophilic chemicals with half-lives of several years (e.g., PCBs, dioxins, chlorinated pesticides) may take more than 20 years to reach steady state. Thus, the half-life is an important consideration in estimating chemical concentration in maternal fat. For dioxins, the half-life is 7-10 years (U.S. EPA, 1994). The mean elimination half-lives of PCBs in humans for several congeners ranged from 6.7 to 9.8 months (ATSDR, 1992). The median half-lives for Arochlor 1242 and Arochlor 1254 were 2.6 and 4.8 years, respectively, in workers occupationally exposed to PCBs during the manufacture of electric equipment (Phillips et al., 1989). Another study on PCB elimination in humans exposed to PCBs in contaminated cooking oil showed elimination half-lives in the range of 4.1 to 6.1 years in the case of Yucheng patients, and 13.7 to 34.2 years for Yusho patients (Masuda et al., 1995). The great variability in PCB half-lives most likely reflects the variability in the half-lives of specific congeners. The measured half-lives for mixtures of congeners will depend on the relative proportions of the congeners in the mixture and on when the measurements were taken. Early measurements will tend to yield shorter half-lives, reflecting the more rapidly eliminated congeners, than later measurements when the slowly-eliminated congeners dominate the mixture. Furthermore, although the half-life of such a mixture will appear to stable when exposure is constant, congeners with longer half-lives will accumulate to a greater degree over time. In this case, the relative toxicities of the congeners must be known to interpret the output of the model. Therefore, assigning a specific half life to mixtures, such as dioxins or PCBs, is meaningless unless all the congeners are known to have similar half-lives. Risk assessors should consult the open literature for the half-lives of chemicals of importance at their site.

9.3.1.2. Biological Elimination Constant for Contaminant in Lactating

Women (k_{elac}) — This elimination constant is the sum of k_{elim} and the daily fraction of

contaminant loss from breast feeding. Equation 9-6 gives the formula for k_{elac} and is from Smith (1987).

$$k_{elac} = k_{elim} + \frac{CR_{milk} f_f f_{mbm}}{f_{fm} BW_{MAT}} \quad (9-6)$$

where:

- k_{elac} = biological elimination constant for contaminant in lactating women (days⁻¹)
- k_{elim} = biological elimination constant for contaminant in adult women (days⁻¹)
- CR_{milk} = ingestion rate of breast milk (kg/day)
- f_f = fraction of contaminant that is stored in maternal fat (dimensionless)
- f_{mbm} = fraction of fat in breast milk (dimensionless)
- f_{fm} = fraction of mother's weight that is fat (kg maternal fat/kg total body weight)
- BW_{MAT} = maternal body weight (kg)

The second term in Equation 9-6 is, essentially, a first-order elimination constant for breast-feeding losses, while k_{elim} represents losses by all other pathways. For highly lipophilic compounds, breast feeding losses can be larger than those by all other pathways. As an example, the breast-feeding loss term in Equation 9-6 is 16 times larger than K_{elim} for dioxin when all the defaults are used and an f_f of 0.9 is assumed for dioxin. Therefore, for highly lipophilic compounds with a long biological half life, assuming that a linear model (first order kinetics) is appropriate, breast milk will constitute the primary route of elimination. Model uncertainty is discussed in Section 9.3.

9.3.1.3. Average Daily Maternal Absorbed Intake of Contaminant (DAI_{MAT}) —

The absorbed maternal intake of the contaminant (mg/kg-day) represents internal intake from all pathways of exposure. Methodology limitations currently exclude

estimation of internal intake from inhalation exposure (see Chapter 10). If dermal exposure is significant, the dermally-absorbed intake (see Chapters 4 and 7) can be added to the orally-absorbed maternal intake (Eq. 9-7), or an equivalent oral intake from dermal exposure can be estimated using the algorithm presented in Chapter 10 of this document and summed with oral intake to derive an aggregate oral intake. The orally-absorbed maternal intake is estimated by multiplying the oral intake (or aggregate oral intake) by the fraction of contaminant absorbed from the gut, as in Equation 9-7.

$$DAI_{MAT} = DI_{MAT} f_{am} \quad (9-7)$$

where:

- DAI_{MAT} = daily maternal absorbed intake of contaminant (mg/kg of body weight/day)
- DI_{MAT} = average daily intake of contaminant ingested by the mother (mg/kg-day)
- f_{am} = fraction of ingested contaminant that is absorbed by the mother (dimensionless)

Values for f_{am} can be found in the open literature. The default value for f_{am} is 1, which represents a conservative assumption.

9.3.1.4. Fraction of Contaminant Stored in Maternal Fat (f_f) — This parameter represents the proportion of the contaminant that is stored in the fat of the mother. The amount of the chemical that partitions into the fat compartment is generally empirically derived from studies of absorption and distribution. For most lipophilic organics, absorption is high and most of the absorbed contaminant is stored in deep compartments, such as the adipose tissue. For these compounds, the fraction of ingested contaminant stored in fat may be >90% (ATSDR, 1992; Sullivan et al., 1991; U.S. EPA, 1994). Information for this parameter can be located in the open literature.

9.3.1.5. Fraction of Mother's Weight That Is Fat (f_{fm}) — The fraction of the mother's weight that is fat is important for estimating the concentration of lipophilic compounds in breast milk. Slim women will generally have smaller fat deposits, suggesting a lower dilution of contaminants (greater concentrations) in fat stores. Changes in the mother's weight, before and during lactation, may influence the concentration of chemicals in fat, in some cases leading to mobilization of chemicals from fat stores (Jensen, 1983; Sim and McNeil, 1992). Both the Smith (1987) and Sullivan et al. (1991) models assume that the fraction of maternal body fat remains constant at approximately 30%.

9.3.1.6. Duration of Mother's Exposure Prior to Nursing (t_{pn}) and Duration of Breast Feeding (t_{bf}) — Maternal exposure duration is partitioned into pre-nursing and nursing phases for the kinetic model that includes breast-feeding contaminant losses (Eq. 9-4). The default for t_{pn} is the exposure duration for the scenario (ED) minus the duration of breast feeding (t_{bf}). This is a conservative default, which assumes that the nursing period occurs at the end of the scenario duration when breast milk concentrations will be highest. The default for t_{bf} is 365 days, which is also somewhat conservative for the U.S. population (NAS, 1991). If a central-tendency estimate is desired, t_{bf} can be set to 180 days. A site-specific duration should be used if local breast feeding practices are known.

9.3.1.7. Maternal Body Weight (BW_{MAT}) — Maternal body weight is the average body weight for the entire duration of exposure. This model does not take into account the changes in body weight during pregnancy and nursing. The default for BW_{MAT} is 60 kg (U.S. EPA, 1997b).

9.3.1.8. Model Performance — Available data are insufficient for adequate assessment of model performance. The dioxin data, however, provide a rough comparison of relative model performance for background conditions. As described previously in this chapter (Section 9.1.1.11997.), dioxin TEQs of 20-27 ppt have been found in human milk fat in highly industrialized countries. The steady-state model (Eq. 9-2) predicts the background dioxin concentrations found in breast milk fat to be 13-38

ppt TEQ, assuming an 8-year half-life, values of 0.9 for f_f and 0.3 for f_{fm} , respectively, and background exposure levels of 1-3 pg TEQ/kg-day for maternal intake (U.S. EPA, 1994) With the same inputs and assuming a 30-year maternal exposure and 6-month nursing period, the kinetic model predicts 12-35 ppt and 8.5-26 ppt with (Eq. 9-4) and without (Eq. 9-3) breast-feeding losses, respectively. All the models generate predictions in the same range as the data, with the kinetic breast-feeding-loss model (Eq. 9-4) at the lower end of the range. The model inputs are too uncertain to distinguish among the model results. The assessor should note, however, that the kinetic breast-feeding-loss model (Eq. 9-4) will predict lower milk fat concentrations with longer breast-feeding durations.

9.3.2. Contaminant Concentration in Breast Milk Fat ($C_{milkfat}$): Biotransfer Factor

Approach. Travis et al. (1988) presented an alternative approach to estimating breast milk contaminant levels using a biotransfer factor. This model assumes an equilibrium tissue concentration of the pollutant, which is proportional to the average daily intake of the substance. The formula for estimating milk fat concentrations of lipophilic compounds is given in Equation 9-8.

$$C_{milkfat} = TDI_{MAT} BTF_m \quad (9-8)$$

where:

- $C_{milkfat}$ = contaminant concentration in breast milk fat (mg/kg)
- TDI_{MAT} = total daily maternal intake of contaminant (mg/day)
- BTF_m = biotransfer factor for breast milk fat (kg milk fat/day)⁻¹

Maternal intake is expressed as total intake per day (independent of body weight).

The biotransfer factor is primarily a function of the octanol-water partition coefficient (K_{ow}) and was developed by Travis et al. (1988) from the following mean regression:

$$BTF_m = 0.00062 K_{ow} \quad (9-9)$$

where:

- BTF_m = biotransfer factor for breast milk fat (kg/day)⁻¹
- 0.00062 = empirical constant (kg/day)⁻¹
- K_{ow} = octanol-water partition coefficient (unitless)

The regression constant was estimated from data on six lipophilic compounds, including PCBs and several organochlorine pesticides (log K_{ow} ² range: 5.16 to 6.5), but did not include any dioxins or furans. Hawker and Connell (1988) report log K_{ow} values of 13 PCB congeners (5.37-7.67) and calculated log K_{ow} for all the remaining PCB congeners; PCB lipophilicity generally increases with the degree of chlorination. Log K_{ow} values for PCDD, PCDF and PCBs can be found in U.S. EPA (1994).

The BTF approach does not appear to work well for dioxin. Assuming a log K_{ow} of 6.6 for 2,3,7,8-TCDD, a BTF_m of 2468 kg/day is predicted. Multiplying this value by an estimated background maternal intake of 10 pg/day (or 1×10^{-8} mg/day) yields (from Eq. 9-5) a breast milk-fat TCDD concentration of about 2.5×10^{-5} mg/kg (25 ppt). This prediction is about 10 times higher than what has been measured in the United States (Jensen, 1987). Thus, this approach may not be as appropriate for PCDDs and PCDFs as the first order kinetics models. The recommended approaches for any lipophilic compound are those based on first order kinetics. Do not use the BTF approach for any compound if k_{elim} and f_f can be found or estimated for use in the equations

²Octanol-water partition coefficient values are generally expressed as the logarithm to the base 10 of the K_{ow} .

presented in Section 9.2.1. Otherwise, use the BTF approach only for compounds in the log K_{ow} range in which it was calibrated (5.2 to 6.5). The BTF approach may be useful for PCB congeners for which elimination constants are not available. Also, as the BTF approach assumes steady-state, it will tend to overestimate breast milk concentrations for shorter exposure durations and should be used only for long-term maternal exposures (> 20 years). Given the potential for overestimation of pollutant concentrations in breast milk, the BTF should be considered as a screening model.

9.3.3. Fraction of Fat in Breast Milk (f_{mbm}). The fat content in breast milk varies throughout the lactation period, with circadian rhythms, during a feeding, and with parity (reviewed in Sim and McNeil, 1992). Daly et al. (1993) suggest that individual feeding patterns (i.e, length of time between feedings) and the degree of breast emptying contribute to the variance of breast milk fat content within women. To normalize for these variations, the concentration of contaminants that partition primarily to the lipid fraction of the breast milk (e.g., PCDDs, PCDFs, PCBs), should be expressed on a milk fat basis (i.e., g/g milk fat).

Jensen (1987) tabulated the average fat content from approximately 47 studies in 19 countries conducted during 1971-1986 and reported average fat content of breast milk to be 1.1-5.0%. More recently, the fraction of lipid in breast milk has been found generally to vary between 2 and 4% (Schechter et al., 1994; Hong et al., 1994; McLachlan, 1993; Bates et al., 1994; NAS, 1991; Butte et al. 1984; Maxwell and Burmaster, 1993; U.S. EPA, 1997b). In development of their models to estimate contaminant concentration in breast milk, Smith (1987) assumed 4% and Sullivan et al. (1991) assumed 3% lipid content. The U.S. EPA (1997b) recommends using approximately 4% as the percentage of fat in breast milk.

9.3.4. Contaminant Concentration in the Aqueous Phase of Breast Milk ($C_{aqueous}$).

To assess the aqueous-phase contaminant contribution to the overall intake from breast milk, Equation 9-2 was adapted for estimating the concentration of contaminants circulating in the aqueous phase of breast milk (Eq. 9-10). Aqueous phase contaminants would include chemicals with appreciable water solubility, such as salts

of metals³, and protein-bound chemicals, such as methylmercury. The concentration of contaminant in the aqueous phase of breast milk is assumed to be proportional to the contaminant concentration in the blood plasma. The contaminant taken up by erythrocytes is assumed to be unavailable for direct transfer to breast milk.

$$C_{\text{aqueous}} = \frac{DAI_{\text{MAT}} f_{\text{pl}} PC_{\text{bm}}}{k_{\text{elim}} f_{\text{pm}}} \quad (9-10)$$

where:

- C_{aqueous} = concentration of contaminant in aqueous phase of breast milk (mg/kg [ppm])
- DAI_{MAT} = daily maternal intake of contaminant (mg/kg of body weight per day [mg/kg-day])
- k_{elim} = biological elimination constant for contaminant in lactating women (days⁻¹)
- f_{pl} = fraction of contaminant (based on total absorbed intake) that is in the blood plasma compartment (dimensionless)
- PC_{bm} = partition coefficient for contaminant concentration between plasma and breast milk aqueous phase (dimensionless)
- f_{pm} = fraction of mother's weight that is plasma (kg maternal plasma/kg total body weight)

DAI_{MAT} and k_{elim} are the same as in Equation 9-2. The applicability of Equation 9-10 is dependent on establishing the value of f_{pl} , for which there is no appropriate general default value. Therefore, if data from the general literature for establishing f_{pl} are not adequate, C_{aqueous} cannot be estimated. The extent to which these data are available in the open literature is unknown.

³ Because of the complexity of the kinetics of bone-seeking compounds, a linear model may be inadequate for predicting breast milk concentrations of lead and cadmium.

9.3.4.1. Fraction of Contaminant That Is in the Blood Plasma Compartment

(f_{pl}) — This parameter represents the steady-state fraction of the total intake of contaminant that is circulating in the plasma. The amount of contaminant that partitions into the blood plasma compartment is generally empirically derived from chemical-specific studies of absorption and distribution. There are no reliable independent predictors of f_{pl} . Information for this parameter must be located in the open literature in order for the model to be used. Concentrations, however, are often given for the whole blood compartment only (plasma plus red blood cells [RBCs]), and concentrations between plasma and RBCs may differ. In such cases, the fraction of contaminant in the plasma subcompartment can be estimated by Equation 9-11, which is simply the weighted fraction of contaminant in the plasma dependent upon the RBC:plasma concentration ratio for that contaminant.

$$f_{pl} = \frac{f_{bl} f_{bp}}{f_{bp} + PC_{RBC} (1 - f_{bp})} \quad (9-11)$$

where:

- f_{pl} = fraction of contaminant (based on total absorbed intake) that is in the blood plasma compartment (dimensionless)
- f_{bl} = fraction of contaminant (based on total absorbed intake) in whole blood compartment (dimensionless)
- f_{bp} = fraction of whole blood that is plasma (kg plasma/kg blood)
- PC_{RBC} = partition coefficient for contaminant concentration between red blood cells and plasma (dimensionless)

Values for f_{bl} must be found in the open literature; there is no appropriate default. Plasma and blood volumes can be used to calculate a default value f_{bp} , which should be generally adequate. Plasma volume is approximately 60% of total blood volume in normal human females (Steinbeck, 1953) and about 63% to 70% in postpartum women (Harrison, 1967; Ueland, 1976); the default value for f_{bp} is 0.65. Specific values for

$P_{C_{RBC}}$ must be found in the open literature. Assuming equal distribution of the contaminant in plasma and RBCs, the default value for $P_{C_{RBC}}$ is 1; this is likely to be the case for most contaminants.

9.3.4.2. Concentration Proportionality Constant Between Plasma and Breast Milk Aqueous Phase ($P_{C_{bm}}$) — This parameter relates the concentration of contaminant in the aqueous phase of breast milk to the concentration of the contaminant in plasma, with the assumption that the concentrations are directly proportional. Specific information for this parameter must be located in the open literature. The default value for $P_{C_{bm}}$ is 1, which should be a reasonable assumption in most cases.

9.3.4.3. Fraction of Mother's Weight that is Blood Plasma (f_{pm}) — Plasma volumes for adult women have been estimated in the range of 37 to 60 mL/kg body weight, averaging about 45 mL/kg (summarized in Altmann and Dittmer, 1964). The average plasma volume of 28 postpartum (6 weeks) women was 45 mL/kg (Ueland, 1976). Given the specific gravity of plasma of 1.026 (Conley, 1974), the default value for f_{pm} is 0.046.

9.3.5. Fraction of Ingested Contaminant that is Absorbed by the Infant (f_{ai}). This parameter represents the absorption of the contaminant in the breast milk by the infant. It is reasonable to assume that the absorption fraction of most ingested lipophilic organic compounds will be high. Smith (1987) assumed 90% absorption of ingested PCDD. Dahl et al. (1995) reported oral absorption of PCBs, PCDDs and PCDFs in breast milk to be >95% for most congeners in infants 1-6 months of age. McLachlan (1993) measured gastrointestinal absorption of PCDDs, PCDFs and PCBs by contaminant mass balance in a nursing infant over the course of 12 days. Absorption was $\geq 96\%$ for the 4 penta- and hexa-PCB congeners and $\geq 90\%$ for the 12 PCDD/PCDF congeners, although absorption appeared to be more variable for the hexa- and higher chlorinated PCDD/PCDF congeners, perhaps because of contamination of diaper blanks. Absorption estimates for chemicals are empirically derived and may be available in the open literature. Empirical absorption estimates should be adjusted for

vehicle-specific differential absorption if data suggest that this may be the case (for experimental vehicles other than milk). In the absence of specific data for estimating f_{ai} , f_{am} can be used as a surrogate. The default value for f_{ai} is 1, which represents a conservative assumption. This default may not be appropriate for salts of metals and other highly polar compounds, as the absorption fraction for these compounds could be very low (ca. <10% in adults).

9.3.6. Ingestion Rate of Breast Milk (IR_{milk}). The daily amount of breast milk consumed by an infant (i.e., the ingestion rate of breast milk, kg/day) varies with numerous factors, predominantly with infant weight and nursing frequency, being higher for larger infants and those that nurse more frequently. NAS (1991) estimated average intake rates of 718-777 mL/day for infants up to 5 months of age. Whitehead and Paul (1981) in a study of 48 British infants aged 1-8 months found that the breast milk ingestion rate ranged from 677 to 922 mL/day; Smith (1987) used 0.8 kg/day in application of the model. Prentice et al. (1994) compiled milk volume measurements from 41 studies published during 1980-1992 from numerous countries for use in a meta-analysis of body mass and lactation performance. Average breast milk volume ranged from 307 to 961 g/day for infants from 1 to 6 months of age, with most studies showing averages of 600-900 g/day. Using 1.03 g/mL as the density of human milk, conversions can be made between the weight and volume of breast milk consumed. U.S. EPA (1997b) recommends using an average breast milk intake for infants 1 to 6 months of 730 mL/day, with an upper percentile intake of 1,029 mL/day. Breast milk intake remains relatively constant until approximately 6-9 months of age, after which it decreases (apparently due to dietary supplementation) (Whitehead and Paul, 1981; U.S. EPA, 1997b). Therefore, U.S. EPA (1997b) recommends using 678 mL/day (12-month time-weighted average) as the mean intake for infants up to 1 year with 1,022 mL/day as the upper percentile rate. The default value for a 6-month breast feeding period is 730 mL/day (1,029 mL/day as the upper percentile rate), which is the 6-month time-weighted average as recommended by the U.S. EPA (1997b).

9.3.7. Body weight of infant (BW_{INF}). The default for BW_{INF} is 8 kg, which is the average for 6-month-old infants (National Center for Health Statistics, 1987; U.S. EPA, 1997b). If a breast feeding duration longer than 6 months is used, the assessor should use the appropriate value from Table 9-3 or consult U.S. EPA (1997b).

9.3.8. Exposure Duration (ED). This approach assumes that the contaminant concentration in milk represents the average over the breast feeding time period (i.e., exposure duration, years). Demographic factors such as maternal marital status, age, education, employment, income, ethnic background and region of the country influence

| TABLE 9-3 Body Weights of Children ^{a,b} | | | |
|--|-----------------------|-------|------------|
| Age | Mean Body Weight (Kg) | | |
| | Boys | Girls | Both Sexes |
| 6-11 months | 9.4 | 8.8 | 9.1 |
| 1 year | 11.8 | 10.8 | 11.3 |
| 2 years | 13.6 | 13.0 | 13.3 |

^a Source: U.S. EPA (1997b)

^b Includes clothing weight

breast feeding practices within the United States (U.S. EPA, 1997b). NAS (1991) reported that, in 1989, breast feeding was initiated in approximately 50% of newborn infants, but was continued until 5-6 months of age in only 20% of the infants. Maxwell and Burmaster (1993) reported that approximately 22% of infants under 1 year are breast fed. In a study of 48 British infants that examined nutritional requirements for growth, Whitehead and Paul (1981) showed that by 4-6 months of age most breast fed

infants transition from being fully breast fed to being partly breast fed because of dietary supplementation in order to maintain a positive growth rate. The National Academy of Sciences report that only 37% of mothers who breast feed are still breast feeding by 5-6 months (NAS, 1991). The risk assessor should consult U.S. EPA (1997b) for further information. Local breast-feeding practices should be considered if adequate data exist. The default value for a central estimate of ED is 6 months. An upper percentile estimate of ED is 1 year.

9.3.9. Averaging Time (AT). Averaging time (years) is the timeframe or portion of the lifetime over which the daily intake is to be averaged. To determine the average dose to the infant, AT should equal ED (Eq. 9-1). If, however, the contribution to total lifetime exposure is desired, such as for estimation of lifetime cancer risk, 70 years is used as the averaging time (U.S. EPA, 1997b).

9.4. UNCERTAINTY IN THE BREAST MILK PATHWAY EXPOSURE TO THE INFANT

Linear 1st order kinetics may yield better predictions for aqueous-phase compounds than for lipophilic compounds, as toxicokinetic processes are generally less complex. Bone-seeking compounds, however, may be an exception. The kinetics of compartmentalization of lead in bone is complex and nonlinear and may not be well-represented by 1st order kinetics (Dalley et al., 1990; O'Flaherty, 1991). An assessment of the potential magnitude or direction of the error has not yet been performed. A better approach for lead would be to add a breast milk compartment to the PBPK model of O'Flaherty (1991); this remains as a research need.

The preferred approach for estimating breast milk concentrations of lipophilic chemicals is the dynamic model presented in Equation 9-4. The BTF approach may be a useful alternative in certain circumstances when elimination constants are not available. However, as the BTF approach can not account for kinetics and will tend to overestimate breast milk pollutant concentrations, it should be considered as a screening model.

Bias in the simplified kinetic models for highly lipophilic compounds when time to steady state and breast-feeding losses are ignored has already been mentioned (Section 9.2.1.). Table 9-4 illustrates the potential over prediction of C_{milkfat} for several different exposure scenarios. Table 9-4 gives the ratio of the steady-state concentration (Eq. 9-2) to the kinetic model prediction (Eq. 9-3) for several different combinations of exposure duration and contaminant half-life. Significant over predictions are evident for the steady-state assumption when the half-life is large and the exposure duration is small.

Table 9-5 gives the ratio of the kinetic model concentration predictions (Eq. 9-3) to the kinetic model prediction that includes breast-feeding losses (Eq. 9-4) for several different combinations of exposure duration, contaminant half-life, and nursing periods.

| TABLE 9-4 | | | | | | |
|--|--|------|------|------|------|------|
| Relative Predicted Contaminant Concentration in Breast Milk for Steady-State Model versus Kinetic Model ^a | | | | | | |
| Biological Half-Life ^b (years) | Total Exposure Duration ^c (ED in years) | | | | | |
| | 30 | 20 | 10 | 5 | 1 | 0.5 |
| 0.5 | 1.00 | 1.00 | 1.00 | 1.00 | 1.33 | 2.00 |
| 1 | 1.00 | 1.00 | 1.03 | 1.00 | 2.00 | 3.41 |
| 4 | 1.01 | 1.03 | 1.22 | 1.73 | 6.29 | 12 |
| 8 | 1.08 | 1.22 | 1.73 | 2.84 | 12 | 23.6 |
| 16 | 1.38 | 1.73 | 2.84 | 5.14 | 23.6 | 46.7 |

^a C_{milkfat} (steady-state, Eq. 9-2) / C_{milkfat} (kinetic, Eq. 9-3); hDI_{MAT} , f_r , and f_m held constant

^b $0.693/K_{\text{elim}}$

^c $t_{\text{pn}} + t_{\text{bf}}$; $t_{\text{bf}} = 0.5$ yrs

TABLE 9-5
Relative Predicted Average Contaminant Concentration in Breast Milk for Kinetic Model, alone,
versus Kinetic Model with Losses from Breast Feeding^a

| Biological Half-Life ^b (years) | t _{br} (years) | Total Exposure Duration ^c (ED in years) | | | | |
|---|-------------------------|--|------|------|------|------|
| | | 30 | 10 | 5 | 1 | 0.5 |
| 0.5 | 0.5 | 1.11 | 1.11 | 1.11 | 1.29 | 1.94 |
| | 1.0 | 1.18 | 1.18 | 1.18 | 1.87 | - |
| 1 | 0.5 | 1.12 | 1.12 | 1.13 | 1.38 | 2.05 |
| | 1.0 | 1.23 | 1.23 | 1.24 | 2.09 | - |
| 4 | 0.5 | 1.14 | 1.15 | 1.17 | 1.47 | 2.15 |
| | 1.0 | 1.27 | 1.30 | 1.35 | 2.29 | - |
| 8 | 0.5 | 1.14 | 1.16 | 1.18 | 1.48 | 2.17 |
| | 1.0 | 1.29 | 1.32 | 1.39 | 2.33 | - |
| 16 | 0.5 | 1.14 | 1.16 | 1.19 | 1.49 | 2.17 |
| | 1.0 | 1.30 | 1.34 | 1.40 | 2.35 | - |

^a C_{milkfat} (Eq. 9-3) / C_{milkfat} (Eq. 9-4); hDI_{MAT} , f_f , and f_m held constant

^b $0.693/K_{\text{elim}}$

^c $t_{\text{pn}} + t_{\text{br}}$

The consequences of ignoring breast-feeding losses are not as severe as those resulting from the steady-state assumption, but can still be significant.

The combined effect of assuming steady-state and ignoring breast feeding losses is illustrated in Table 9-6, in which the output of Equation 9-2 (steady state assumption) is compared to the output of Equation 9-4 (t_{pn} and t_{bf} considered). The overestimation of $C_{milkfat}$ exceeds 30% for all scenarios and is particularly large for longer durations and half-lives. As an example, for a dioxin (half-life = 8 years) exposure scenario that begins at the start of breast feeding, $C_{milkfat}$ could be overestimated by a factor of 16 or greater by ignoring the kinetic elements.

Given the well-documented benefits of breast feeding, any estimation of risk to the infant from contaminants in maternal milk needs to be free of bias. If a linear model adequately describes the kinetic behavior of the substance in the body, both time to steady state and breast feeding losses should be considered, given the overestimation of infant dose otherwise. The simple linear models presented here, however, are unlikely to be accurate across a wide range of chemical properties and physiological processes. Model uncertainty may be substantial. The adequacy of linear algebraic models for predicting human breast milk concentrations of highly lipophilic compounds is unknown. Although, in laboratory animal studies, the pharmacokinetics of TCDD and related compounds appears to be highly non-linear and dose-dependent, linear behavior was observed at lower doses and some of the nonlinear behavior may have been a result of the acutely toxic effects (wasting syndrome) at the higher doses (Roth et al., 1994). Whether or not the linear models are biased in any given direction remains as a topic for further research.

An implicit assumption in the breast milk model is that body weight and fat content remain constant over the period of breast feeding. Postpartum, lactating mothers are unlikely to have constant body weight or constant body fat. Many consciously attempt to lose both fat and weight and some gain weight and fat. Differences in diet and in activity, compared to the pre-partum period, may significantly

| TABLE 9-6 Combined Relative Predicted Average Contaminant Concentration in Breast Milk for Steady-State Model versus Kinetic Model with Losses from Breast Feeding ^a | | | | | | |
|--|-------------------------|--|------|------|------|------|
| Biological Half-Life ^b (years) | t _{bf} (years) | Total Exposure Duration ^c (ED in years) | | | | |
| | | 30 | 10 | 5 | 1 | 0.5 |
| 0.5 | 0.5 | 1.11 | 1.11 | 1.11 | 1.73 | 3.88 |
| | 1.0 | 1.18 | 1.18 | 1.19 | 2.49 | - |
| 1 | 0.5 | 1.12 | 1.13 | 1.17 | 2.77 | 7.01 |
| | 1.0 | 1.23 | 1.23 | 1.28 | 4.18 | - |
| 4 | 0.5 | 1.14 | 1.39 | 2.02 | 9.21 | 25.9 |
| | 1.0 | 1.28 | 1.57 | 2.34 | 14.4 | - |
| 8 | 0.5 | 1.23 | 1.99 | 3.36 | 17.8 | 51.1 |
| | 1.0 | 1.39 | 2.28 | 3.94 | 28.1 | - |
| 16 | 0.5 | 1.57 | 3.30 | 6.11 | 35.1 | 101 |
| | 1.0 | 1.78 | 3.80 | 7.20 | 55.4 | - |

^a C_{milkfat} (Eq. 9-2) / C_{milkfat} (Eq. 9-4); hDI_{MAT} , f_f , and f_m held constant

^b $0.693/K_{\text{elim}}$

^c $t_{\text{pn}} + t_{\text{bf}}$

alter the distribution of contaminants to breast milk. As an example, significant body fat loss from dieting and exercise may tend to “dump” fat-stored compounds with consequences that are not fully known; some may be stored again, some may be eliminated more readily, and some may go into the breast milk. This issue contributes to the overall uncertainty of the model, but does not necessarily indicate a bias in one direction or the other.

A potential source of bias, however, is the assumption that breast milk fat and maternal body fat are in equilibrium and equal in contaminant concentration. Milk fat appears to be synthesized in the mammary glands (cite...?), which may result in lower contaminant concentrations in milk fat than are present in the general body fat stores.

Unless equilibration of de novo milk fat with body fat is rapid, the model would tend to over estimate infant exposure.

Physiological factors such as maternal age, parity, length of lactation, and life style factors such as cigarette smoking and alcohol consumption, which influence transfer of compounds to breast milk (see §9.2.4.) are not explicitly included in the model. The overall impact of these factors on the concentration of contaminants in breast milk is difficult to assess.

Uncertainties in model input variables also can contribute substantially to uncertainty in the output. In particular, partitioning factors and chemical half lives can vary among measurements by factors of 2 or 3. Given these uncertainties and the large uncertainties in toxicity estimation, estimations of risk based on these models are probably precise only to within an order of magnitude, at best. Risk assessors are referred to Chapter 10 for quantitative approaches for the uncertainty analysis and risk characterization.

9.5. REFERENCES

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RISK ASSESSMENT

10.1. INTRODUCTION

Risk assessment is an approach utilized by U.S. EPA to evaluate environmental concerns. Risk assessment has been defined by NAS (1983) as a four-step process (see Figure 10-1) consisting of hazard identification, dose-response assessment, exposure assessment, and risk characterization. In the hazard identification step the problem and the potential toxic effects are defined and the data needs are determined. The next step, dose-response assessment, consists of establishing and quantifying the relationship between the adverse health effect and exposure to or dose of a toxic agent, and characterizing the overall scientific confidence in the dose or exposure concentration of the toxic agent to the study group and the health effects data. As discussed in Chapter 2, the exposure assessment step consists of delineating the pathways and routes of exposure that relate a source to an exposure event, identifying exposed individuals, quantifying their exposures, and characterizing the overall scientific confidence in these data, e.g., identifying sources of uncertainty in the step. In risk characterization, the results from the three previous steps are evaluated and integrated. This is translated into an overall conclusion about the likelihood of an adverse health effect occurring due to an exposure (NAS, 1983; NRC,1994). The risk characterization is then utilized by a risk manager to make a decision. It should be noted that the risk characterization, which attempts to provide a synthesis of the science to the risk decision-maker, is but one factor that enters into a the final decision. Other factors could include economic, political, and technologic considerations.

The U.S. EPA has developed a number of guidelines for human health risk assessment that are applicable to assessing human health risks from exposures arising from combustor emissions. Table 10-1 presents a brief summary of the guidelines.

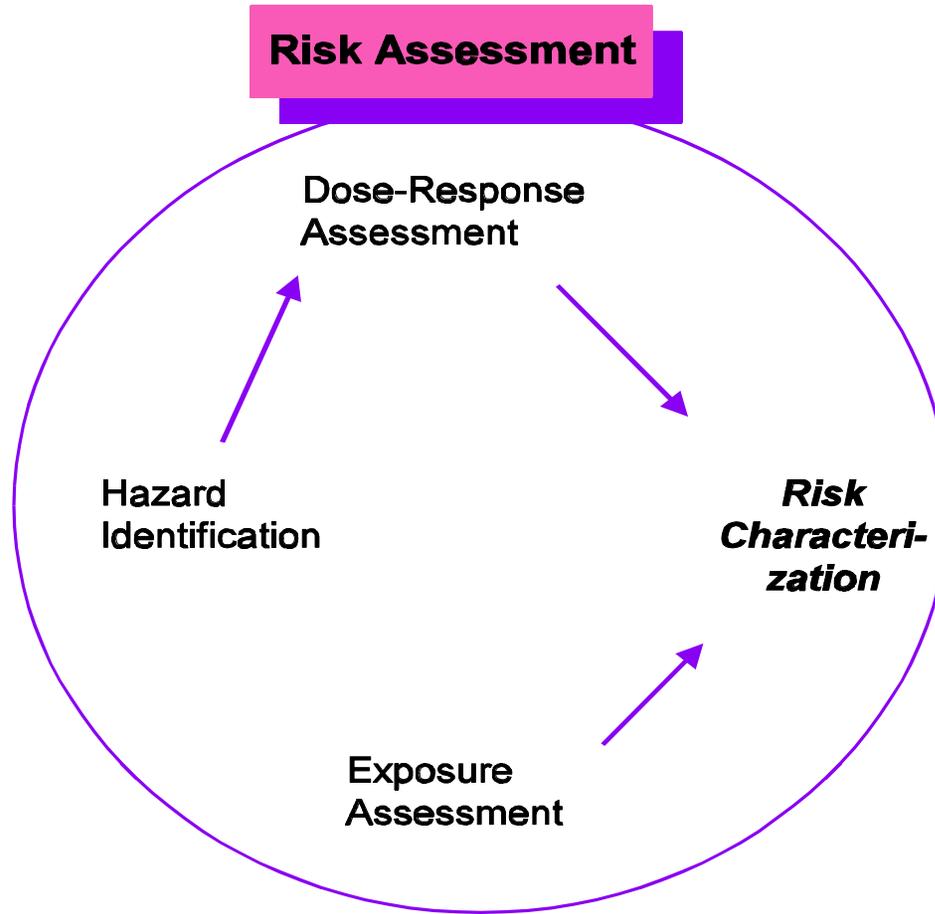


Figure 10-1. This figure illustrates the risk assessment paradigm as described in 1983 by NAS. Figure adapted from NAS, 1983

TABLE 10-1

U.S. EPA Risk Assessment Guidelines

Carcinogenicity

The Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1986a) and the proposed revisions (U.S. EPA, 1996a) are intended to serve as a guide for Agency evaluation of suspect carcinogenic agents in assessing the likelihood that the agent is a human carcinogen and in quantitative estimation of potency.

Mutagenicity

The Guidelines for Mutagenicity Risk Assessment (U.S. EPA, 1986b) provide guidance for the assessment of the weight of evidence that an agent is a potential human mutagen capable of inducing heritable genetic lesions and assessment of the resulting impact on public health.

Chemical Mixtures

The Guidelines for the Health Risk Assessment of Chemical Mixtures (U.S. EPA, 1986c) provide approaches for assessing both carcinogenic and noncarcinogenic human health outcomes from exposures to mixtures of chemicals.

Developmental Toxicity

The Guidelines for the Health Risk Assessment of Suspect Developmental Toxicants (U.S. EPA, 1986d) are designed to guide EPA assessors in the evaluation of potential developmental toxicity associated with human exposure to environmental pollutants. The Guidelines discuss all embryonic and fetal effects from *in utero* exposure and deal with maternal effects, as well.

Reproductive Toxicity

The Guidelines for Reproductive Toxicity Risk Assessment (U.S. EPA, 1996b) discuss the scientific basis for concern about exposure to agents that cause reproductive toxicity and describe the principles and procedures to be followed in conducting risk assessments for reproductive toxicity. They include the female (non-pregnant and pregnant) and male reproductive systems.

Exposure

The Guidelines for Assessment of Exposures (U.S. EPA, 1992a) provide the Agency with a general approach and framework for carrying out human or nonhuman exposure assessments for environmental pollutants.

10.2. EXPOSURE ASSESSMENT

The U.S. EPA's Guidelines for Exposure Assessment (U.S. EPA, 1992a) established a broad framework for conducting exposure assessments. The exposure assessment step of combustion risk assessment consists of evaluating the

environmental fate of emitted pollutants, identifying exposure routes of concern, determining the bioavailable concentrations of emitted pollutants in exposure media, evaluating exposure rates (e.g., consumption rates, inhalation rates) and finally estimating exposures to pollutants.

Exposure scenarios developed for a site-specific assessment may include exposure via multiple routes and pathways. This document has been concerned with the assessment of exposures to combustor emissions. Chapter 2 discussed the creation of exposure scenarios and developed a framework for application of the methodology. Chapters 3-9 presented models designed to estimate contaminant concentrations in environmental and biological media and, ultimately, human intake of contaminants via relevant pathways of exposure. In this methodology, daily pollutant intake has been calculated independently for the following routes and pathways: oral via produce, livestock, fish, breast milk, soil and water, dermal via soil and water, and inhalation. A given individual or population may experience exposure by one or more of these pathways.

10.2.1. Estimation of Individual Total Exposure. To calculate total exposure to an individual exposed by multiple pathways, estimates must be combined across pathways and routes. In the absence of data to the contrary and if the risk assessor judges it to be appropriate, this methodology recommends that chemical exposures be summed across pathways and routes. This is consistent with Agency guidance for adding risks across pathways, contained in Chapter 8 of the Risk Assessment Guidance for Superfund: Volume I—Human Health Evaluation Manual (Part A) (U.S. EPA, 1989) and the Guidelines for Health Assessment of Chemical Mixtures (U.S. EPA, 1986c).

The focus of this section is on *how* to combine intake across exposure pathways. It does not address the question of *when* to combine intakes across pathways. Decisions regarding whether it is appropriate to combine exposures by different pathways are made by the risk assessor and risk manager during the development of the exposure scenarios, a topic that is discussed in Chapter 2. (In general, risks

should be added across pathways whenever it is reasonable to expect an individual to experience exposure by a given set of pathways.)

The risk assessor should be aware that predicting the risks posed to a specific individual is highly uncertain. Both uncertainty and variability associated with the individual could involve different activity patterns resulting in variable exposure rates, toxicodynamic uncertainty, and variable nature of an individual's general health. Many of these factors cannot be modeled at present and, as a result, predicting risk to a specific individual is uncertain.

10.2.1.1. Combining Exposures from Multiple Routes — Route-to-route conversion should only be attempted for dermal exposures at this time. Adequate inhalation-to-oral conversion methods, particularly for steady-state conditions, have not yet been developed. A general outline of the oral-to-inhalation extrapolation process and a discussion of route-to-route extrapolation issues can be found in Gerrity and Henry (1990) and in the EPA's Reference Concentration methodology document (U.S. EPA, 1994b). Until such methodology is developed, inhalation and oral risk characterization should be carried out separately. The assessor should note, however, that total risk will appear to be smaller by not combining all routes of exposure.

Multiple-route exposures can be combined in two different ways: summing the absorbed daily doses or summing the (external) oral equivalent daily doses. Both approaches require an estimate for the oral absorption fraction but the latter is adopted here as it is simpler for comparison with standard toxicity benchmarks based on ingestion (external dose).

In order to determine the health risk associated with daily intake of contaminant by ingestion or dermal contact, the daily intake is either multiplied by the contaminant's cancer slope factor (for carcinogens) or compared with the contaminant's RfD for noncarcinogenic effects. Cancer slope factors and RfDs are available for oral exposure, but not dermal exposure. Therefore, dermal intake must be converted to the equivalent oral intake (U.S. EPA, 1989).

A number of factors might contribute to differences in toxicological effectiveness between oral and dermal exposures at equal dosages. The most obvious relates to differences in absorption rates between the two routes. Other potential contributing factors include differing sensitivity of absorption sites to damage and differences in toxicokinetics (i.e., distribution, metabolism, elimination) between exposure routes. Ideally, the conversion from dermal to equivalent oral dose would be based on experimentally derived values relating the doses that produced a particular toxicity by the different routes. In practice, however, the conversion will usually be based on absorption factors because of a general absence of appropriate data.

In this methodology, daily dermal intake (DDI) is calculated as an absorbed dose (see Chapter 4). Oral intake and the RfD, by contrast, are based on ingested (external) dose. The contaminant's oral absorption factor can be used to convert the absorbed dermal dose to an equivalent external oral dose, assuming equivalent toxicological effectiveness of absorbed doses. The DDI can be transformed to an equivalent oral daily intake (DI) by dividing the DDI by the oral absorption factor, as shown in Equation 10-1:

$$DI = \frac{DDI}{AF_o} \tag{10-1}$$

where:

- DI = daily intake (oral equivalent) (mg/kg-day)
- DDI = daily dermal intake (mg/kg-day)
- AF_o = oral absorption factor for contaminant (unitless)

Contaminants lacking data on oral absorption are assumed to be 100% absorbed from the gastrointestinal tract (AF_o = 1), so the equivalent oral dose would be equal to the DDI. Note that this is a conservative assumption with respect to oral ingestion but not for dermal-to-oral conversion. Equivalent oral DI values from dermal

pathways can be added to DI values from oral pathways to determine total intake of contaminant by these routes. The assumption of equivalent effectiveness of absorbed doses between exposure routes, however, does not hold in some cases, such as when effects occur at the portal of entry or when removal, inactivation, or activation of the compound before reaching the target organ varies with the exposure route.

When this assumption is used, therefore, the data to support it should be characterized in the final step of the assessment.

10.2.1.2. Exposure Duration Adjustments — The models presented in earlier chapters of this methodology derived daily contaminant intake rates by various pathways on the basis of estimated contaminant concentrations in environmental media and human activity patterns. Both activity patterns and media levels are subject to change over time. Activity patterns are defined in exposure scenarios. The most common activity changes are associated with exposure as both a child and an adult. For example, the potential dermal exposure during childhood may be quite different from that experienced by an adult. Scenarios, however, may also include activity changes within one or both of these broad time frames. In order to arrive at an intake representative of the entire duration of a scenario, a time-weighted average is calculated. This is illustrated in the following equation for a simple scenario that includes both childhood and adult exposure:

$$DI_w = DI(\text{child}) \frac{ED_c}{ED_s} + DI(\text{adult}) \frac{ED_a}{ED_s} \quad (10-2)$$

where:

- DI_w = time-weighted daily intake for pathway during exposure (mg/kg-day)
- DI = daily intake for pathway (mg/kg-day)
- ED_c = duration of childhood exposure (years)
- ED_s = duration of scenario (years)
- ED_a = duration of adult exposure (years)

This equation can be easily modified to encompass alternative partitions of the total exposure duration. If data were available regarding the change in contaminant emission rates over time, averaging over the entire duration of the scenario would produce a more realistic estimate of intake than an estimate based on emission rates at any one point in time. For example, a risk assessor may decide to subdivide childhood into specific phases such as, breast-fed infant up to 1 year of age, 2-6 years of age, 7-12 years of age, and 13-18 years of age.

When risk is characterized, the classification of exposure duration for a given pollutant ultimately should consider the data set used to generate the dose-response estimate. If there are a number of toxicologic evaluations, the risk assessor should choose the dose-response curve from a study that best applies to the exposure duration being evaluated. Typically, the Agency-verified data are presented on EPA's IRIS database. For noncarcinogens, no further duration adjustments of DI_w are necessary. However, the DI_w does need to be categorized as chronic (typically considered 7 years to lifetime; U.S. EPA, 1989) or subchronic (typically thought to be 2 weeks to 7 years; U.S. EPA, 1989), depending on the duration of the exposure scenario (D_s). Chronic DI_w values are compared with RfD values, while subchronic DI_w values, if calculated, are compared with subchronic RfD values. For all of these subchronic RfDs, see the Health Effects Assessment Summary Tables (HEAST) (U.S. EPA, 1998b). Acute exposures should be compared with estimates of short-term health effects; for assessments of combustor emissions, acute exposures, if considered, are generally evaluated for the inhalation route only (see Chapter 3).

Significant acute exposures resulting from combustor emissions are thought to potentially occur only through the inhalation route. As described in Chapter 3, during periods of operational perturbation, the magnitude of the emissions may increase and compounds emitted from the source may change. Given the state-of-the-art of commercial combustion sources in the United States, these are generally infrequent events of an extremely short duration. Atmospheric conditions may also change over short periods of time resulting in a low dispersion of emitted pollutants. While the types

of pollutants emitted would be unchanged, the predicted concentrations in the local atmosphere may be elevated for these short time periods. The nature and duration of these time periods depends on the site of the facility, local meteorology and topography.

Predicted or measured chemical concentrations in the surrounding atmosphere should be compared with appropriately derived short-term, dose-response estimates. These short-term exposures in general should not be averaged over a lifetime. Obviously, a mixture of chemicals could be emitted. Dose-response data for acute exposures to chemical mixtures, if available, should also be considered.

For carcinogens, exposure is usually averaged over the entire lifetime of the individual (assumed to be 70 years), even if the actual exposure duration is shorter (U.S. EPA, 1995a). This is because cancer risk is generally described in terms of lifetime probabilities of contracting the disease. To make this adjustment, the following equation may be used:

$$DI_{LW} = DI_W \frac{ED_s}{D_L} \tag{10-3}$$

where:

- DI_{LW} = lifetime-weighted daily intake for pathway (mg/kg-day)
- DI_W = time-weighted daily intake for pathway during exposure (mg/kg-day)
- ED_s = duration of scenario (years)
- D_L = duration of lifetime (default = 70 years)

Although appropriate in most circumstances, there are times when adjustment to lifetime average exposure is not recommended for a carcinogen. For example, childhood may be the critical exposure period for some carcinogens, in which case the risk would be underestimated by averaging over the entire lifetime. These exceptional instances should be carefully evaluated on a case-by-case basis.

10.2.1.3. Total Daily Intake Due To Indirect Exposure To Combustor

Emissions — Total daily intake (TDI) of a contaminant attributable to indirect exposure to emissions from the combustor for a particular exposure scenario is estimated by summing the oral equivalent daily doses. Equation 10-4 presents the formula for summing doses (appropriately weighted for time as in Eq. 10-2) for all pathways relevant to the exposure scenario.

$$TDI = \sum_{i=1}^n DI_{(W, LW) i}$$

(10-4)

where:

TDI = total daily intake for an exposure scenario including n exposure pathways (mg/kg-day)

$DI_{(W, LW) i}$ = time-weighted daily intake by i th pathway (mg/kg-day)
[DI_W for noncarcinogens, DI_{LW} for carcinogens]

The results of this equation can be used in the development of individual risk assessments described in Chapter 2 (e.g., Maximum Exposed Individual).

Although oral absorption of a particular contaminant may differ for different vehicles (water, food, or soil), vehicle-related adjustments are not generally recommended (U.S. EPA, 1989), as RfDs and oral cancer slope factors are generally derived to apply to all oral routes of exposure rather than to specific media. When vehicle-related toxicity differences are adequately supported by the data, separate toxicity values have been derived for different vehicles (e.g., cadmium has both food- and water-based RfD values; U.S. EPA, 1998a). In these cases, the pathways should be sorted according to vehicle (e.g., water vs. food or soil for cadmium) and the DI values within each group summed to obtain vehicle-related TDI values.

10.2.1.4. Cumulative Exposures — It is important to recognize that there may be sources of exposures to chemicals other than from emissions of these chemicals from the modeled combustion sources. Cumulative exposures occur when the

chemical exists naturally in the local environment, or when the chemical is ubiquitous in the environment although it may not be natural to the environment. Examples of the former are mercury or other metals, and examples of the latter are dioxins and PCBs. This concern, in general, has been expressed in terms such as “exposures from multiple sources”, “cumulative exposures”, or “background exposures”. These terms have been used in different contexts and may have different meanings in these contexts. Cumulative exposures may be defined as the total chemical exposure that results from all sources an individual comes into contact with, through multiple exposure routes over a period of time. The quantification of cumulative exposure includes consideration of all routes and sources of exposure as well as contact rates and bioavailability of a pollutant within different media and over a specified temporal period. Cumulative Risk may be narrowly defined as the likelihood of an adverse effect that results from cumulative exposure to a single chemical. Alternatively, cumulative risk may encompass an evaluation of the effects that result from exposure to multiple stressors (chemical pollutants or otherwise) to a given individual over time.

The term “Background Level” may be defined alternatively as the concentration of a chemical in an environmental medium (air, water, or soil) that occurs naturally (i.e., is not the result of human activities) or the concentration of a chemical in a defined area over a period of time before the introduction of a specific anthropogenic source only. Background exposure will be defined here in terms of the second definition offered; it is the cumulative exposure experienced prior to the introduction of a specific anthropogenic source. (TDI defines the exposure that results from the source only).

If and how the risk assessor considers background or cumulative exposures depends on the nature of the question posed by the risk manager. It may be useful in communicating the risks of a site-specific assessment to compare the TDI with an estimate of background or cumulative exposures. Assessors may be interested in background exposures in at least two ways: addressing how incremental impacts of a single source compare with background impacts in the same geographic region, or

addressing how incremental impacts of a single source compare to the general population background exposure distribution.

The first of these two assessment options is site-specific. In this case, background exposures can be thought of as the exposures an individual would face if the source in question were not in existence. Individuals living in the vicinity of the source would not behave differently; they would just be exposed to environmental media concentrations that would be lower because the source in question would not be in operation. For example, if there is a subsistence fishing scenario pertinent to a particular source, the subsistence fishers would be consuming fish at the same rate whether or not the source were present. The fish concentrations to which the individuals were exposed would be a function of the concentrations of the contaminant in the water body where the fish were caught, which in turn resulted from the cumulative impacts of all other sources in the geographic region (or, in a different instance, could have resulted from natural levels of the contaminant in the environment).

For the second of these assessment needs, background exposure may be thought of in a more generic sense and not necessarily specific to a site or source. For example, a risk assessor could devise a scenario for a specific source, estimate the incremental daily dose from that source, and then compare that dose to a generic background exposure distribution, which could be calculated considering the distribution of medium specific contact rates across the nation and the distribution of chemical concentration ratios in the medium. In the example in the previous paragraph, an exposure resulting from subsistence fishing could be calculated as a function of subsistence consumption and fish concentrations that result only from the source in question. This exposure could be compared with an average national exposure from fish consumption, calculated assuming national average fish concentrations and average, rather than subsistence, fish consumption rates. Alternatively, the site- and source-specific exposure could be compared with an exposure calculated by assuming the same subsistence behavior and a national

average fish concentration. There are numerous approaches to consider background impacts in a site-specific assessment. This section will not give prescriptive guidance, but rather will provide the risk assessor with a background in different options.

As seen in these examples, a background exposure estimate requires two quantities: contact rates and exposure media concentrations. Contact rates could be contact rates derived for a specific site, or generic values determined from different data sets. A site-specific contact rate could be important if unique behaviors, such as subsistence fishing, are associated with the source in question. Four options are presented for estimating background exposure media concentrations:

1. *Generic Exposure Media Concentrations:* A risk assessor could construct a generic background exposure media concentration. For example, the Dioxin Exposure Reassessment Document (U.S. EPA, 1994a) derives typical concentrations of the dioxin-like compounds in air, soil, and various food products for the United States, and the Mercury Study Report to Congress (U.S. EPA, 1997) derives typical concentrations of mercury in air, soil, and food products such as fish. The mercury report also predicts exposures based on these data. Use of generic contact behaviors and generic background concentrations based on measured media concentrations allows one to derive a general background exposure for any combination of pathways. This could be accomplished through estimation of the distribution of concentrations that occur in a specific area (e.g., the United States). The distribution of background exposures can then be estimated by multiplying the distribution by the distribution of contact rates.
2. *Measurement of Exposure Media Concentrations:* Measurement of concentrations of the contaminant in question in all relevant exposure media associated with a site would be optimal, but is costly and may not be feasible if the source in question has been in existence for several years. For example, a measurement of dioxins or mercury in air and soil in the vicinity of an operating incinerator would reflect the impacts of the incinerator, as well as any other sources that are present. Measurements in environmental/exposure media in the vicinity of a closed incinerator could still be influenced by past emissions from the incinerator. This would be the case if measuring soil around a closed incinerator. On the other hand, measurements of air concentrations around a closed incinerator would be an appropriate reflection of background air concentrations for that site. The measurement of exposure media concentrations is usually feasible (but still costly) if the assessment is

prospective in nature, i.e., that it evaluates a new source not yet emitting the contaminant. Here a careful monitoring program could give estimates of environmental media prior to emissions from a new combustion source.

3. *Modeling of Exposure Media Concentrations:* There are at least two ways in which background exposure media concentrations could be estimated by models alone. One is to model the impacts from all major sources in the area except for the source in question and then adds impacts of points of interest. This assumes that the impacts from several sources are independent. The model ISC3, recommended for use in this document, can, in fact, model multiple sources. This document does not discuss the procedures for using the ISC3 model in this mode. (This option and the following RELMAP option raise additional questions such as: Did the assessor identify all sources? Are the source emission estimates correct? and so on.) Another possibility is use of the Regional Legrangian Model of Air Pollution (RELMAP) (Eder et al., 1986; Clark et al., 1992). EPA's Office of Research and Development has developed this national model. RELMAP takes, as input, emissions into the air from specifically defined sources in the United States, and predicts, for any location in the United States, amounts of depositions and air concentrations for modeled contaminants. Air concentrations and depositions could then serve as the input for modeling impacts to the terrestrial and aquatic environment, using the steady-state models discussed in this assessment. The RELMAP was used to predict national fate of mercury emissions in U.S. EPA (1997), and is currently being used in a similar manner for sources of dioxin release. Drawbacks of this approach include the real possibility that not all sources have been identified or properly quantified, as well as its low precision. The smallest scale that such a regional modeling exercise can use is about 40 km². Exposure media concentrations modeled by RELMAP or ISC3 would be the "background" concentrations, on top of which the source in question will be adding impacts.
4. *A Combination of Modeling and Limited Monitoring:* This may be the most reasonable way to estimate background exposure media concentrations for a specific site, if site-specific data are available. For example, if a historical combustor source were no longer operating, than air concentrations measured in the vicinity of the source could give an estimate of background air concentrations. These could then be routed through the terrestrial and aquatic environments to predict soil and food concentrations for background exposure estimation, using the models in this document. Careful monitoring of soil and air concentrations in the vicinity of the source while it is still operating is another possibility. Specifically, if several air monitors in all directions from a combustor

source were sampled on several days, during which time wind-rose data were also taken, one could probably identify air concentrations most and least likely to be impacted by the source in question. Soil concentration data several miles away may be an appropriate measure of impacts to soils unaffected by the source in question. Again, these intermediate exposure concentrations could be used with the steady-state models of this document to model the full range of terrestrial and aquatic impacts.

Once contact rates and exposure media concentrations are decided, the risk assessor can generate a background exposure estimate to suit the particular assessment. Then, the assessor faces critical decisions on proper use and interpretation of these estimates. One option that has been alluded to in previous paragraphs is to do a simple comparison. Risk managers can compare the background dose to the site-specific, predicted incremental dose and determine the most useful and appropriate method of using the data.

The other option is to add the incremental exposure that results from the source (TDI) to the background exposure resulting in a new cumulative exposure estimate. This may be an appropriate option in at least two circumstances: 1) the health endpoint is triggered by a threshold dose—there may arise a circumstance in which the background exposure alone or the incremental exposure (TDI) alone would not trigger the threshold, but the addition of the two may lead to the exceedence of the threshold; 2) a risk management decision hinges on a non-threshold health impact, such as a cancer endpoint, in which the addition of background plus incremental exposure may lead to a level of concern (from a risk management standpoint) for a specific set of exposure assumptions. These exposures may be summed through Equation 10-5 to estimate cumulative exposure:

$$CE = TDI + \sum_{i=1}^n BI_i$$

(10-5)

where:

CE = Cumulative exposure intake for exposure scenario including n

background exposure pathways (mg/kg-day)

BI_i = daily background intake by i th pathway (mg/kg-day)

The only prescriptive guidance regarding background in this methodology is that the risk assessor should consider background impacts in an indirect exposure assessment, although there may be circumstances in which this is not necessary.

There have been many Superfund site-specific assessments in which only incremental impacts were considered in the establishment of cleanup levels. On the other hand, heightened awareness of the ubiquitous nature of contaminants commonly emitted from combustors, such as mercury or dioxins, coupled with an awareness that even the background levels of these contaminants approach levels of concern, has required site-specific combustor risk assessments to take background impacts into consideration.

10.2.2. Population Exposure. The population exposure is the aggregate exposure to the affected individuals. U.S. EPA's (1992a) Exposure Assessment Guidelines recommend assessing the exposure and risk experienced by the aggregate population. Several potential approaches to describing population exposure are presented in Chapter 2 of this methodology. One way is to simply present the distribution of the individual exposures predicted for all individuals within the exposed population. For example, for inhalation exposures U.S. EPA's Human Exposure Model (HEM) can predict the distribution of inhalation exposures experienced by the population around a facility. (The HEM only accounts for inhalation exposures.) For combinations of large populations and large numbers of pollutants that are transferred through multiple environmental compartments, estimating individual exposures for the entire population may be very resource intensive. The isopleth approach also presented in Chapter 2 of this document can effectively be used to estimate and present population exposures and the resulting risks. However, the resources needed to complete the approach for large numbers of pollutants may not be available to the risk assessor. A third approach assumes that the exposure predicted for the "average" individual in the study area represents the population mean and the distribution of the exposure is not estimated.

A fourth procedure combines knowledge of the “commodity shed” with the distribution of daily consumption rates of the commodity. This method could be used for any medium to which a significant fraction of the population is exposed. Although most applicable for foods, it could apply to other sources of exposure such as drinking water or soil.

10.3. TOXICITY ASSESSMENT

Toxicity assessment consists of the evaluation of a particular contaminant’s ability to cause adverse effects in exposed individuals—hazard identification—and the estimation of the relationship between the actual exposure to a contaminant and the increased likelihood of adverse effects—dose-response assessment (U.S. EPA, 1989). The purpose of the following sections is to summarize these two steps in the risk assessment process as they relate to both cancer and noncancer toxicity. The concepts put forward in these sections are not unique to combustor emissions but can be applied in any toxicity assessment scenario. Toxicity assessments for specific substances can be found in the U.S. EPA’s Integrated Risk Information System (IRIS; U.S. EPA, 1998a).

The first step in the toxicity assessment process, hazard identification, determines the type of effects produced by a contaminant and whether those effects are adverse. Hazard identification is a qualitative evaluation of all the available human and experimental animal data to determine the range of adverse effects associated with exposure to a given contaminant. Unique to the cancer assessment is the qualitative classification of the potential of a contaminant to cause cancer in humans; a parallel concept does not exist (formally) for noncancer assessment.

The second step in toxicity assessment—dose-response assessment—defines the relationship between the exposure level of the contaminant and the associated biological effects. The result of this assessment is a quantitative measure in the form of a media concentration or dose of the contaminant associated with a given level of risk. The formal quantitative measures are the Reference Dose (RfD) and Reference Concentration (RfC) for oral and inhalation noncancer assessment, respectively, and

the slope factor and unit risk for cancer assessment. Detailed explanations of the underlying concepts, methodologies and assumptions for these quantitative estimates is beyond the scope of this document and can be found elsewhere [RfD (U.S. EPA, 1988a; Barnes and Dourson, 1988), RfC (U.S. EPA, 1994b), slope factor/unit risk (U.S. EPA, 1986a, 1988b, 1996a)]

The U.S. EPA's approach to assessing the risks associated with noncancer toxicity has traditionally differed from its approach to assessing carcinogenic risks because of different assumptions about the mechanisms of action involved. For most carcinogens, the assumption is that even a single molecular event can evoke changes in a single cell that can lead to uncontrolled cellular proliferation. This mechanism is referred to as nonthreshold, as there is theoretically no level of exposure for such a chemical that does not pose a small, but finite, probability of generating a carcinogenic response. Noncancer effects, however, are presumed to arise from threshold mechanisms. That is, homeostatic, compensating, and adaptive mechanisms must be overcome before a recognizable toxic endpoint is manifested. The threshold concept is that some finite level of exposure to a substance will not result in an adverse effect for any individual. The key word in the interpretation of this concept is adverse, such that, even if it can be shown that one molecule of a substance destroys a protein molecule, such an effect would be considered biologically insignificant and would not be judged to be adverse.

Common to both types of assessment is a statement of the confidence held in the quantitative estimates. The confidence judgment is based on the quality and completeness of the entire body of data supporting the quantitative estimate. The statements of confidence should be interpreted in the context of the likelihood that the quantitative estimate will *not* change when new data become available. The confidence statement is not a commentary on the quality of the assessment or on the relative protectiveness of the quantitative estimate; additional data could result in lower or higher numbers. As an example, additional data could identify a more sensitive

endpoint (lowering the NOAEL) or could fill in a data gap (lowering the uncertainty factor).

A significant practical aspect of the cancer/noncancer mechanistic dichotomy when assessing exposures is that quantitative potency estimates for carcinogenicity allow for estimation of incremental risk in the human population given a specific exposure level while noncancer potency estimates do not. Currently, noncarcinogenic quantitative estimates only identify the exposure level below which adverse effects are unlikely; an RfD or RfC does not say anything about incremental risk for higher exposures. The Benchmark Dose or other dose-response models, combined with a probabilistic treatment of uncertainty (Price et al., 1997; Swartout et al., 1998), may provide a basis for estimating risk above the RfD or RfC in the future. However the risk is expressed, as long as a threshold is assumed, the total exposure (including background) for any given contaminant must be known for assessment of noncarcinogenic risks.

10.3.1. Hazard Identification for Carcinogens. The U.S. EPA has recently published (U.S. EPA, 1996a) proposed revisions to the 1986 Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1986a). Hazard identification in the proposed revisions to the cancer guidelines (EPA Proposed Cancer Guidelines, U.S. EPA, 1996a) is highlighted by an expanded weight-of-evidence narrative, which culminates in a classification of the substance as to the likelihood that it is a human carcinogen. Proposed changes include:

- a greater focus on biological information other than tumor findings,
- a revised classification system,
- a consideration of the agent's mode of action,
- use of biologically-based extrapolation models,
- mathematical models other than the linearized multistage model, and
- a two-step dose-response assessment process.

The revised classification system focuses on the likelihood that the agent is a human carcinogen, which is reflected in the language. Determination of this classification is dependent on an expanded and more inclusive weight-of-evidence assessment. Also, the existence of a hazard is no longer strictly a yes/no decision, but

can involve a consideration of dose, depending on the mode of action of the carcinogen. That is, some carcinogens may be determined to act by indirect (threshold) mechanisms rather than by direct genotoxic action. For dose-response assessment, selection of mathematical model is liberalized and low-dose extrapolation has been decoupled from high-dose modeling (see Section 10.3.3., following). The reader is referred to U.S. EPA (1996a) for a detailed discussion of these topics.

10.3.2. Hazard Identification for Noncarcinogens. Unlike carcinogen risk assessment, no formal guidelines exist for noncarcinogen risk assessment and so, the latter will be presented here in somewhat greater detail than the former. Methodology documents for both the RfD and RfC, however, are available (U.S. EPA, 1988a, 1994b), as well as a few related publications (Barnes and Dourson, 1988; Dourson, 1994; Swartout et al., 1998).

In the vast majority of cases, hazard identification for noncancer effects is not a yes/no process, as for carcinogenic effects, but is dependent on dose. Virtually all substances will eventually produce adverse effects as the dose is increased. Thus, noncancer hazard identification is indistinguishable from dose-response analysis; the existence of a hazard cannot be determined independently from the dose-response analysis. A qualitative aspect of noncancer hazard identification, however, exists conceptually, as a weight-of-evidence (WOE) approach for determining the likelihood of occurrence of specific effects in humans. Guidance on how to conduct a WOE is limited (U.S. EPA, 1988a; Barnes and Dourson, 1988) and a formal noncancer WOE is not included in noncancer assessments⁴ (U.S. EPA, 1998a). An assessment of the strength of the data, however, is discussed throughout an RfC or RfD document on IRIS (U.S. EPA, 1998a) culminating in the confidence statement described previously. The identification of a critical effect, on which an RfD or RfC is based, is largely a procedural issue rather than a WOE issue. The critical effect is always the adverse

⁴ The lack of a formal WOE is now being addressed, somewhat, with the recent inclusion on IRIS (U.S. EPA, 1998a) of text devoted to the synthesis and evaluation of major noncancer effects.

effect at the LOAEL of the study defining the RfD—the principal study. The principal study is almost always the one yielding the lowest RfD when the appropriate uncertainty factor scenario is considered. Biological considerations may override the procedural approach when specific mechanisms or effects are judged to be more appropriate for application to human risk assessment.

10.3.3. Dose-Response Assessment for Carcinogens. The dose-response assessment step in carcinogen risk assessment is to define the relationship between the dose of an agent and the likelihood of a carcinogenic effect. Dose-response assessment usually entails an extrapolation from the generally high doses administered to experimental animals or exposures noted in epidemiologic studies to the exposure levels expected from human contact with the agent in the environment. It also includes considerations of the validity of these extrapolations. Extrapolation is ordinarily carried out first by fitting a mathematical model to the observed data and then by extending the model (or a bound on the risks it predicts) from the observed range down toward risks expected at low exposure. The models are generally, but not always, nonthreshold. That is, risk diminishes with dose, but does not become zero until dose becomes zero. The proposed revised carcinogen risk assessment guidelines allow for different approaches in different situations (U.S. EPA, 1996a).

Dose-response assessment includes (1) selection of the appropriate data sets to use; (2) derivation of estimates at low doses from experimental data at high doses using an extrapolation model; and (3) choice of an equivalent human dose when animal data sets are used. A more detailed description of the dose-response assessment for carcinogens can be found in other U.S. EPA documents (U.S. EPA, 1986a, 1988b, 1996a).

In the EPA Proposed Cancer Guidelines (U.S. EPA, 1996a), dose-response assessment is a two-step process. The default assumption remains low-dose linear, but the upper anchor for the extrapolation has changed. Dose response in the range of the observations is first modeled to obtain a point of departure, from which low-dose extrapolation begins. For oral exposure, the cancer potency factor (CPF) is estimated

as the slope of the line from the point of departure to the origin (zero risk at zero dose) as in Equation 10-6.

$$CPF = \frac{R_{pd}}{D_{pd}} \quad (10-6)$$

where:

CPF = cancer potency factor

R_{pd} = response at point of departure (unitless)

D_{pd} = dose at point of departure (mg/kg-day)

The default for R_{pd} is the lower 95% confidence bound on the dose associated with a 10% risk derived from modeling the observations (in terms of human equivalent dose), but could be different depending on the situation. The carcinogen dose associated with a specific predicted human risk can then be calculated from Equation 10-7.

$$RSD = \frac{TIR}{CPF} \quad (10-7)$$

where:

RSD = risk-specific dose (mg/kg-day)

TIR = target incremental risk

CPF = cancer potency factor

Equations 10-6 and 10-7 are included as an example of the procedure for calculating carcinogen risk and apply to the oral route of exposure. The equations for inhalation and dermal exposure will be similar but with different units. Also, these equations will be different for nonlinear models of low-dose risk and will depend on the

particular model used. The reader is referred to U.S. EPA (1996a) for a more thorough discussion of these topics.

10.3.4. Dose-Response Assessment for Noncarcinogens. Noncancer dose-response assessment centers on the no-observed-adverse-effect level (NOAEL) associated with the LOAEL for the critical effect. The NOAEL is defined as the highest experimental dose of a chemical at which there is no statistically or biologically significant increase in frequency or severity of an adverse effect in individuals in an exposed group when compared with individuals in an appropriate control group. The NOAEL is then divided by a series of uncertainty factors that reflect specific major areas of uncertainty in the RfD and RfC. If a NOAEL has not been identified, the LOAEL is used, with application of an additional uncertainty factor. The formulas for calculation of RfCs and RfDs are given in Equations 10-10 and 10-11, respectively.

More recently a benchmark dose (BMD) or concentration (BMC) has been used instead of a NOAEL to derive RfDs or RfCs. The BMD/C is defined as the statistical lower confidence limit on the dose estimated to produce a predetermined level of change in response relative to controls (Crump, 1984). The BMD/C incorporates information on the slope of the dose-response curve and sample-size uncertainty into the quantitative estimate. The BMD approach is particularly useful when a NOAEL is not defined. Current usage of the BMD/C is as a replacement for the NOAEL terms in Equations 10-10 and 10-11. A discussion of the BMD methodology and its strengths and weaknesses can be found in the draft guidance document for the use of the BMD in risk assessment (U.S. EPA, 1996c).

Uncertainty factors are reductions in the dose rate (RfD) or concentration (RfC) used to account for several areas of scientific uncertainty inherent in most toxicity data bases. Uncertainty factors of up to 10 each are applied to extrapolate from test animals to humans, to provide protection for sensitive human subpopulations, to account for the effects of exposure duration, to estimate a NOAEL from a lowest-observed-adverse-effect level (LOAEL) and to account for the lack of a complete data base. There is no standard description for the modifying factor, as it is situation specific. A detailed

description of uncertainty factors is beyond the scope of this document and can be found elsewhere (U.S. EPA, 1988a; Barnes and Dourson, 1988).

10.3.4.1. Reference Dose (RfD) Calculation —The U.S. EPA's formal definition of the RfD is:

an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effect during a lifetime.

The RfD is derived from the NOAEL by application of uncertainty and modifying factors that reflect various types of data sets used to estimate RfDs (U.S. EPA, 1988a; Barnes and Dourson, 1988). The RfD is calculated as follows:

$$RfD = \frac{NOAEL}{\prod UF_i \times MF} \quad (10-8)$$

where:

- RfD = Reference Dose (mg/kg-day)
- NOAEL = no-observed-adverse-effect level (mg/kg-day)
- $\prod UF_i$ = product of individual (i) uncertainty factors (unitless)
- MF = modifying factor (unitless)

10.3.4.2. Reference Concentration (RfC) Calculation — The RfC value for inhalation exposure to a chemical is expressed as a concentration in air as milligrams per cubic meter (mg/m³). The RfC is calculated as follows:

$$RfC = \frac{NOAEL_{HEC}}{\prod UF_i \times MF} \quad (10-9)$$

where:

- RfC = Reference Concentration (mg/m³)
- NOAEL_{HEC} = no-observed-adverse-effect level, human equivalent concentration (mg/m³)
- $\prod UF_i$ = product of individual (i) uncertainty factors (unitless)
- MF = modifying factor (unitless)

The RfD and RfC methodology differ primarily in the manner of expressing the NOAEL. The RfC methodology explicitly provides for dosimetry adjustments among species and for different exposure scenarios, such that the experimental NOAEL is scaled specifically for humans (U.S. EPA, 1994b). Case-specific data applicable to this scaling can be used to reduce the overall uncertainty factor. Such adjustments can also be made for RfDs but are not explicit in the methodology.

10.3.4.3. Interpretation of Noncancer Assessments — Although the noncancer risk assessment approach assumes thresholds—even for the most sensitive individual in the population—the RfD is not an estimate of the human population threshold. Although not stated explicitly in the RfD methodology, the RfD is an implicit estimate of a NOAEL in a study of a sensitive human subpopulation (NOAEL_{HS}; Swartout et al., 1998). This definition arises by considering the requirement for reducing the overall uncertainty factor to unity, which is a NOAEL in a human study comprising the presumed sensitive subpopulation (U.S. EPA, 1988a; Barnes and Dourson, 1988). Thus, the actual human risk at the RfD is the residual risk at the NOAEL_{HS}, which can be zero or nonzero; the upper limit depends on the power of the study to detect an effect. Even if the latter were determinable, the residual risk applies only to the sensitive subpopulation studied. A determination of the human population risk would require an estimate of the proportion of the human population comprising the sensitive subpopulation.

In addition, the RfD should be interpreted as a lower-bound estimate of the NOAEL_{HS} (Swartout et al., 1998). This conclusion follows from the conceptual nature

of uncertainty factors, each of which are considered to be loose upper bounds on the factor required to lower the dose producing an effect to account for missing information. As an example, an uncertainty factor of 10 is used to account for the effects of prolonged exposure on toxicity when lifetime studies are not available (subchronic-to-chronic UF). The expectation, however, is that the true reduction in the NOAEL when the chronic study is performed will be less than 10 most of the time; the value of 10 is thus meant to be protective. It follows, then, that the (multiplicative) application of each additional factor of 10 will increase the degree of protection of the RfD with respect to anticipating the $NOAEL_{HS}$. That is, the assessment of the likelihood that the RfD is less than the $NOAEL_{HS}$ depends on the number of uncertainty factors used in the RfD derivation. A rough idea of the relative likelihood of any RfD exceeding the $NOAEL_{HS}$ can be appreciated by assuming that each uncertainty factor is independent and identically lognormally distributed with a 95th percentile equal to 10. That is, the probability that the reduction in the NOAEL will exceed 10-fold when the data is acquired satisfying one area of uncertainty is 0.05. The value of two and three multiplicative 10-fold uncertainty factors (100 and 1000) has a probability of 0.01 and 0.005, in their respective joint distributions (Swartout et al., 1998). Recognizing this issue, the U.S. EPA has modified the standard values for combined uncertainty factors when four or five areas of uncertainty apply to 3,000 and 10,000, respectively (Dourson, 1994). The result is that, for more recent assessments, RfDs have moved closer to becoming probabilistically equivalent in estimating the $NOAEL_{HS}$. When evaluating specific RfDs, the assessor must pay close attention to the description of the uncertainty factors to determine whether or not adjustments have been made to account for compounded conservatism in the uncertainty factors.

Finally, the risk of noncancer effects above the RfD cannot be estimated with current methodology, although an approach has been published that may be useful (Price et al., 1997). Exposure-response relationships over a range of doses or exposure durations are only appreciated *qualitatively*. As an example, the steepness of the dose-response curve has no influence on the value of the resulting RfD. A NOAEL

associated with a steep dose-response slope is more likely to be subthreshold than a NOAEL associated with a gradual increase in response. The latter, however, has a little more room for error than the former with respect to other sources of error and uncertainty.

10.4. RISK CHARACTERIZATION

10.4.1. Introduction. Risk characterization is the summarizing and essential final step of the risk assessment process. In risk characterization, the major scientific evidence and bottom-line results from hazard identification, dose-response assessment, and exposure assessment are evaluated and integrated into an overall conclusion about risk (NRC, 1983, 1994).

This section will show how the exposure information can be integrated in a quantitative manner with hazard and dose-response information to estimate risk for individuals and populations. It also will discuss how quantitative risk estimates can be integrated with qualitative and quantitative information regarding uncertainty and variability to produce the risk characterization. The general approach is based on Agency guidelines for exposure assessment and risk characterization (U.S. EPA, 1989, 1992a,b, 1995b,c,d).

Various individuals and groups may be significantly impacted by the results of the risk characterization. These potential stakeholders include industry scientists and decision-makers, local government representatives, local residents, citizen action groups, national environmental advocacy groups, and national industry advocacy groups. Some issues with which they may be concerned include the number of people exposed, the range of uncertainty around the exposure estimates, the critical variables driving the assessment, the existence of data gaps, the bottom-line conclusion, whether the risk characterization supports a regulatory decision, and whether the risk assessment has been peer reviewed as well as the quality and thoroughness of the peer review. The economic and social ramifications of the risk assessment require that the risk characterization communicate the results clearly, highlighting the important issues and uncertainties, and exploring their implications for different audiences. The

emphasis in the risk characterization process should be on clarity of communication, transparency in decision making, consistency of policy, and reasonableness of the assumptions incorporated into the assessment (U.S. EPA, 1995c).

10.4.2. Risk Estimation. This section discusses how exposure estimates developed with this document can be used to estimate risk. Risk is the result of a combination of hazard and exposure. For chemical pollutants emitted from combustors, the hazard is a property of the pollutant and exposure results from contact with the pollutant (Presidential/Congressional Commission on Risk Assessment and Risk Management, 1997). Risk can be ascribed to individuals, populations, or defined subgroups of a population (U.S. EPA, 1992a, 1995b). Individual risk, on the other hand, is the risk accruing to an individual represented by a defined exposure scenario. Section 10.4.2.1. describes how to calculate the individual risk associated with a given scenario for both carcinogens and noncarcinogens. This section also discusses how to incorporate results from a direct inhalation exposure analysis into the calculation of individual risks.

Different exposure scenarios will lead to different levels of estimated risk. In addition, stochastic variation inherent in most input parameters of the methodology will contribute further variation. As a result, individual risks will be distributed within any exposed population. Section 10.4.2.2. discusses ways to represent the variability inherent in individual risk estimates.

Population risk is the aggregate risk experienced by the exposed population; it may include estimates of the number of individuals expected to be affected during a specified period of time or estimates of the distribution of risks to specific subgroups. It takes into account not only the risk associated with the various scenarios, but also the number of people represented by each scenario. Estimation of population risk is discussed in Section 10.4.2.3.

Risk can also be determined for specified subgroups within the exposed population. The subgroup of interest may be highly exposed, highly susceptible, or both. Once identified, the subgroup can be treated as a population in itself, and

individual and aggregate risks (i.e., risk incorporating consideration of subgroup size) for the subgroup can be determined. Issues associated with estimation of risk to specific subgroups are discussed in Section 10.4.2.3.1.

10.4.2.1. Calculation of Individual Risk — Individual risk is the risk accruing to an individual in a defined exposure scenario. Individual risk is calculated differently for noncarcinogenic toxicants than for carcinogens. The different treatment follows from assumptions made regarding the mechanisms by which these effects are exerted. Noncarcinogens are assumed to operate by threshold-dependent mechanisms. Carcinogens, by contrast, are generally assumed to operate by a linear (nonthreshold) mechanism, although EPA methodology is flexible enough to accommodate nonlinear mechanisms of carcinogenicity, and even those with apparent thresholds.

For estimation of risk to noncarcinogens, TDI (or the CE, if the latter were calculated) is compared with the RfD to characterize the risk to human health. For carcinogens, TDI is used to estimate excess carcinogenic risk. The excess risk (ER) is derived from the daily incremental dose of the contaminant above the background dose and the human cancer risk factor as established by U.S. EPA methods . It is defined as the incremental upper bound lifetime cancer risk above background to a hypothetical population in which all individuals are continuously exposed to a concentration equal to the daily intake of the contaminant. For example, an ER of 10^{-6} means that lifetime exposure to that specific concentration (or administered dose) would produce an upper-bound excess cancer risk of one in a million.

Exposure to members of a chemical class or a chemical congener may be estimated from emission data using the proportion of the total mass of the chemical class that the congener comprises. Unless congener-specific data are available, all of the congeners of the chemical class (e.g., PAHs or PCBs) are typically assumed to have the same environmental transport characteristics. Furthermore, for the purposes of risk assessment, the congener is assumed to comprise the same proportion of the total chemical class in deposition, soils, plants, and animals as it does in emissions. This allows estimation of exposure to the congener as well as to the total chemical

class. Potential health effects resulting from exposure to the congener or the chemical class can be evaluated using the RfD or cancer risk slope for the congener.

Although the focus of this methodology is to quantify exposure to combustor emissions by indirect routes and characterize the resulting risk, the reality is that individuals in the exposed population will also receive direct inhalation exposures. Results from direct inhalation exposure analysis can be incorporated into the calculation of individual risk for both carcinogens and noncarcinogens.

10.4.2.1.1. Noncarcinogenic Toxicants. For noncarcinogenic toxicants, risk is assessed by comparison of TDI (or the CE) with the RfD. This is done by calculating a hazard quotient (HQ), as follows:

$$HQ = \frac{TDI}{RfD} \tag{10-10}$$

where:

- HQ = hazard quotient (unitless)
- TDI = total daily intake (mg/kg-day)
- RfD = reference dose for oral exposure (mg/kg-day)

For a chemical like cadmium that has separate RfDs for food and water vehicles, a hazard quotient can be determined according to the following equation (if the vehicle-specific RfDs are not based on portal-of-entry effects):

$$HQ = \sum_{k=1}^m \frac{TDI_k}{RfD_k} \tag{10-11}$$

where:

- HQ = hazard quotient for m exposure vehicles, k (unitless)
- TDI_k = total daily intake by k th vehicle (mg/kg-day)

$RfD_k =$ reference dose for oral exposure by k th vehicle (mg/kg-day)

The RfD (or subchronic RfD) used to calculate the HQ should correspond to the duration of exposure in the scenario being considered. If exposure to the contaminant from sources other than the combustor is important, then the CE should be used to calculate the HQ for risk estimation.

The HQ merely expresses the exposure relative to the RfD and, by itself, says nothing about risk. Expectations of risk are dependent on the nature of the RfD, particularly on the magnitude of the total uncertainty factor (UF). That is, the RfD does not represent the same level of risk in every case. The RfD could be several-fold lower than the population threshold or it could be associated with a finite risk, perhaps as high as 10%. The primary indicators of the plausible risk at the RfD are the size of the population studied and the magnitude of the UF. Small studies imply greater residual risk at the NOAEL, simply as a result of sample size uncertainty. A smaller UF implies a smaller margin of protection. That is, as each individual uncertainty factor is assumed to be protective, multiplicative combinations of uncertainty factors provide a greater *relative* level of protection. As an example, a risk assessor may be more concerned with an HQ of 1 for nitrate with a UF of 1 (and a LOAEL less than 2-fold higher than the NOAEL) than an HQ of 10 for dichloropropene with a UF of 10,000. Furthermore, the risk embodied in the HQ refers only to the potential that some individuals may be affected and cannot address the absolute level of risk simply because the RfD is not expressed in terms of risk levels.

The HQ reflects the level of concern associated with exposure to a single contaminant. However, combustor emissions will generally contain a mixture of many contaminants. It will usually be desired to assess risk associated with exposure to the emissions as a whole. In practice this means that the risks associated with exposure to the individual contaminants will be summed to produce an estimate of risk posed by the mixture (U.S. EPA, 1989). The simplifying assumption of additivity among emission constituents fails to take into account potential synergistic and antagonistic interactions

among constituents, but is neutral with respect to conservativeness (U.S. EPA, 1986c). The risk associated with a mixture of contaminants is calculated as the hazard index (HI):

$$HI = \sum_{i=1}^n HQ_i$$

(10-12)

where:

- HI = hazard index for mixture of n chemicals (unitless)
- HQ _{i} = hazard quotient for i th chemical (unitless)

The guidelines for adding risks across chemicals are included in the Guidelines for the Health Assessment of Chemical Mixtures (U.S. EPA, 1986c) and RAGS (U.S. EPA, 1989). Strictly speaking, it is appropriate to sum risks across noncarcinogenic chemicals only when those chemicals act on the same target organ by the same mechanism of action. In practice, however, as an initial screening method it is acceptable to calculate an initial HI based on all chemicals of concern in the combustor emissions (U.S. EPA, 1989). If this initial HI is less than 1, then intake of the mixture by indirect routes is not expected to present a health hazard. If the initial HI is 1 or more, then HQs for the chemicals of concern should be segregated according to target organ of the chemical and (if sufficient data are available) mechanism of action, and target-based HI values calculated. A target-based HI of greater than 1 may or may not indicate a potential health risk due to indirect exposure to the mixture. Interpretation of the HI is, again, dependent on the nature of the RfD for each component of the mixture.

10.4.2.1.2. Carcinogens. For chemicals classified as carcinogens and assumed not to exhibit a threshold, the ER due to indirect exposure to combustor emissions may be determined using Equation 10-13 (if risks are estimated to be below 0.01) or 10-15 (any risk level) (U.S. EPA, 1989):

$$ER = TDI \cdot CRF \tag{10-13}$$

$$ER = 1 - e^{-(TDI \cdot CRF)} \tag{10-14}$$

where:

ER = excess risk due to indirect exposure to a contaminant (unitless)

TDI = total daily intake of contaminant by indirect routes (mg/kg-day)

CRF = human cancer risk factor for contaminant (mg/kg-day)⁻¹

ER is the unitless probability of an individual developing cancer from indirect exposure to combustor emissions. Because cancer risk factors are typically derived as upper 95th percentile values, ER as calculated above will generally be an upper bound estimate of risk (i.e., the true risk is not likely to exceed ER and will probably be lower).

Background exposures are not taken into account when calculating ER because ER is an expression of incremental risk due to the facility and not an expression of total carcinogenic risk. It may be useful, however, to compare background exposure risks with TDI to determine the fraction of exposure to a given carcinogen that is contributed by the facility.

Equations 10-13 and 10-14 calculate ER for a single contaminant. However, combustor emissions are mixtures of many contaminants. In order to calculate ER for a mixture of contaminants, the estimates of ER for the individual mixture constituents are summed as follows (U.S. EPA, 1989):

$$ER_{Mix} = \sum_{i=1}^n ER_i$$

(10-15)

where:

ER_{Mix} = excess risk due to indirect exposure to combustor emissions for a mixture of n chemicals (unitless)

ER_i = excess risk for i th chemical (unitless)

This calculation is an approximation because it does not take into account the joint probabilities of the same individual developing cancer from two or more carcinogens. It is appropriate for use in cases where ER_{Mix} is less than 0.1 (expected to be the vast majority of cases). See U.S. EPA (1989) for guidance when ER_{Mix} exceeds 0.1. This approach assumes independence of action by the carcinogens in a mixture (i.e., it is assumed that no synergistic or antagonistic interactions occur between mixture constituents). Other limitations are discussed in the Guidelines for the Health Assessment of Chemical Mixtures (U.S. EPA, 1986c) and RAGS (U.S. EPA, 1989).

The fate and transport of individual pollutants is modeled individually. Elevated concentrations of individual pollutants may impact the fate and transport of other emitted pollutants. For example, two metals may compete for the same binding site of a given cell; one metal may be preferentially taken up at the receptor to the exclusion of the second, or the mixture of both metals may result in a reduced uptake of each. This is considered an uncertainty in this model.

10.4.2.1.3. Incorporating Results from a Direct Exposure Risk Analysis.

Although the focus of this methodology is to quantify exposure to combustor emissions by indirect routes and characterize the resulting risk, the reality is that individuals in the exposed population will likely also receive direct inhalation exposures. Following is a brief presentation of how risk from direct inhalation exposure to carcinogenic and noncarcinogenic combustor emissions can be quantified and subsequently added to

the risks accruing from indirect exposure. This discussion is included for illustrative purposes only; it is not meant to be a complete discussion of this issue.

The air models discussed in Chapter 3 calculate long-term average ambient air concentrations. For the purposes of estimating direct inhalation risk, it is important that the ambient air concentrations of the pollutant represent the sum of *both* the vapor phase and the fine particulate phase (i.e., the sorbed phases). This was discussed in Chapter 3. Except as noted below, the combined vapor and particulate phase concentrations should generally be used directly for estimating risk.

For carcinogens, the inhalation risk is best computed by multiplying the compound specific inhalation unit risk (IUR) by the average (over the exposure period) concentration of the contaminant in air at the point of exposure. This procedure is illustrated in Equation 10-16:

$$ER = IUR \cdot C \tag{10-16}$$

where:

ER = excess risk due to direct inhalation exposure to a contaminant (unitless)

IUR = inhalation unit risk for contaminant (mg/m³)⁻¹

C = average ambient air concentration of contaminant (mg/m³)

For noncarcinogens, risk is estimated using the hazard quotient (HQ), as follows:

$$HQ = \frac{C}{RfC} \tag{10-17}$$

where:

HQ = hazard quotient (unitless)

- C = average ambient air concentration of contaminant (mg/m³)
RfC = reference concentration for contaminant (mg/m³)

Interpretation of the HQ was discussed in Section 10.4.2.1.1.

The ER (carcinogens) or HQ (noncarcinogens) from direct inhalation of a contaminant can be added to those accruing from indirect routes to obtain an estimate of overall risk associated with exposure to the contaminant from combustor emissions.

In general, the ambient air concentration (which should include both particulates and vapors, as stated before) should not be adjusted in order to calculate the inhalation risk, unless the particle sizes are greater than approximately 10 microns. Below this size, particles are considered inhalable and represent an inhalation exposure. Above this size the particles are considered non-respirable (U.S. EPA, 1994b Appendix G; Kennedy and Trochimowicz, 1984). In general, only fugitive dust emissions or resuspended dust (e.g., from mechanical disturbance of soil) would be expected to have a significant particle component in the size range larger than 10 microns. If significant exposures to particles much larger than 10 microns are projected to occur, then the portion of the ambient air concentration represented by particles above 10 microns should be considered along with other oral exposures for the purpose of estimating risk.

10.4.2.2. Distributions of Individual Risk — Individual risk is the risk accruing to an individual in a defined exposure scenario. A given population may include individuals described by any number of different exposure scenarios. Each of these scenarios will be associated with a different level of risk. In addition, the stochastic variation inherent in most input parameters of the methodology will lead to further variation in risk estimates. There will, therefore, be a distribution of individual risks within any exposed population.

In order to capture the variability of individual risk within the exposed population, individual risk is determined for both central-tendency and high-end portions of the distribution (U.S. EPA, 1995b). Central-tendency estimates are estimates of risk for

persons in the middle of the risk distribution, and as such generally reflect central estimates of exposure. Central tendency is best estimated by the median (50th percentile). For normally distributed data, the arithmetic mean is also an appropriate estimator of central tendency, because it corresponds to the median in this distribution. Similarly, for log-normally distributed data, the geometric mean is an appropriate estimator of central tendency because it corresponds to the median of the distribution.

The central-tendency estimate may be derived in a number of different ways (U.S. EPA, 1995b). If complete information on the population distribution of exposures is available, then the median value can be taken directly from the distribution and used to calculate risk. If this information is not available, but sufficient data are available regarding variability in the exposure parameters, then the distribution of exposures can be estimated using probabilistic modeling techniques, such as Monte Carlo analysis (see Section 10.5.2.). Alternatively, the central-tendency exposure can be satisfactorily estimated by using central-tendency estimates (preferably medians) for all input parameters in the exposure model (even though this may not correspond to any actual exposure scenario in the exposed population).

High-end estimates are plausible estimates of the individual risks for persons at the upper end of the risk spectrum (U.S. EPA, 1992a). They are used to convey estimates of risk in the upper range of the distribution while avoiding estimates that are beyond the true distribution. The upper 90th or 95th percentile of the risk distribution is generally used. The high-end estimate may be derived in different ways, depending on the amount of data available (U.S. EPA, 1995b). If complete information on the population distribution of exposures is available, then the upper 90th or 95th percentile value can be taken directly from the distribution and used to calculate risk. If this information is not available, but sufficient data are available regarding variability in the exposure parameters, then the distribution of exposures can be estimated using probabilistic modeling techniques, such as Monte Carlo analysis (see Section 10.5.2.). If data are not adequate to perform Monte Carlo analysis, the high-end exposure can be estimated by using high-end exposure estimates for a few of the most sensitive input

parameters and central-tendency estimates for the remainder. Using high-end estimates for all parameters would be expected to push the estimate beyond the high end of the true distribution (U.S. EPA, 1995b). The choice of high-end exposure estimates should be internally consistent; for example, the same individual should not be assigned high-end food intake and low body weight.

Exposure estimates representative of central tendency and high end in the exposed population, derived as described above, should be entered into the equations of Section 10.4.2. to estimate the central-tendency and high-end risks of individuals in the exposed population. Because the cancer risk factor (or unit risk) used to calculate risk will be an upper bound for most chemicals, these are estimates of the upper-bound risk for the given exposure levels.

10.4.2.3. Population Risk — Population risk refers to the aggregate risk to the exposed population. It takes into account not only the risk associated with the various exposure scenarios, but also the number of people represented by each of the scenarios.

Population risk is estimated differently for carcinogens and noncarcinogens (U.S. EPA, 1992a, 1995b). For carcinogens, there are two general approaches that can be used. One is to simply sum the individual risks for all individuals within the exposed population. If individual risk has not been determined for all members, then this quantity can be approximated by multiplying the average individual risk by the population size. This produces an estimate of the upper bound on the probabilistic number of cancer cases in the population of interest over a specified time. Note that this is not the same as an actuarial prediction of cases in the population, which is a statistical prediction based on a great deal of empirical data.

An alternative way to estimate population risk for carcinogens is to base the estimate on the amount of contaminant entering the food supply per year. This approach is probably most practical for pathways involving ingestion of locally produced food. This would involve estimating the annual amount of food produced in various growing regions within the study area, computing the contaminant level in the

food from each growing area, and adding up the products of contaminant concentration and the amount of food produced for each growing region. The population risk is computed as follows:

$$\text{Population Risk} = \frac{\text{CRF} \cdot \text{Ds}}{\text{BW} \cdot \text{L}_d} \sum_{i=1}^n (\text{FP}_i \cdot \text{Cf}_i)$$

(10-18)

where:

- CRF = cancer risk factor (mg/kg-day)⁻¹
- Ds = duration of exposure scenario (years)
- BW = body weight (kg)
- L_d = lifetime (years)
- n = number of growing regions (unitless)
- FP_i = average annual food production in growing region i/365 days per year (kg/day)
- Cf_i = contaminant concentration in food from growing region i (mg/kg)

This approach assumes that all food produced in the study area is consumed (at any location inside or outside the study area) and that all resulting individual risks are in the linear range of the dose-response curve (i.e., directly proportional to the amount consumed). A similar approach could also be followed for the dairy products ingestion and fish ingestion pathways, if dairy farming and fishing (recreational, subsistence, commercial) are important activities in the study area.

Either approach to estimating population risk yields the number of incremental cancer cases expected to occur in the population over a 70-year period. The second approach has the advantage of accounting for exposure that may occur as a result of exporting food outside of the study area. However, neither approach accounts for the exposure/population risk that may occur from contamination of food produced outside of the study area. Although the individual risks outside the study area may be below

levels of concern, the population risks could be important if significant long-range transport occurs. This issue can be evaluated by examining how much of the emitted contaminant is deposited in the study area. If 90% of the contaminant is deposited in the study area, then for carcinogens approximately 90% of the population risk is accounted for. However, long-range transport and impacts of incinerator emissions are not well understood; the local vs. long-range impacts may not be linearly proportional to the relative amounts deposited.

As stated previously, neither approach accounts for exposure and risk from outside the area. To account for this, the second approach may be slightly modified using the commodity-shed approach described previously. This approach may provide a better estimate of exposure for areas that are net local importers of select commodities because it provides an estimate of exposure from outside the area. For example, within a given 50-km radius around a combustion source, assume there is only a single commercial beef farm and the quantity of beef produced on the farm is much lower than the total amount of beef consumed by the local population. For pollutants that do not exhibit a threshold, the population risk can be estimated by summing individual risks for all members of the population. The product of the slope factor, arithmetic mean of the exposure, and population size will also serve as an estimate of risk.

Characterization of the population risks posed by threshold-acting pollutants may be accomplished through comparison of the population exposure range with the threshold level. The number of individuals in the population exposed above the specified level of risk (e.g., RfD or LOAEL) is sufficient to estimate population risk. For example, population risk can be characterized in terms of the number of individuals estimated to have an HQ (or HI for a mixture of chemicals) greater than 1 based on chronic (or subchronic, if desired) exposure (U.S. EPA, 1992a, 1995b). This range of predicted individual exposures occurring within the population can be determined using the commodity-shed approach.

10.4.2.3.1. Subpopulations of Special Interest. Risk can be determined for specified subgroups within the exposed population. Particular subgroups may be of interest because they are highly exposed, highly susceptible, or both (U.S. EPA, 1995b). A highly exposed subgroup is one that receives significantly higher exposure than the larger population. For example, subsistence fishermen would represent a highly exposed subgroup for a contaminant that accumulates in fish. A highly susceptible subgroup is one whose members are more sensitive to the toxic effects of the contaminant than are other members of the population. For example, pregnant women may be a highly susceptible subgroup for many contaminants. An example of a subgroup that is both highly exposed and highly susceptible might be young children exposed to environmental lead.

A particular subgroup may be selected for further analysis based on *a priori* interest or as a result of discovery during the assessment process. Once identified, the subgroup can be considered as a population in itself. Individual and aggregate risks for the subgroup can be determined using the methods presented in Chapter 2, treating the subgroup as the entire population.

10.5. UNCERTAINTY AND VARIABILITY IN THE RISK CHARACTERIZATION

The previous section described how to calculate numerical estimates of risk associated with the modeled indirect exposure to combustor emissions. This section will discuss how to integrate these estimates with qualitative information derived from the modeling exercise in order to produce the risk characterization. The purpose of the qualitative component of the risk characterization is to put the quantitative component in its proper context. Discussion of confidence in the risk estimate, including major uncertainties, limitations, and assumptions and their influence on the assessment is essential to ensure appropriate interpretation of the numerical risk estimate (U.S. EPA, 1992b, 1995b,c).

The qualitative component, therefore, consists of a discussion of the strengths and weaknesses of the quantitative risk estimate, based primarily on evaluation of uncertainty. It is important to distinguish here between variability and uncertainty.

Variability arises from true heterogeneity in characteristics within a population (U.S. EPA, 1995b). Variability is an inherent trait of the population being studied and cannot be reduced by improvements in risk assessment methodology. The risk assessor should make sure that the existing variability is adequately represented in the risk characterization. Use of multiple descriptors of risk and, in particular, both central-tendency and upper-percentile estimates of individual risk (discussed in Section 10.4.2.), is intended to capture the variability present in the population being studied. Distributional analyses using tools such as Monte Carlo techniques may be useful in assessing the impacts of population variability, if scientifically justified.

By contrast, uncertainty represents lack of knowledge about the true value of a risk estimate (U.S. EPA, 1995b). Imprecise measurement techniques, sampling error, use of models, and use of assumptions to bridge data gaps all contribute to uncertainty. Uncertainty can be reduced by additional study. Monte Carlo analysis and comparable probabilistic modeling procedures can be used to analyze the uncertainty associated with a particular risk estimate. More limited information regarding uncertainty can also be obtained by other methods, such as incorporating mass-balance checks in fate and transport models.

By incorporating critical information regarding uncertainty, the risk characterization synthesizes an overall conclusion about risk that is complete, informative, and useful for risk managers and other decision makers (U.S. EPA, 1992b, 1995c). It also presents a clear and transparent basis for communication of the results of the risk assessment with the public and concerned stakeholders (U.S. EPA, 1995c).

10.5.1. Sources of Uncertainty. There are numerous sources of uncertainty in the risk assessment process (U.S. EPA, 1992a, 1995a,b). One source that is especially relevant to the Indirect Exposure Methodology presented is the use of models. This methodology makes extensive use of models to predict the fate and transport of chemicals in the environment. Uncertainty in a model is an inverse function of the demonstrated accuracy of its predictions. Evaluations that assess the accuracy of model predictions through comparison with real-world data are the primary means of

addressing this type of uncertainty. Validation exercises have been conducted for portions of the Indirect Exposure Methodology, and the results were presented in Chapter 11. An alternative way to gauge model uncertainty is to compare the model in question to other models that have been developed. Owing primarily to the paucity of suitable data with which to test model validity, there remains substantial uncertainty associated with use of the models of this document.

Another important source of uncertainty is the use of assumptions to bridge data gaps. This methodology is data intensive and relies heavily upon use of site-specific data. It is anticipated that appropriate data will frequently be unavailable and that, in many cases, resources will not be adequate to allow for the collection of additional data. Therefore, default values have been supplied for most of the input parameters. Rationale for these values, including all assumptions made and sources of relevant data used as the bases for these values, are presented in the appropriate chapters of this document. Although the use of these defaults enables a risk assessor to estimate indirect exposure using minimal data, it also adds uncertainty to the estimate. To the extent that the risk assessor can replace the defaults with more site-related assumptions or, ideally, site-related data, uncertainty will be reduced accordingly. Any assumptions used in place of defaults should be explained in full, including sources and general logic used in the derivation.

Even in situations where data are available, there is uncertainty associated with the results. The quantity, quality, and representativeness of the data all influence the uncertainty associated with use of the data. Even the highest quality data will be accompanied by some degree of error because scientific measurements are inevitably made on a sample taken from a study population rather than on a complete population. Sampling error of this type can be addressed by standard statistical techniques, but all uncertainties associated with data used in the models should be fully described.

The models described in this methodology can be divided into groups; the assumptions, variability, and uncertainty in each group can then be evaluated separately. The groups include the following: Emissions or Source Term, Atmospheric

Dispersion and Deposition, Terrestrial Fate, Aquatic Fate, Exposure Estimate, Estimate of Size of Exposed Population, Dose-Response, Modeling, and finally, Identification of Sensitive Subpopulations.

10.5.2. Quantitative Evaluation of Uncertainty. Probabilistic modeling techniques provide powerful tools for estimating overall ranges of uncertainty associated with calculated risk estimates, and for examining the influence of particular assumptions, input values, or pathways on the overall results. Occasionally, for simple multiplicative models, an analytic approach can be taken by assuming that all inputs are lognormal (Slob, 1994). The analytic approach is convenient in that determination of output distribution percentiles does not require the use of random sampling techniques, such as Monte Carlo. Another analytic approach that may be useful for estimating the central tendency and one or two “upper bounds” of the output is discrete probability calculus, which can be used to estimate joint variability and uncertainty (Bogen, 1995); this method, however, does not give distribution percentiles, but averages of selected portions of the distribution. An intermediate approach is stochastic response-surface analysis, which combines aspects of the analytic approach and random-sampling techniques (Isukapalli et al., 1998); this approach may be of use for very large and complex models where computing resources become limiting. In most cases, however, a complete Monte Carlo analysis will be required to estimate the distribution of model outputs.

Furthermore, an attempt should be made to characterize uncertainties in a probabilistic fashion even when data are minimal. This almost always involves judgment, which means that there will be a subjective component in most uncertainty distributions. Subjective probability can be dealt with by using Bayesian techniques or fuzzy sets (Zadeh, 1984); a discussion of these approaches, however, is beyond the scope of this document. Subjective probability can also be characterized in a frequentist manner, much the same as for natural variability, as long as the subjective nature of the distribution and its impact on the overall result are clearly presented. Often, uncertainty in the value of a specific characteristic for an individual is

represented by the variability in the population. That is, the individual is treated as a random selection from the general population when there is otherwise no information to place the individual in the population distribution.

In the assignment of any uncertainty distribution one should strive to follow the principle of maximum entropy (Shannon, 1949; Jaynes, 1986). This principle, which is based on information theory (Shannon, 1949), in effect says that ignorance ought not to be underestimated and that distributions assigned to any input should not require more information than is available (Boyd and Regulinski, 1979). As an example, the uniform distribution reflects maximum entropy when only minimum and maximum values can be estimated and nothing is known about the relative likelihood of values between the extremes (Englehardt and Lund, 1992). Also, if only a mean value is available, an exponential distribution is the maximum-entropy choice (Tribus, 1969; Englehardt and Lund, 1992). The entropy inherent to any distribution is dependent on the information content of the functional form of the distribution (Rényi, 1955). Formal representation of the information content for most distributions has not yet been developed. The principle of maximum entropy, nevertheless, can be followed in spirit. As an example, it is not hard to see that the information requirement for a log-normal distribution is greater than that for a triangular.

There are at least two alternatives to a full probabilistic characterization of inputs. One option is a nominal range sensitivity analysis. This process consists of varying each input from its low to high value while keeping all other inputs at their nominal values and assessing the impact on the output of the model. The reader is referred to Morgan and Henrion (1990) for a full description of this technique. Another option is the use of partially characterized distributions, in which the assessor need only estimate the expected value and a specific upper (or lower) bound or percentile (Bogen, 1995). This approach simplifies input characterization and provides an analytic solution, eliminating the need for a Monte Carlo simulation yet still providing a probabilistic output. A presentation of the details of this approach is beyond the scope of this document. The reader is referred to Bogen (1995), who presents two different

methods for performing this kind of analysis with specific attention to the consideration of joint uncertainty and variability.

An alternative to probabilistic modeling for quantitative evaluation of uncertainty is to conduct mass balance checks. Although mass balance analyses will not provide detailed information regarding uncertainty, they will allow the risk assessor to gauge the reasonableness of model predictions and thereby address some of their inherent uncertainties.

10.5.2.1. Probabilistic Modeling Techniques — Probabilistic modeling techniques, such as Monte Carlo and Latin Hypercube assessments, are generic statistical methods that generate a distribution for an output of a mathematical model using the distributions of the input variables. Computer simulations are used to repeatedly generate outputs based on parameter inputs, where values for parameters are selected from their distributions. The outputs are compiled and expressed as a frequency distribution. In the context of exposure assessment, for example, a Monte Carlo application could involve developing distributions for each of the parameters in the exposure equation and generating a distribution showing how the exposure levels vary in the exposed population. The final distribution can be interpreted as the probabilities of one individual (randomly selected from the exposed population) experiencing various exposures. Since exposure levels are a function not only of the exposure parameters but also of the concentration in exposure media, another application of the Monte Carlo method would be to estimate the distribution of exposure media concentrations using mathematical models for fate and transport.

Monte Carlo and related methods are used for analysis of both uncertainty and variability. As noted previously, uncertainty results from lack of knowledge about the true value of a parameter, whereas variability is the change in a parameter value across a population or situation. The same parameters can have elements of both uncertainty and variability. For example, the contaminant concentration in soil can be uncertain because of measurement or modeling error and spatially variable because of

differences in deposition at various locations. Distinction between these elements can be made in a variety of ways.

The probabilistic assessment of joint uncertainty and variability in the exposure assessment can be dealt with by at least two different techniques. The simplified 2-point distributional characterization of inputs (Bogen, 1995) has been mentioned previously. Another approach is a two-dimensional Monte Carlo analysis (e.g., Keenan et al., 1995). In the framework of Monte Carlo simulation, the impacts of uncertainty and variability can be systematically addressed using a two-dimensional or nested loop simulation approach. As in any Monte Carlo assessment, analytic (closed-form) distributions, with user-specified parameters, are applied to the input variables. In the two-dimensional approach, the parameters of these distributions are themselves assigned distributions, which represent the uncertainty in the parameters. The outer loop addresses the uncertain parameters and applies the user-specified probability models to make random selections for these terms. For a given selection of the uncertain parameters, the inner loop allows all of the population exposure variables to vary, and a distribution of population exposure or risk is obtained. When this process is repeated for other selections of the uncertain variables, a family of curves representing potential distributions of risk in the population is obtained. These results can then be applied, for example, to estimate the fraction of the population with exposure above a specified level and to establish error bounds on this fraction. This approach requires developing distributions of uncertainties, in addition to population variability, and can be quite difficult. In cases where statistically based survey or measurement data are available, statistical likelihood functions may be used to allow a non-subjective quantification of uncertainties. However, such data are frequently lacking. Otherwise, it may be possible to select distributions via professional judgment, but the assessment should clearly state that the outcome is largely dependent on judgment used to develop the distributions.

An alternative to the double-looping approach is to use sensitivity analysis to demonstrate uncertainty and approximate error bounds. The distinction between

uncertainty and variability should be clearly shown in the final display of a distribution generated from a Monte Carlo simulation. For example, uncertainty bands can be drawn around the distribution of variability.

Special care must be taken when variables are dependent on one another or when the same variable appears more than once in the formula. In the former case, some variables may be correlated. That is, one variable may co-vary with another, such that high values for one variable are associated with high values of another (positive correlation) or with low values for the other (negative correlation). In the absence of evidence to the contrary, variables are usually assumed to be independent. Strong correlations between sensitive variables (those that contribute more to the variance of the output), however, will have a fairly large effect on the output distribution, so particular attention should be given to identifying theoretical or empirical correlations. Where dependencies can be quantitatively described, a useful approach is to determine a distribution for one variable and use values from this distribution to compute the second variable (using a conditional distribution for the second variable given knowledge of the first variable). When the same variable appears more than once in the formula, the assessor must ensure that the same value is used for each instance. If multiple assignments are inadvertently made, they will inappropriately alter the shape of the resulting probability distribution.

It is often difficult to find appropriate distributions for Monte Carlo assessments. One problem is that distributions derived from national data may not represent local conditions. To the extent possible, distributions or frequency histograms derived from local surveys should be used. When distributional data are drawn from a national or other surrogate population, it is important that the assessor address the extent to which local conditions may differ from the surrogate data. In addition to a qualitative statement of uncertainty, the representativeness assumption is appropriately addressed as part of a sensitivity analysis.

Another problem is that many surveys (both local and national) addressing issues such as food consumption were conducted over a short time period for each

respondent and, therefore, may not represent long-term trends (the respondents' usual behavior). Generally, environmental risk assessments for chronic health effects address risk as a function of the long-term average exposures of individuals, and thus are most appropriately conducted using data on long-term average, "usual" behavior. Similar problems arise when distributions of concentration data arise from short-term monitoring periods or when factors such as soil ingestion are measured using protocols of only several days.

Finally, values near the tail of a distribution may be especially sensitive to the form of distribution selected. Tails of many commonly used distributions extend to infinity. The assessor should consider using empirical distributions when substantial data are available, or infinite-tail distributions truncated at plausible bounds.

Probabilistic techniques can be a powerful tool for evaluating variability and uncertainty in exposure assessments. The results, however, can be misleading unless careful attention is paid to the distinction of variability and uncertainty, to the qualification of the data and theoretical concepts used to define both types of distributions, and to the interrelationships among the input variables. The risk assessor must provide an adequate description and justification for the form and parameterization of each distribution used in the analysis. Confidence in the Monte Carlo analysis is directly related to confidence in the distributions used.

Examples of the use of probabilistic modeling techniques in the analysis of uncertainty and variability in exposure assessment include studies by Belcher and Travis (1989), McKone and Ryan (1989), McKone and Bogen (1991), Burmaster and Stackelberg (1991), Anderson et al. (1992), Paustenbach et al. (1991, 1992a,b), Cullen (1995), and Keenan et al. (1995). The study by Keenan et al. (1995) includes use of a nested-loop approach to characterize uncertainty and variability separately.

10.5.3. Mass Balance Checks. Mass balance checks can be used as a means of evaluating some aspects of uncertainty in the modeling. A mass balance would be violated, for example, if the mass of contaminant estimated to enter a medium (e.g., soil) exceeds the mass being emitted from the stack. The ISC3 air emissions model is

designed on mass balance principles, and therefore should not lead to impossible air concentrations or deposition rates that exceed emission rates. Depositions are subtracted out of the airborne reservoir of particle-bound contaminants as the depositions occur. However, some of the media transfer models, which use the output from the air models, are based on simple transfer/partitioning approaches, which do not have built-in mass balances. If these models are properly parameterized, then the possibility of meaningful mass balance violations is minimized. This is discussed below. However, it is generally recommended that risk assessors make mass balance checks to ensure that reasonable predictions are being made. These checks can be made in various ways. One way is to compare estimates of the amounts of contaminant in the various media (i.e. soil, vegetation, and biota) within the study area (i.e., the area within the outer isopleth boundary, as described in Chapter 2) to the amount emitted from the stack. Comparable time frames must be used. For example, the amount of contaminant in the beef annually produced from the study area should not exceed the amount of contaminant emitted during the year (except in an unusual circumstance where a large cattle ranch begins operation within the study area several years after incineration begins, and accumulation in the environment to that point could lead to large withdrawals by the cattle initially). In addition to fate and transport mass balance transfer, one should also be aware of mass balance violations when estimating exposures from given media concentrations. For example, the amount of impacted beef ingested by populations in the study area should not exceed the amount of beef produced in the study area.

Because the fate and transport and the food chain algorithms do not contain built-in mass balance checks, mass balance violations could occur. Contaminants estimated to be deposited onto soils partition between a sorbed phase and a dissolved phase. Transfers occur into below-ground and above-ground vegetation with a biotransfer factor. Bioconcentration factors take concentrations in one medium (e.g., water concentrations), and translate them to a concentration in another medium (e.g., fish). In this simple framework, mass balances are considered but are not rigorously

maintained. For example, soil-to-plant transfers are not explicitly modeled as a loss for soil concentration estimation. However, there is an overall loss constant for the soil concentration algorithm, which explicitly considers leaching, erosion, runoff, degradation, and volatilization. The loss via plant uptake could be estimated and added to the degradation rate constant; otherwise, plant uptake loss is not explicitly considered.

There are other examples where exchanges between media and sinks are not rigorously modeled. However, this particular type of theoretical mass balance issue is not normally expected to be a fatal flaw for any contaminant evaluated. First, dissipation from key media is modeled with loss rate constants; these key media include soils, vegetation, and surface waters (water column and benthic sediments). Guidance has been presented for proper parameterization of these dissipation factors. Second, all transfer and bioconcentration parameters have been empirically developed from appropriate data sets; these key transfer factors include soil and air to plants, plants to animals, and aquatic media concentrations (water or sediment) to fish. These empirical factors are, by design and definition, approximations of observed phenomena.

Another type of mass balance violation could occur with improper parameterization. For example, the aquatic impact requires the methodology user to estimate the land area draining into an impacted water body as well as a contaminant deposition rate that represents depositions over that entire area. If one selects a deposition rate that would occur at the point of maximum deposition (e.g., within a few hundred meters of the stack) as representing deposition over a drainage basin that is millions of square meters in area, or one estimates a drainage basin size much too large for an impacted water body (which is defined in this methodology in terms of flow rates and volumes), one could very easily obtain results that obviously violate mass balance considerations — that an impacted surface water body receives more contaminant over a multi-year period in runoff, erosion, and direct deposition than is emitted from the stack.

Proper parameterization of the model is the key to not violating principles of mass balance. The following are offered as points to consider for mass balance concerns:

- 1) *No parameter is trivial:* All parameters used in the modeling should be presented for others to scrutinize. Careful attention should be paid to the stack emission rate assumed for air transport modeling, as every subsequent media concentration is proportionally related to it. All fate, transport, and transfer parameters specific to the contaminant are important. Ensure that all parameters are in the proper units. If an air concentration is presented to the risk assessor in units of $\mu\text{g}/\text{m}^3$, and the food chain models require units to be in pg/m^3 , then an oversight in converting will result in all media concentrations (i.e., plants, animal food products, and water and fish of the surface water body) being overestimated by a factor of a million.
- 2) *Do reality checks with estimated media concentrations:* This is, of course, easier said than done. It means that risk assessors should evaluate their predicted concentrations with observed concentrations in the literature. If predicted concentrations exceed observations by an order of magnitude, for example, one should very carefully evaluate model input parameters for mistakes. Particularly, if the observed data are from contaminated sites.

10.6. THE COMPLETED RISK CHARACTERIZATION

The completed risk characterization incorporates noteworthy conclusions regarding uncertainty with numerical risk estimates. It is a synthesis of the risk estimation and uncertainty analysis phases of the risk assessment, ultimately yielding an overall conclusion about the resulting risk.

The risk characterization is the mechanism by which the risk assessor will convey his judgment to the risk manager, who will integrate the risk characterization with other considerations (e.g., economic, legal, social) in order to make and justify regulatory decisions (U.S. EPA, 1995b). The risk characterization also forms the basis for communication of risk to the public (U.S. EPA, 1995b). By providing a clear and transparent record of the reasoning that produced the risk assessment, the risk characterization equips stakeholders in environmental issues with sufficient information to evaluate the significance of environmental risks independently. It is critical to both these applications that the numerical risk estimate not be separated from the statement

of confidence, and that the latter include full disclosure regarding the uncertainties embedded in the risk estimate.

The risk characterization should address the “big picture” questions that relate to the analysis. Some important issues that might be addressed include: how well exposures are characterized (e.g., identification and characterization of critical modeling assumptions, strengths and weakness of supporting arguments, availability of analytical measurements of pollutants in environmental media of concern, and comparison of predicted media levels to measured values); effects of location and exposure factors on exposure estimates; the range of exposures predicted for different groups; identification of the most important pathways and routes of exposure for the general, highly exposed, and highly susceptible human populations; identification of the emission constituents that pose the greatest threat to human health; the existence of other local sources of exposure to the pollutants posing the greatest threat; and the relative risk to general, highly exposed, and highly susceptible human populations of combustor emissions in relation to other sources. These are the types of issues with which risk managers and stakeholders are concerned, and the risk characterization should provide them with as much guidance as possible regarding these issues.

The final scientific step of the process involves an evaluation of the risk assessment by scientific peers and a response to their comments. Peer review is an important part of gaining widespread acceptance of the conclusions reached through the risk assessment process. Reviewers can examine and comment on the scientific reasoning as well as the scientific judgments made in the document. It is important that the reviewers are independent and have the appropriate scientific experience. For example, U.S. EPA employs several different levels of external review depending on the importance of the product. Some scientific reports are reviewed by large groups of individuals whose expertise includes health effects assessment, exposure assessment, fate and transport characteristics, and emissions assessment.

10.7. REFERENCES

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APPENDICES

- A. Model Validation
- B. Derivation of Kinetic Breast Milk Exposure Model
Incorporating Breast Feeding Losses
- C. Glossary

MODEL VALIDATION

A.1. INTRODUCTION

The lack of model validation is an issue for essentially all fate and transport models of chemicals in the environment, including those used for multiple-pathway exposures. Therefore, the main purpose of this chapter is to describe efforts to validate the multiple-pathway models, specifically indirect pathways. This effort is limited to the fate and transport models, rather than the exposure models. Further, the exercises presented here are focused on how well the fate models predict observed concentrations. Other ways to evaluate the validity of models include sensitivity analysis, issues of generic predictability, and the qualitative reliability of the observed data sets referenced (it will be assumed that the published data described in this chapter are valid). Finally, it should be understood that model validation is an ongoing process and the exercises in this chapter are by no means expected to establish model validity beyond any doubt. Users of this methodology are encouraged to subject models to any number of tests, validation or otherwise, as they use the models described in this document to conduct indirect exposure assessments.

A.2. OVERVIEW OF MODEL VALIDATION

In this document, the word validation refers to an exercise in which the following holds true:

1. An impacted media concentration is known. A concentration of a contaminant in a medium that can be predicted by indirect fate models, such as a concentration in soil, vegetation, water, sediment, biota, or ambient air, is known through a site-specific monitoring program. Model predictions of these concentrations have often been termed the dependent model results in a validation exercise.
2. The source causing this impact is known. Source-term information has often been called the independent model input in a validation exercise. For example, if the concentration of a contaminant in ambient air represents the known dependent quantity, then the independent, or source, term could be the emissions from one or more tall stacks. Specifically, source-term information would translate to the level of emissions (in units of mass/time such as g/sec) of the particular contaminant from the identified stacks. The

model validation exercise would take these known emissions, put them into an air dispersion model along with other parameters (e.g., stack heights, exit velocities, site-specific meteorological data, etc.), and predict ambient air concentrations. In other model validation exercises, however, the source is likely not going to be incinerator emissions. For example, if underground vegetables were the impacted medium, then the independent source term could be the concentration in the soil in which the vegetables were growing. One could also start with ambient air concentrations. In that case, the air concentrations would be used to predict the soil concentrations, which in turn would be used to predict the vegetable concentrations. In any case, the source term needs to be known and the model user needs to be reasonably certain, or at the very least needs to assume, that the source directly impacts the affected medium.

3. All other model parameters are assigned values using the best available information. Site-specific information is most appropriate, if it is available. Chemical-specific parameters, such as bioconcentration/biotransfer parameters, should be assigned values using information in this document, the companion Parameters Guidance Document, or other literature sources.
4. Model predictions of the impacted media are compared with observations. Once all the parameters are assigned values, the model is run and its predictions of the dependent medium concentration are compared with real-world observations. This is the final step in a model validation exercise.

Model validation needs to be distinguished from model calibration. Calibration exercises, like validation exercises, require real-world measurements of independent source terms and dependent media impacts. What distinguishes the two is that a calibration exercise is conducted in order to determine values for one or more key model input parameters. The model is forced to duplicate the observed data by adjusting the value of key input parameters until this duplication is achieved. As described in step 3 above, in a validation exercise all model parameters are assigned values; none are adjusted to fit the observed data.

An example of a calibration exercise in the realm of indirect exposure modeling is the calibration of the air-to-leaf transfer factor for the vapor phase, B_v , for dioxins and furans reported in Lorber (1995). Air concentrations of these compounds above experimental grass pots were measured, as were the final concentrations in grass harvested after three weeks of growth. All other model parameters necessary for the

prediction of the concentration of dioxins and furans in the grass, including the physical parameters (mass of grass harvested, fresh to dry weight conversion, etc.), vapor/particle partitioning in the air, and particle deposition algorithms, were assigned values based on site-specific measurements or the literature. The B_v was then adjusted until the model predictions of grass concentrations matched the observed concentrations.

This chapter reviews several model validation exercises that have been conducted and published and presents one exercise not otherwise published. The previously conducted validations are for dioxins and furans and were reported in EPA's Exposure Reassessment Document for Dioxin-Like Compounds. This reassessment, when completed, will replace EPA's current draft exposure document on dioxin entitled *Estimating Exposures to Dioxin-Like Compounds* (EPA/600/6-88/005Ca-Cc, June 1994). As it is still under development, it will be referred to throughout this exposure pathways document as the "dioxin exposure reassessment." The fate models described in that document are substantially similar to the fate models of this document; differences in the two approaches will be noted below. Rather than fully duplicate the text from the dioxin exposure reassessment, summaries including final results are presented below. The dioxin document also presents a validation exercise involving nondioxins. This exercise tests the vapor/particle partitioning model on PCBs, PAHs, and organochlorine pesticides, and is duplicated in this chapter as well. The one exercise conducted uniquely for this document is an air-to-plant model validation exercise for PAHs.

A.3. ISSUES IN VALIDITY OF THE AIR DISPERSION MODEL

Air dispersion and deposition analysis is performed using the ISC3 model. The model is intended to give approximate estimations of atmospheric dispersion and wet and dry deposition flux, rather than absolute values. The model predicts future states based on known characteristics of geographical location, local meteorological conditions, temporal rates of emissions, and the physical description of the facility.

Atmospheric dispersion in ISC3 is modeled with the common Gaussian plume method. Downwind concentrations of the contaminants are calculated as a function of stack height, the mass emission rate, the wind speed, and general atmospheric conditions. The Gaussian model assumes that the emission concentrations predicted by the model will fit a normal distribution. The principal assumptions in the Gaussian model are (Kapahi, 1991):

- ! The air concentration of the chemical at a fixed distance from the source is directly proportional to the emission rate from the source;
- ! The air concentration of a given chemical is inversely proportional to the wind speed corresponding to the effective height of release of the chemical into the air;
- ! The predicted ground-level concentration of the chemical approaches zero at large distances from the initial point of release;
- ! The model is steady state;
- ! The model assumes constant wind speed, wind direction, and atmospheric stability over time and space for a given period.

In general, the stochastic features of the Gaussian plume model predict annual average ambient air concentrations of chemical emissions from industrial sources to within one order of magnitude of measured values and, in some cases, within a factor of three to fourfold of field measurements (Cohrssen and Covello, 1989). This modeling error spans both sides of the predicted concentration; that is, the actual concentration may be plus or minus this amount of predicted value. In 1978, the American Meteorological Society published a position paper stating that Gaussian plume air dispersion models should predict average concentrations to within a factor of two in the absence of complicating factors (complex terrain, building effects, etc.) (AMS, 1978). This factor-of-two accuracy is often cited when describing the capabilities of the Gaussian plume model.

EPA undertook an extensive effort to validate the ISC model (the forerunner of the ISC3 model) in 1981 (U.S. EPA, 1981), with particular attention to the validation of

the gravitational settling/dry deposition option and the building wake effects options. Three sets of deposition experiments were used to test the dry deposition algorithm, and three sets of diffusion experiments were used to test the building wake effects option of the model. The details of these validation tests are too extensive to provide here; they can be found in U.S. EPA (1981). Some principal findings and conclusions of this work are:

1) The accuracy of the gravitational dry deposition algorithms generally conform to the factor-of-two accuracy attributed to air dispersion modeling. On average, the ISC model predicted the maximum deposition to within 30 percent for all three data sets. These very positive results were explained in part, however, by the relatively large gravitational settling velocities of the glass microspheres used in one experiments and the larger droplets used in another of the experiments. For these large diameter particles, the effects of atmospheric turbulence were small in comparison to the effects of gravitational settling. The match between predictions and observations was best within 800 meters of the source of release for this reason. Measurements further downwind at beyond 4 kilometers, where the droplets had smaller diameters and their deposition was now dominated by atmospheric turbulence, were not as well matched by the model, although the calculated deposition still showed to be within a factor of 2 of measurements.

2) In testing of the building wake effects, it was found that the building wake effects option significantly improved the performance of the ISC model over that of the corresponding models at the time time, CRSTER and MPTER, that did not have the building wake effects option. The model performance, as measured by ratios of calculated to observed concentrations (RCOs), and root mean square errors, suggest that the fit of predictions and observations was not as good as for the deposition experiments, with a general trend of underpredicting the

concentrations. Still, the RCOs showed that predictions still were mostly within a factor of two, with most RCOs between 0.5 and 2.0. The complexities at each of the three tested sites and the permutations of options tested by U.S. EPA (1981) makes it difficult to generalize further on results.

The most sensitive aspects to variability in modeled predictions of ambient air impacts, if emissions are held constant, are stack height (height of the release), and terrain (flat versus complex topography). To investigate modeling variability, U.S. EPA placed a prototype hazardous waste incinerator in both flat and elevated terrain in geographical areas around the United States (U.S. EPA, 1991; analysis conducted with the Industrial Source Complex, or ISC, model, which was a forerunner of the ISC3 model). The stack height was varied at these locations. Numerous runs were made at 12 specific sites to compare and contrast the influence of stack height and terrain on predicted ambient air concentrations of various emission rates of specific inorganic pollutants. A series of tables were developed from this sensitivity analysis, from which estimates of variability as a function of stack height and terrain can be inferred. When the hypothetical incinerator was modeled in flat terrain (i.e., no topography within a distance of 5 km is above the height of the stack) and the stack height was varied from 4 meters to 120 meters, the variability in the predicted ambient air concentration spanned two orders of magnitude (100). The lower stack height resulted in a predicted ambient air concentration that was 100 times greater than the concentration predicted using the tallest stack height. When the incinerator was located in complex terrain over the same range of physical stack heights, the variability in estimated ground level concentration of the subject pollutant spanned two orders of magnitude (100-fold). In the latter case the stack height was adjusted for terrain by subtracting from the physical stack height the influence of terrain on plume rise. From this limited analysis, it can be assumed that the predictions of spatial ground-level ambient air concentrations of contaminants in general could span two orders of magnitude, depending on changes in stack height or terrain.

The most uncertain aspect of the modeling is the estimation of dry- and wet-deposition flux of contaminants. Settling velocities and scavenging coefficients estimated for specific particle size diameters provide the most uncertainty (Cohrssen and Covello, 1989; Doran and Horst, 1985). Seinfeld (1986) found that particles more than 20 microns in diameter settle primarily by gravity, whereas smaller particles deposit primarily by atmospheric turbulence and molecular diffusion. Considerable, but nonquantifiable, uncertainty exists with respect to deposition velocities of particles 0.1 to 1.0 micron in diameter (Seinfeld, 1986). The uncertainty is difficult to define. The wide variation of predicted deposition velocities as a function of particle size, atmospheric turbulence, and terrain adds to this uncertainty (Sehmel, 1980). However, Gaussian plume dispersion models have been field validated for their ability to spatially predict dry deposition flux over some specified distance (Doran and Horst, 1985). In a series of field experiments conducted by Pacific Northwest Laboratory (Doran and Horst, 1985), zinc sulfide was used as a depositing tracer gas and sulfur hexafluoride was used as a nondepositing tracer gas to compare and contrast modeling results with field measurements of dry deposition and atmospheric diffusion of the gases. The tracer was released from a height of 2 meters, and all releases were made under relatively stable atmospheric conditions. Five sampling stations were located from 100 to 3,200 meters downwind of the release. The results of these experiments showed good agreement with the predicted versus the measured deposition of the tracer ZnS. The overall correlation coefficient between predicted and measured deposition concentration was found to be 0.82 (Doran and Horst, 1985), but the models marginally overpredicted deposition flux near the source of release and underpredicted deposition flux at 3,200 meters.

Travis and Yambert (1991) have evaluated the uncertainty in modeling the dry deposition flux of particulates using four standard Gaussian plume dispersion models. Since deposition flux is dependent on deposition velocity for a given particle mass and diameter, comparisons were made between model-generated deposition velocities and measured values in the literature for particles ranging from 0.01 to 30 microns in

diameter. It was found that measured deposition velocities exhibit variability spanning roughly two orders of magnitude. Comparison of predicted deposition velocities to measured values showed that most measured data exceeded the predicted data for all four models. Moreover, the models underestimated the mean deposition velocities for particles between 0.05 and 1.0 microns in diameter.

Similar uncertainty probably exists with regard to rainfall scavenging of particles. Seinfeld (1986) has calculated scavenging coefficients in terms of the removal efficiency of particles of a given size by rain droplets having a given momentum. Seinfeld (1986) found that the scavenging coefficient of a given particle diameter corresponding to a given rainfall intensity can be calculated based on physical laws, but there is a complete absence of research data to verify these calculations.

A.4. MODEL VALIDATION EXERCISES FOR DIOXINS AND FURANS

The dioxin exposure document described the fate models and demonstrated them in a series of scenarios. The scenarios were crafted to account for the magnitude of the source strength, the assignment of all fate parameters, and the exposure behaviors of the individuals who may have been impacted by their proximity to the sources. Some of the model validations below have taken results from these scenarios and compared them in a broad sense to similar quantities in the literature. This falls somewhat outside our description of model validation in that not all the independent source term data and dependent model results were from one site.

Another consideration is that the fate models in the dioxin exposure document are not identical to the models described in this methodology. The models in both documents are substantially similar, however, particularly in the use of empirical, simple models (such as the use of bioconcentration factors) and the assumption of steady state. One could consider the models of the dioxin document a specific application of indirect exposure methods. Relevant deviations in the modeling procedures of the dioxin document from those in this document will be described as necessary.

A.4.1. Air-to-Soil Modeling. One of the scenarios demonstrated in the dioxin document was termed the background scenario. Air concentrations and soil concentrations were input as source terms, and the models predicted the impacts to the aquatic environment (water, sediment, fish) and to terrestrial biota (vegetation and animals). The air and soil concentrations were taken from an actual rural site in Ohio. If one can assume that the soil concentrations resulted from depositions of airborne dioxins, then one can use the same data to test the air-to-soil modeling algorithms. The air data alone become the source-term independent data and the soil data become the dependent model result.

Data were available on the 17 dioxin-like dioxin and furan congeners. A total toxic equivalent concentration, abbreviated as total TEQ or simply TEQ, is often calculated from individual congener concentrations. The total TEQ is calculated as the sum of the TEQ concentrations of each of the 17 dioxin-like congeners. The TEQ concentration of an individual congener is calculated as the congener's actual concentration times its toxic equivalent factor, or TEF. These TEFs relate the toxicity of the individual congener to that of 2,3,7,8-TCDD. For example, the TEF for 2,3,7,8-TCDF is 0.1, which means that this congener is judged to be 1/10 as toxic as 2,3,7,8-TCDD. Individual congener and TEQ concentrations are displayed for this exercise.

The TEQ air and soil concentrations from this site were 0.019 pg/m³ and 1.37 pg/g, respectively. By modeling the deposition of the 17 congeners, the goal will be to see how well the model predicts the soil concentration of each congener, as well as the TEQ soil concentration. The reservoir of soil for this exercise will be a 7.5-cm depth, which was the depth of the soil sampling at the rural site in Ohio, and the assumed soil bulk density will be 1.50 g/cm³ (actual bulk density information was not available). The soil dissipation rate assigned to all dioxin congeners in the dioxin document is 0.0277 yr⁻¹, which corresponds to a half-life of 25 years. Since deposition was not monitored at the rural site, it will be estimated as the particle-bound airborne reservoir times a velocity of deposition. Koester and Hites (1992) measured a dry deposition rate of 0.002 m/sec for dioxins in Indiana. They also measured wet deposition and found it

roughly comparable for two sites. On this basis, dry deposition in this exercise will be modeled using the 0.002 m/sec velocity and wet deposition will be assumed equal to dry deposition.

The results of this validation exercise are shown in Table A-1. The soil concentrations appear to be predicted reasonably well, with modeled concentrations somewhat lower but within the realm of field observations. Specifically, 11 of the 17 observed concentrations were higher than model predictions. All but three congeners

| TABLE A-1 | | | |
|---|--------------------------------------|-------------------------|--------------------------|
| Results of the Air-to-soil Model Testing for Dioxins and Furans | | | |
| Congener | Observed Air (pg/m ³) | Observed Soil (pg/g) | Predicted Soil (pg/g) |
| 2,3,7,8-TCDD | 1.4·10 ⁻³ | 0.39 | 0.03 |
| 1,2,3,7,8-PCDD | 5.2·10 ⁻³ | 0.14 | 0.19 |
| 1,2,3,4,7,8-HxCDD | 7.9·10 ⁻³ | 0.35 | 0.31 |
| 1,2,3,6,7,8-HxCDD | 9.3·10 ⁻³ | 0.82 | 0.36 |
| 1,2,3,7,8,9-HxCDD | 1.4·10 ⁻² | 1.23 | 0.54 |
| 1,2,3,4,6,7,8-HpCDD | 2.3·10 ⁻¹ | 17.7 | 9.1 |
| OCDD | 9.0·10 ⁻¹ | 161.0 | 36.2 |
| 2,3,7,8-TCDF | 2.8·10 ⁻³ | 0.64 | 0.06 |
| 1,2,3,7,8-PCDF | 6.5·10 ⁻³ | 0.17 | 0.20 |
| 2,3,4,7,8-PCDF | 7.4·10 ⁻³ | 0.21 | 0.26 |
| 1,2,3,4,7,8-HxCDF | 1.3·10 ⁻³ | 0.16 | 0.50 |
| 1,2,3,6,7,8-HxCDF | 1.6·10 ⁻² | 0.11 | 0.59 |
| 1,2,3,7,8,9-HxCDF | 2.8·10 ⁻³ | 0.15 | 0.11 |
| 2,3,4,6,7,8-HxCDF | 9.2·10 ⁻³ | 0.67 | 0.36 |
| 1,2,3,4,6,7,8-HpCDF | 6.9·10 ⁻² | 4.06 | 2.74 |
| 1,2,3,4,7,8,9-HpCDF | 1.4·10 ⁻³ | 0.27 | 0.58 |
| OCDF | 6.7·10 ⁻³ | 10.7 | 2.70 |
| TEQ | 1.9·10⁻² | 1.37 | 0.70 |

were modeled to within a factor of 5 of observations, and the three other congeners were about a factor of 10 from observations (i.e., either observations were 5 to 10 times higher than predictions, or predictions were 5 to 10 times higher than observations). The four highest observations are matched with the four highest predictions as follows: 17.7 ppt observed 1,2,3,4,6,7,8-HpCDD versus 9.1 ppt modeled, 161.0 versus 36.2 ppt for OCDD, 4.06 versus 2.74 ppt 1,2,3,4,6,7,8-HpCDF, and 10.7 versus 2.70 ppt OCDF. The observed TEQ soil concentration of 1.37 ppt matches well with the predicted TEQ concentration of 0.7 ppt.

Although the soil model appears to work reasonably well considering only impact of particle depositions, vapor impacts are not considered, which would increase predictions of soil concentrations. As noted above, soil concentrations may generally be underpredicted, although for six congeners the model predictions were higher than observations. Direct vapor deposition could impact soils, but at the rural site in Ohio all samples were taken in grassy areas, and with a vegetative cover it is speculated that there would be little direct vapor deposition. Therefore, detritus production would be a mechanism for vapor impacts to soils. Barbour et al. (1980) list a detritus production rate for a setting described as tallgrass prairie as 520 g/m²/yr. Given the concentrations predicted to occur in grass because of vapor transfers, one can estimate the loadings of dioxin corresponding to detritus production of this magnitude. The predicted TEQ concentration in leafy vegetation due to vapor transfers was 0.27 pg/g dry weight given the rural air concentrations at the site in Ohio. This concentration times the detritus rate leads to a loading of 112 pg TEQ/m²/yr. In contrast, the dry and wet deposition loading estimated by dry and wet deposition of particle-bound dioxins is 2,130 pg TEQ/yr. Therefore, on a TEQ basis, vapor impacts via detritus production would be only about 5% of loadings by dry and wet deposition of particle-bound dioxins. Particle-bound dioxins also impact vegetation, and detritus production might be considered as an additional loading. However, since 100% of atmospheric depositions are loaded into the soil model, detritus production is inherently

handled, and considering it separately would double-count the impact of particle-bound dioxins.

Another factor to consider is the representativeness of the air concentrations. The air concentration profile was the average of three samples, one taken in March 1994, one in April 1994, and one in June 1995. It has been observed that air concentrations are higher during winter months in one site (Reed et al., 1990), and if that were also the case at this site in Ohio, perhaps the inclusion of additional winter samples would lead to a higher air concentration profile and higher predicted soil impacts.

In summary, this section has shown that the air-to-soil model based on deposition of particle-bound dioxins appears to work reasonably well. Vapor impacts would occur primarily through dieback of vegetative materials, but the additional increment to soil concentrations is estimated to be less than 10% by this route. Inclusion of wintertime air concentrations in the average air profile could lead to higher predictions of soil concentrations and a superior match of predicted and observed soil concentrations.

A.4.2. Air-to-Plant Modeling. Jones and Duarte-Davidson (1997) present the results of an extensive monitoring study of dioxin concentrations in air and grass, as well as deposition fluxes, from three sites over three time periods between 1992 and 1993 in the United Kingdom. The three sites include a rural background site, an urban site, and an industrial site. Two subsets of this data, which are appropriate for air-to-plant model validation purposes, were presented by Jones and Duarte-Davidson (1997). Specifically, this includes concurrently measured concentrations of dioxin and furan congeners, and homologue groups, for air and grass sampled for two of the sites, the industrial and rural background site, for one of the sampling periods, September 14 - October 30, 1993. They also presented the results of their deposition collection for those two sites/sampling periods. Results for the rural site are used for model evaluations in this section. In an expanded version of the exercise, Lorber and Pinsky (1998) evaluate three air-to-life models for dioxins on both sites.

Air samples were taken using standard General Works high-volume samplers which took weekly samples of 300-500 m³ air for 4-6 week sampling periods. The glass fiber filters and the polyurethane foam plugs of these samplers (measuring, in theory, the vapor and particle phases, respectively) were collected weekly and composited for each full sampling period to allow for a single measurement of total air concentration of the dioxins, representing around 2000-3000 m³ (depending on the time of the individual sampling periods) of air volume. A bulk deposition sample for each site/sampling period was also collected using "upturned frisbee" collectors. Grass was mowed at the beginning and end of each sampling period; the second cutting represented the grass yields over the sampling period. Data site used here are shown in Table A-2.

The models that will be evaluated here were described in Chapter 6. First, total dioxin concentrations are partitioned into a vapor and a particle phase, using the vapor/particle partitioning model provided in Chapter 3, based on aerosol particle densities and the saturated liquid vapor pressure of the contaminant. This model is evaluated for dioxins in Section A.4.6., and then for other organic contaminants in Section A.5. Total plant concentrations are the sum of vapor phase and particle phase impacts. The particle-phase impact model is a simple reservoir mixing model: particle-bound dioxins deposit using a deposition velocity (0.2 cm/sec) to mix in a reservoir of plant matter (the grass yield), and then dissipate (weather) from the plant with a fixed dissipation rate, set equal to a half-life of 14 days in this application. Vapor phase impacts are modeled in either of two ways, both described in Chapter 6. The first is, quite simply, a bioconcentration approach: plant concentration equals the vapor phase air concentration times an air-to-leaf bioconcentration factor, B_v . This factor was calibrated (Lorber, 1995) for the dioxin-like compounds based on experimental data on the transfer of dioxins to Welsh Ray Grass (Welsch-Pausch et al., 1995). The partitioning of dioxins between a particle and a vapor phase for various airsheds (where the airsheds are defined by particle densities), and the air-to-leaf bioconcentration factor B_v , are shown in Table A-3. The background airshed vapor/particle partitioning scheme was used in this exercise. The second model is the

Appendix A
Model Validation

vapor deposition model. It is, in fact, analogous to the model for particle phase impacts to plants; plant

| TABLE A-2 | | | | | | | |
|--|------|------------|-------|---|------|------------|-------|
| Observed Data for the Air-to-Plant Model Validation Exercise | | | | | | | |
| Compound | Air | Deposition | Grass | Compound | Air | Deposition | Grass |
| 2378-TCDD | 0.01 | <0.46 | 0.72 | TCDD | 0.72 | 73 | 66 |
| 12378-PCDD | 0.03 | 2.3 | 1.3 | PCDD | PCDD | 0.56 | 54 |
| 123478-HxCDD | 0.04 | 2.3 | 0.93 | HxCDD | 0.65 | 38 | 26 |
| 123678-HxCDD | 0.08 | 4.8 | 2.3 | HpCDD | 0.71 | 41 | 22 |
| 123789-HxCDD | 0.1 | 3.8 | 1.8 | OCDD | 2.5 | 166 | 94 |
| 1234678-HpCDD | 0.82 | 41 | 22 | TCDF | 1.6 | 24 | 93 |
| 2378-TCDF | 0.33 | 12 | 14 | PCDF | 0.45 | 18 | 13 |
| 12378-PCDF | 0.06 | 2.5 | 1.8 | HxCDF | 0.45 | 18 | 13 |
| 23478-PCDF | 0.1 | 4.1 | 2.2 | HpCDF | 0.22 | <1.8 | <0.22 |
| 123478-HxCDF | 0.3 | 11 | 5.6 | OCDF | 0.42 | 28 | 13 |
| 123678-HxCDF | 0.1 | 4.5 | 2.2 | Units: air - pg/m ³ deposition - pg/m ² -day grass - pg/g. Grass yield = 89 g/m ² dry weight | | | |
| 123789-HxCDF | 0.02 | 1.8 | 0.61 | | | | |
| 234678-HxCDF | 0.14 | 4.8 | 2.6 | | | | |
| 1234678-HpCDF | 0.53 | 19 | 12 | | | | |
| 1234789-HpCDF | 0.11 | 2.9 | 1.1 | | | | |

| TABLE A-3 | | | | | |
|---|------------------------------|-------|-------|-------|----------------------|
| Fate and Transport Parameters for the Dioxin-like Congeners | | | | | |
| Congeners | Particle fractions, ϕ^* | | | | B _v * |
| | C C | B | B+LS | U | |
| 2378-TCDD | 0.1 | 0.29 | 0.49 | 0.75 | 6.55*10 ⁴ |
| 12378-PCDD | 0.44 | 0.74 | 0.87 | 0.95 | 2.39*10 ⁵ |
| 123478-HxCDD | 0.78 | 0.93 | 0.97 | 0.99 | 5.20*10 ⁵ |
| 123678-HxCDD | 0.78 | 0.93 | 0.97 | 0.99 | 5.20*10 ⁵ |
| 123789-HxCDD | 0.78 | 0.93 | 0.97 | 0.99 | 5.20*10 ⁵ |
| 1234678-HpCDD | 0.93 | 0.98 | 0.99 | 0.997 | 9.10*10 ⁵ |
| OCDD | 0.98 | 0.995 | 0.998 | 0.999 | 2.36*10 ⁶ |
| 2378-TCDF | 0.09 | 0.27 | 0.47 | 0.73 | 4.57*10 ⁴ |
| 12378-PCDF | 0.27 | 0.57 | 0.75 | 0.91 | 9.75*10 ⁴ |
| 23478-PCDF | 0.38 | 0.69 | 0.84 | 0.94 | 9.75*10 ⁴ |
| 123478-HxCDF | 0.63 | 0.86 | 0.93 | 0.98 | 1.62*10 ⁵ |
| 123678-HxCDF | 0.63 | 0.86 | 0.93 | 0.98 | 1.62*10 ⁵ |
| 123789-HxCDF | 0.74 | 0.91 | 0.96 | 0.99 | 1.62*10 ⁵ |
| 234678-HxCDF | 0.74 | 0.91 | 0.96 | 0.99 | 1.62*10 ⁵ |
| 1234678-HpCDF | 0.86 | 0.96 | 0.98 | 0.99 | 8.30*10 ⁵ |
| 1234789-HpCDF | 0.92 | 0.98 | 0.99 | 0.997 | 8.30*10 ⁵ |
| OCDF | 0.98 | 0.995 | 0.998 | 0.999 | 2.28*10 ⁶ |

* C C: Clean continental; B = Background; B+LS: Background plus local sources; U = urban
B_v: Air-to-leaf biotransfer factor, (pg PCDD/g leaf dry)/(pg PCDD/g air)

concentrations are modeled by assuming a vapor-phase reservoir of dioxins depositing onto, mixing in, and dissipating from a plant reservoir. This approach has been described and parameterized for vapor phase 2,3,7,8-TCDD impacts to grassy plants by Trapp and Matthies (1995) and Smith et al. (1995a). Their critical deposition velocity terms were 0.50 and 0.76 cm/sec, respectively, and their dissipation rates were 0.374 and 0.159 day⁻¹ (half-lives of 1.8 and 4.4 days). This model is applied to 2,3,7,8-TCDD only, using the parameterization of these two authors.

Of 25 air:grass observed data points, 17 dioxin-like congener concentrations and 8 homologue group concentrations, only 22 could be used for this exercise. In order to obtain independent data points, the congener-specific data were subtracted from their respective homologue groups. For example, 2,3,7,8-TCDD concentrations in air and plants were subtracted from the TCDD homologue group concentrations in air and plants. In doing so for all congeners and their respective homologue groups, it was found that, in three instances, HpCDF, HxCDF, and HpCDF, subtraction of the congener concentrations from the homologue group concentrations resulted in negative air concentrations. There was obviously some measurement error in this data set. The air:grass pairs for these three homologue groups were, therefore, not considered further. The remaining 22 data pairs were found to be highly correlated, with a correlation coefficient of 0.92. Generation of dioxin toxic equivalent (TEQ) concentrations were developed using the International Toxicity Equivalency Factors (U.S. EPA, 1989). Model goodness-of-fit was evaluated using the absolute and signed difference between the natural logs of the measured and modeled grass concentrations. The signed error, or bias, measures the systematic tendency of the model to under or overpredict; a bias near 0 suggests that the model underpredicts and overpredicts by about the same amount. The absolute error calculation describes model variation; how close the model predictions come to the observations, regardless of whether the model over or underpredicted.

Figure A-1 shows the comparison between predicted and observed grass concentrations of the 22 congener/homologue pairs of this exercise. Grass

concentrations were predicted as the sum of vapor plus particle impacts, where the particle phase impacts were modeled using the deposition approach as previously described, and the vapor phase impacts were modeled using the air-to-leaf bioconcentration factor approach. The testing of the vapor deposition approach will be described shortly. The predictions and observations were converted to a log basis because of the wide spread of concentrations, with grass concentrations ranging from less than 1 ppt to nearly 100 ppt. Observed grass concentrations are on the x-axis and predicted grass concentrations on the y-axis. The dashed line shows where the predicted equals observed would occur.

As seen in this figure, the model provided a very good fit to the data. The predicted TEQ concentration by the model was 6.6 pg/g dry, compared with the observed concentration of 6.0 pg TEQ/g dry. The bias was 0.012, giving a bias factor of $e^{0.012} = 1.01$ and suggesting that there appeared to be no particular bias in either under or overpredicting grass concentrations. The absolute error was 0.396, meaning that the predicted grass concentrations tended to be within a factor of about 1.5 ($e^{0.396}$) of measured concentrations.

Figure A-2 shows the comparison of predicted and observed deposition of dioxin; again a dashed line shows the perfect fit between observed and predicted. It is clear that the modeled rates of deposition were consistently higher than the measured rates. There was a high degree of correlation between measured and modeled rates, however, with a correlation coefficient of 0.99. The absolute error and bias were 1.12 and 1.06, respectively (for all but one congener/homologue, the model overpredicted deposition), suggesting that the model predictions were, on average, approximately three times higher than observed ($e^{1.12}$ equals about 3). This would indicate a systematic bias, either that the model tended to overpredict depositions or that the measurements tended to under-represent depositions to plants (or a combination of

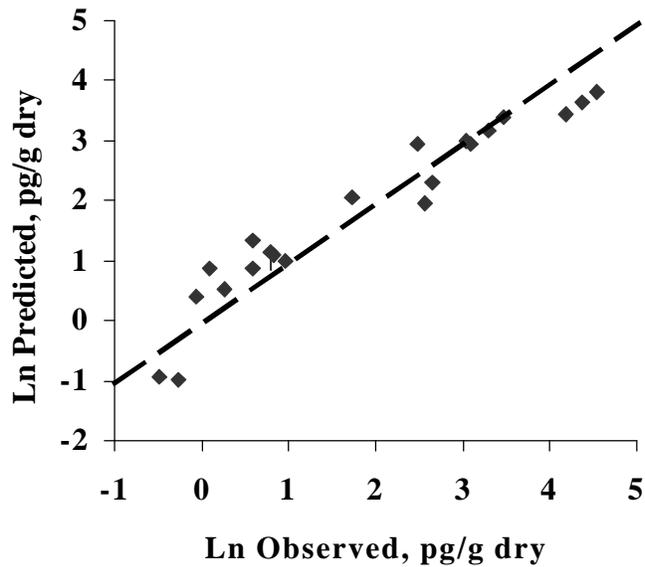


FIGURE A-1

Comparison of Observed Grass Concentrations of Dioxins/furans and Concentrations Predicted by the Particle and Vapor Phase Impacts Models Described in Chapter 6. The Perfect Match of Observed and Predicted Is Shown in the Dashed Observed = Predicted Line.

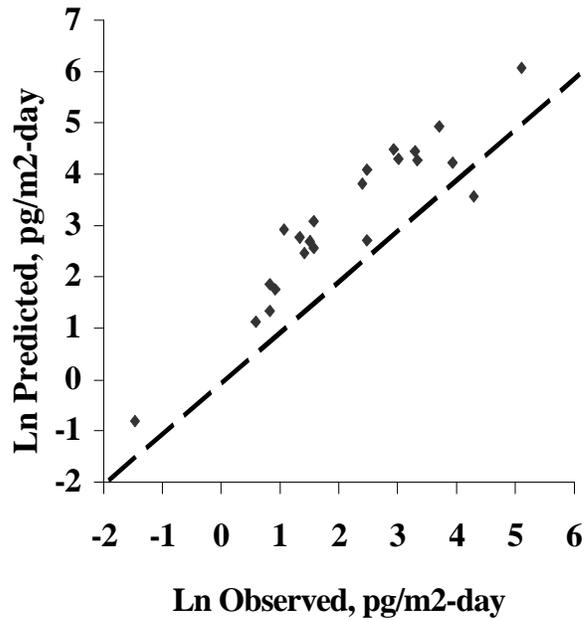


FIGURE A-2

Comparison of Observed Dioxin/furan Deposition and Deposition Predicted by the EPA Model. The Perfect Match of Observed and Predicted Is Shown in the Dashed Observed = Predicted Line.

both). If the model tended to overpredict deposition, this may have been due to the assumption of a deposition velocity that was too high. Measured deposition velocities can be calculated from the data of Jones and Duarte-Davidson (1997) simply as the deposition flux divided by the air concentration (with proper conversions). Average velocities calculated this way were 0.06 cm/sec for the rural site data shown in Figure A-2; lower than the 0.20 cm/sec applied in the modeling exercise. Actually, the discrepancy is larger: 0.20 cm/sec was applied to the particle phase concentration, while 0.06 cm/sec was calculated from total air concentrations. Another key modeling parameter that may have caused overestimation in deposition fluxes was the modeled particle phase fraction. As shown in Section A.4.5., measured particle phase fractions tend to be significantly lower than modeled fractions. If the smaller measured particle phase fractions were used perhaps with 0.06 cm/sec deposition velocity, then modeled deposition amounts would be similar to measured amounts.

Table A-4 shows the comparison of the measured grass concentration of 2,3,7,8-TCDD with the modeled vapor transfer concentration using the vapor bioconcentration model and the vapor deposition model parameterized by Trapp and Mattheis (1995) and Smith et al. (1995a). It is clear from this table that the vapor deposition algorithm, as parameterized by these two research groups, predicts concentrations that are over an order of magnitude lower than predictions made by the vapor bioconcentration algorithm, and even lower still than observed grass concentrations. Critical parameters include the deposition velocity and the rate of degradation on the plant. The degradation term is more likely inappropriately assigned by these researchers, at least for this field data set. That rate was based on a controlled chamber study, that included an uptake and a degradation phase (McCrary and Maggard, 1993). The degradation phase was conducted in outdoor bright sunlight (personal communication with J. McCrary, and U.S. EPA, 1994). Degradation rates derived under these sunlight conditions may not be appropriate for most conditions. A longer half-life would improve model predictions. However, no data other than McCrary's could be found for the degradation value.

| TABLE A-4 | |
|--|---|
| Model Results Comparing the Vapor Transfer Model and the Vapor Deposition Model with the Field Data for 2,3,7,8-TCDD (Concentrations in pg/g Dry Weight) | |
| Description | 2,3,7,8-TCDD grass concentrations, pg/g dry |
| Observed data | 0.76 |
| vapor bioconcentration model ^{3,5} | 0.35 |
| Smith et al. (1995a) model ⁷ | 0.01 |
| Trapp and Mattheis (1995) model ⁸ | 0.02 |

A.4.3. Soil Concentrations and Concurrent Concentrations in Bottom Sediments and Fish. The Connecticut Department of Environmental Protection (CDEP, 1992) established a program in 1986 for monitoring TCDD, TCDF, and other dioxin-like congeners of comparable toxicity in several environmental matrices near resource recovery facilities (RRFs). Matrices monitored include ambient air, residues and leachate from the ash disposal sites, surficial soils, surface water surficial bottom sediments, and whole fish. The purpose of the program is to evaluate the impact of RRFs. Eight locations were evaluated through 1990, with one location serving as a baseline or reference site. This section will examine the soil, sediment, and fish data from that program.

Two key quantities examined are the ratio of soil concentration to bottom sediment concentration and the ratio of fish lipid concentration to organic carbon normalized bottom sediment concentration. The first ratio is compared to an analogous ratio in the dioxin document's background scenario. In this scenario, soil concentrations within a watershed and air concentrations are input as source terms, and the fate models predict concentrations in the water body (water, sediment, fish)

and the terrestrial biota (vegetation, animal fats). The aquatic impacts in this scenario are modeled as a function of both soil erosion from the watershed and deposition of airborne dioxins directly into the water body. The second ratio is the definition of the biota sediment accumulation factor, or BSAF, which is described as one option for fish tissue concentration modeling in the indirect models of this document. One can derive the BSAF from the Connecticut data because the important site-specific quantities, the organic carbon content of the bottom sediments and the fish lipid fractions, were measured by the CDEP.

In general, the dioxin document models that predict impacts to water bodies are quite similar to the aquatic impact models of this assessment. The most important similarities include the use of the Universal Soil Loss Equation for unit area soil losses coupled with a sediment delivery ratio and an enrichment ratio to predict the delivery of contaminants to a water body; the modeling of the deposition of airborne contaminants to the water body as a second source term; the assumption of equilibrium between the bottom sediments and the water column; the use of partitioning parameters (i.e., K_{ow} or K_{oc}) to model the partitioning among bottom sediment, suspended sediment, and water; and the overall assumption that the system is in steady state. The aquatic models of this assessment are more generalized in that certain quantities, such as the volatilization loss of contaminants from the water body to the atmosphere, are modeled, whereas volatilization loss (and other quantities) are not modeled in the dioxin document's aquatic modeling framework. This and other differences are not expected to be significant for the dioxin-like compounds. For example, dioxins are tightly bound to sediments such that escape from the water via volatilization is insignificant.

Table A-5 summarizes the key results from the CDEP (1992) data. The $C_{sed}:C_{soil}$ ratio is the ratio of sediment concentration to soil concentration, and the second ratio is the BSAF. The contaminants examined include 2,3,7,8-TCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PCDF, and the total toxic equivalents, or total TEQ. The CDEP (1992) calculated the concentrations of all 17 dioxin and furan dioxin-like congeners, which allowed for the calculation of the TEQ ratios in Table A-5. The background

| TABLE A-5 | | | |
|---|-------------|----------|---------|
| Summary of the Results from Eight Sites of the Connecticut Department of Environmental Protection Sampling, Including Soil, Sediment, and Fish Concentrations, and the Key Concentration Ratios of Sediment to Soil and the Biota Sediment Accumulation Factor (BSAF) Ratio | | | |
| Dioxin congener | Soil | Sediment | Fish |
| 2,3,7,8-TCDD | | | |
| Number of samples | 770.56 | 3462.16 | 5211.06 |
| Mean concentration, ppt | | | |
| C_{sed}:C_{soil} Ratio: | 3.86 | | |
| BSAF: | 0.86 | | |
| 2,3,7,8-TCDF | | | |
| Number of samples | 776.77 | 34617.52 | 5212.53 |
| Mean concentration, ppt | | | |
| C_{sed}:C_{soil} Ratio: | 2.59 | | |
| BSAF: | 0.25 | | |
| 2,3,4,7,8-PCDF | | | |
| Number of samples | 773.56 | 3465.62 | 5211.49 |
| Mean concentration, ppt | | | |
| C_{sed}:C_{soil} Ratio: | 1.58 | | |
| BSAF: | 0.47 | | |
| TEQ | | | |
| Number of samples | 778.42 | 34622.69 | 5213.1 |
| Mean concentration, ppt | | | |
| C_{sed}:C_{soil} Ratio: | 2.69 | | |
| BSAF: | 0.24 | | |

Source: CDEP, 1992

demonstration scenario modeled all 17 congeners, allowing for a prediction of the TEQ ratios.

Key observations from the background demonstration scenario in the dioxin document and the results of the CDEP (1992) program are:

(1) The predicted sediment-to-soil ratios of 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PCDF for the background demonstration scenario of the dioxin exposure document were 2.55, 1.82, and 2.43. The differences in the sediment:soil ratios of these congeners are due to slightly different organic carbon partition coefficients assumed for the three congeners. These ratios compare with the 3.86, 2.59, and 1.58 calculated from the Connecticut data set for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PCDF, respectively. The ratio for total TEQ was calculated at 2.69, compared with the predicted 2.64. The predicted ratios appear to be in the same ballpark as the observed ratios, and it is judged that this result tends to support the model's approach.

One of the key uncertain model parameters in the dioxin document, as well as in this document, in the soil-to-sediment models is the soil enrichment ratio. It was assigned a value of 3.0 in the dioxin document, which means that concentrations in soil eroding from the watershed are three times higher than concentrations on the field. If the soil enrichment ratio is set to 1.0, then sediment:soil ratios would be predicted to be less than 1.0. The closer match of observed and predicted sediment:soil ratios with an enrichment ratio of 3.0 does not necessarily validate the models approach to predicting sediment impacts based on soil erosion, however. The background demonstration of the dioxin document suggests that nearly all surface water impacts were from the erosion of basin soils; sensitivity analysis showed that less than 5% of the water body impact was from deposition of airborne dioxins. However, sediment concentrations in water bodies in actuality are also a function of other direct, industrial-related discharges. The impact of industrial sources on the sediments in the CDEP (1992) data is unclear, although CDEP (1992) did observe that the resource recovery facilities do not appear to be influencing soils, sediments, or fish in their monitoring program (CDEP, 1992).

In summary, the CDEP (1992) data appear to indicate that bottom sediment concentrations exceed surface soil concentrations by more than a factor of 2.0 in environmental settings that do not appear to be impacted by industrial activities. The models also predict a similar enrichment of sediment concentrations, due mainly to the use of a soil enrichment ratio, by a factor of 3.0.

(2) The overall BSAF ratios for the three dioxin compounds and the TEQ ratio, ranging from 0.24 to 0.86, are higher than the BSAF used in the dioxin document, which is 0.09 for 2,3,7,8-TCDD, 0.072 for 2,3,7,8-TCDF, and 0.144 for 2,3,4,7,8-PCDF. Higher BSAFs in the CDEP (1992) data are expected because the fish species sampled were bottom feeders, except for the yellow perch. The selected BSAF of 0.09 for 2,3,7,8-TCDD is mainly supported by Lake Ontario data (U.S. EPA, 1990a), which were on brown and lake trout, smallmouth bass, and white and yellow perch, all column feeders. [The BSAF for other dioxin congeners was based on the bioequivalency factor, or BEF, approach suggested by U.S. EPA (1995). This is a ratio approach like the TEF used to assign BSAF or other aquatic bioconcentration/biotransfer factors for other dioxin congeners given a value for 2,3,7,8-TCDD.] Bottom feeders are expected to have more exposure to contaminants because of their direct contact with sediments. This implies that use of the BSAF for site-specific assessments should consider whether fish are bottom feeders or column feeders. If they are bottom feeders, then a higher BSAF would be in order.

One other study considered the relationship between watershed soils and bottom sediments. Smith et al. (1995b) evaluated sediment core data from the Hudson River National Estuary Research Reserve system located on the lower (southern) Hudson River. They also took surface soil cores near the estuaries studied. Using principal component analysis, as well as a mass balance approach, they concluded that the CDD/CDF concentrations in the river sediments were dominated by soil erosion (76% of total influx) and sewage-containing effluents (19%). In doing their mass balance exercise, they used an organic enrichment factor of 1.6 for calculating the contribution of watershed soil dioxins to the river sediment load. This is analogous to

the enrichment ratio described above and supports a value greater than 1.0. However, it does suggest that the value may not be as high as 3.0 if other sources of bottom sediments, such as sewage effluents, are known to impact the sediment.

A.4.4. Transfer of Dioxins from Soils to Below-Ground Vegetables. This section describes a validation of the transfer algorithm from soils to below-ground vegetables. The dioxin exposure document's model for predicting the concentration of dioxins in below-ground vegetation is the same as the general model in this methodology: a soil concentration times an empirical root concentration factor (RCF), equals the below-ground vegetation concentration. The dioxin document introduces an empirical adjustment factor, VG_{bg} , which considers that the empirical algorithm used to develop values of RCF for the dioxin congeners was developed from laboratory data on the transfer of organic contaminants into root hairs, whereas below-ground vegetation is bulky. The RCF would model transfers into the outer layers of bulky below-ground vegetation (such as carrots or potatoes), but not their inner parts. On the basis of data, the dioxin document assigned a value of 0.25 to the VG_{bg} parameter for underground bulky vegetation. The VG_{bg} parameter is also described in Chapter 6 of this document.

Data from Muller et al. (1994) were used to validate this model. Specifically, carrots were grown in pots with soil of two concentrations, a control soil and a contaminated soil. Muller et al. (1994) provided graphs showing the congener group concentrations for soil and for three parts of the carrot: peel, cortex, and stele. The precise concentrations from these graphs were unavailable. However, the graphs were digitized by Cambridge Environmental (58 Charles Street, Cambridge, MA; concentration values contained in discussions in a public comment provided to U.S. EPA), and those concentrations were used in this exercise. Data in this article also included the soil organic carbon content, 8.1%.

Part of this data set was used in conjunction with the model described above. The VG_{bg} was taken out of the equation and the soil concentration data were input into the model to predict the peel concentrations. The cortex and stele concentrations were not used in the validation exercise. The predicted peel concentrations were compared

with the observed concentrations. Since the data were available by congener groups and not individual congeners, the values for the parameters RCF and K_{oc} were estimated as the congener-specific value if only one dioxin-like congener was in the congener group (e.g., 2,3,7,8-TCDD), or as the average of the congener-specific values of the multiple dioxin-like congeners in the congener group (e.g., the three HxCDDs). Finally, the data in Muller et al. (1994) were given only in dry-weight terms without discussion of the dry-weight fraction of their experimental carrots, and the model predicts a fresh weight. For this exercise, it was assumed that carrots are 15% dry weight; the fresh weight was divided by 0.15 to estimate the dry-weight concentration.

Table A-6 shows the data that went into this validation exercise and the results. It would appear that the model works reasonably well. The difference in peel concentrations due to soil concentration is apparent in both the data and the model predictions, and the magnitude of the difference appears to be captured. With one exception, the predictions and observations are within a factor of 4 of each other, with the exception being a factor of 5. Thirteen of 20 predictions/observations are within a factor of 2 of each other. The biggest discrepancies are the HpCDF and OCDF congener groups, with predictions exceeding observations by a factor of about 4 for both the control and contaminated soils. Generally, it is concluded that these data support the use of the Briggs et al. (1982) RCF empirical formulation to predict the peel concentration of dioxin-like compounds in underground bulky vegetation.

A.4.5. An Update of the Air-to-Beef Model Validation Exercise. An original version of the air-to-beef model validation exercise can be found in a journal article (Lorber et al., 1994) as well as in an earlier version of the dioxin document (U.S. EPA, 1994). The current dioxin exposure document updates this exercise. This section provides an overview of the exercise, the changes made, and the final results.

The air-to-beef model of the dioxin exposure document represents one of the two approaches presented in this document to model animal fat concentrations. One approach is termed the “biotransfer” approach. Animal fat concentrations or whole-

animal concentrations are predicted as a function of the mass intake of the contaminant—i.e., the mass intake (in g/day or some other mass/time units) of the contaminant times the biotransfer factor equals the animal tissue (whole or lipid-based) concentration. The other option, which is used in the dioxin exposure document, is the bioconcentration approach. Animal fat concentrations are predicted as a function of the concentration of the contaminant in the animal's diet (i.e., the weighted average

TABLE A-6

Data and Results of the Soil to Below-ground Vegetable Validation Exercise

| Congener Group | K _{oc} (L/kg) | RCF | Control Soil | | | Contaminated Soil | | |
|----------------|------------------------|--------|--------------|-------------------------|--------------------------|-------------------|-------------------------|--------------------------|
| | | | Soil (ppt) | Observed Peel (ppt dry) | Predicted Peel (ppt dry) | Soil (ppt) | Observed Peel (ppt dry) | Predicted Peel (ppt dry) |
| TCDD | 3.98·10 ⁶ | 5200 | 11 | 1.7 | 1.2 | 24.3 | 2.9 | 2.6 |
| PCDD | 2.69·10 ⁶ | 3900 | 6.8 | 1.2 | 0.8 | 80.5 | 5.6 | 9.6 |
| HxCDD | 2.12·10 ⁷ | 18600 | 23.5 | 1.6 | 1.7 | 176.7 | 7.3 | 12.7 |
| HpCDD | 6.17·10 ⁷ | 43700 | 45.6 | 1.6 | 2.7 | 238.6 | 5.4 | 13.9 |
| OCDD | 9.77·10 ⁷ | 62200 | 85.4 | 3 | 4.5 | 297.4 | 6.3 | 15.6 |
| TCDF | 7.76·10 ⁵ | 1500 | 21.8 | 11.9 | 3.5 | 270.7 | 36.7 | 43 |
| PCDF | 2.88·10 ⁶ | 4080 | 34.8 | 5.9 | 4.1 | 361.9 | 24.8 | 42.1 |
| HxCDF | 6.17·10 ⁶ | 7410 | 38.5 | 3.2 | 3.8 | 418.4 | 22 | 41 |
| HpCDF | 3.86·10 ⁷ | 29400 | 49 | 1.2 | 3.1 | 667.2 | 12.2 | 41.8 |
| OCDF | 3.89·10 ⁸ | 180000 | 46.6 | 0.4 | 1.8 | 687.3 | 5 | 26.2 |

concentration in pg/g or a similar mass/mass concentration unit multiplied by the bioconcentration factor).

The premise of this exercise to test the beef food chain model is that airborne reservoirs of these compounds in rural environments are the “source term” explaining concentrations found in beef. The principal assumption in the validation exercise is that one can define an “average” rural air profile of dioxins, route this profile through the food chain model, and predict an “average” beef concentration. This exercise does not qualify as a validation exercise in the traditional sense, as described in the introduction to this chapter. However, this exercise was undertaken for these reasons: (1) the ubiquitous nature of dioxins in the environment leads to the possibility of true average air and beef fat dioxin concentrations; (2) a comprehensive site-specific data set (i.e., air concentrations, vegetation concentrations, cattle fat concentrations, and other data) was not available; (3) beef and air concentration data that are judged to be reasonably representative for U.S. conditions were available; and (4) dioxins in animal fat were judged by U.S. EPA (1994) and by researchers around the world to be the most important matrix of exposure to these compounds; hence it was desired to demonstrate that the modeling approach for this route of exposure would lead to appropriate concentrations.

Figure A-3 presents an overview of the air-to-beef food chain model. This approach is analogous to the terrestrial food chain models of this methodology. For this exercise, air dispersion models are not employed; the ambient air concentrations are the source terms. Besides using the bioconcentration option for animal fat concentrations, the only other noteworthy deviation from the methodologies of this document is that the soil-to-above-ground plant algorithms are not considered. Dioxin impacts to plants are only from air-to-plant transfers (vapor and particle phases). The dioxins are tightly bound to soils and soil-to-above-ground plant transfers are not expected to occur. The key components of the current model validation exercise were:

1. Source Term: Air concentrations. These are the source terms for this exercise. They are routed into cattle vegetation and the cattle fat

concentrations are predicted from the vegetation (and the soil concentrations; see below). The air profile used was the same rural air

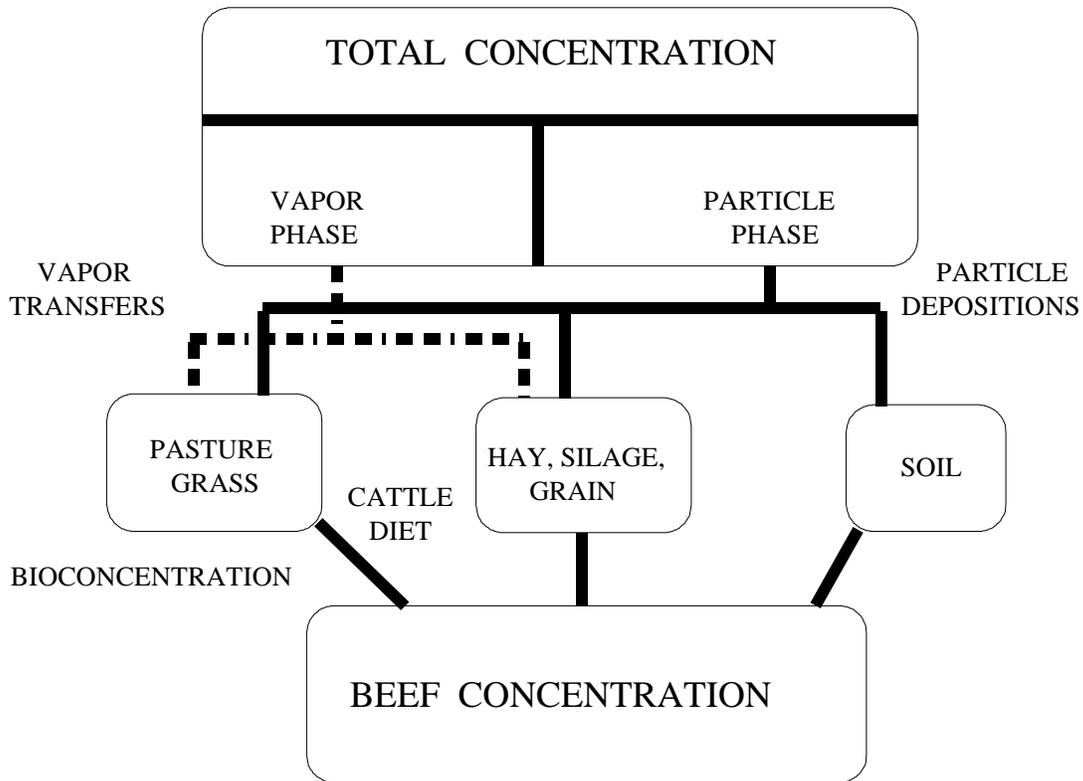


FIGURE A-3

Overview of Model to Predict Beef Concentrations from Air Concentrations

profile used in the background scenario of the dioxin document referred to above. The original air-to-beef model validation exercise crafted a rural profile based on a compilation of data for U.S. urban settings. The dioxin exposure document describes why the rural profile is superior to this crafted air profile, and why it can be considered reasonably representative of rural air concentrations in general. The overall TEQ concentration in this air profile is 0.019 pg TEQ/m³.

2. Source Term: Soil concentrations. Although soil was demonstrated in sensitivity analyses exercises in the exposure document to be much less important than cattle vegetative feeds, it is the second primary source of dioxins in cattle. The measured soil concentrations used in the background scenario in the exposure document were used in these model validation exercises, and soil concentrations were modeled from deposition of the airborne reservoir of dioxins. The overall TEQ concentration in the soil is 1.37 pg TEQ/g.
3. Predicted Media Concentration: Beef concentrations. The original validation exercise used an average profile of dioxins in whole beef generated from 14 samples of beef from three literature reports of grab samples. A far superior data base on this dependent model result was generated in a collaborative national survey of beef fat from slaughterhouses conducted by USDA and U.S. EPA (Winters et al., 1996). The overall TEQ concentration in this profile is 0.18 pg TEQ/g whole beef. This was calculated from the USDA/EPA survey, assuming nondetects were equal to ½ the detection limit and that whole beef is 19% fat.
4. Key model parameters. Model sensitivity analyses as well as actual field experimentation showed that vegetation concentrations of the lower chlorinated dioxins (the tetra through hexa congeners) tend to be dominated by vapor transfers rather than particle depositions. Therefore, final beef concentrations of the lower chlorinated congeners will be similarly sensitive to assignment of the air-to-leaf transfer factor, B_v. The original values for B_v for the dioxins were derived using an empirical algorithm relating this parameter to an organic contaminant's octanol-water partition coefficient, K_{ow}, and its Henry's Law Constant (U.S. EPA, 1992). McCrady and Maggard (1993) showed that a value of B_v for 2,3,7,8-TCDD calculated this way was 40 times higher than the value they obtained experimentally. Therefore, in the first version of the air-to-beef model validation exercise (Lorber et al., 1994; U.S. EPA, 1994), the B_v values for the dioxins were calculated by first using the empirical algorithm and then dividing each value by a factor of 40. The calibration exercises described in Lorber (1995) suggested that the B_v for dioxins should be even lower, by about a factor of between 2 and 4. This was, in fact, the basis for the guidance

given in Chapter 5 of this methodology that assignment of B_v for organic contaminants can be estimated by using the empirical algorithm and then dividing the final result by a factor of 100 (i.e., the factor of 40 and then the additional “real world” factor of between 2 and 4). The final B_v values for the dioxins were very similar to those described in Lorber (1995). There was an additional slight adjustment when the vapor/particle partitioning was slightly refined, which led to a recalibration of the B_v . Other key parameters that were varied from their original versions included the vapor/particle partitioning of the ambient air concentrations of dioxins and the beef bioconcentration factors. As with model validation, all parameters were assigned values and none were calibrated for this exercise.

Further details on the construct of the modeling exercise can be found in the dioxin exposure document. Table A-7 shows the original and current model predictions for leafy vegetation and compares them against four available data sets. The data on hay in the United States (Reed et al., 1990) seem to conflict with the other available data on the table; they have significantly higher concentrations of the congeners (of the ones that were quantified—most were nondetects), particularly OCDD. These data could have been influenced by a local source, or the particular type of hay may have had much higher particulate dioxin contributions than other grass data sets. The two data sets from the U.K. are reasonably similar, with the more recent (Kjeller et al., 1996) showing lower concentrations. In fact, these data were used by the authors (among other data) to suggest that emissions of dioxins are being reduced in the U.K. The data set on alfalfa is consistent with these data on grass in the U.K.

It is easily seen that the current set of model predictions of dioxins in grass is much more in line with these two U.K. observations and the U.S. alfalfa observation than are the predictions in the 1994 data set. There was a general reduction in the concentrations predicted between 1994 and the current predictions, due primarily to reductions in the air-to-leaf vapor transfer factor, B_v . There were noticeable improvements in some of the congeners, particularly the predictions for 2,3,7,8-TCDF and 1,2,3,7,8-PCDF, and to a lesser extent but still noticeable, improvements in 1,2,3,7,8-PCDD, 1,2,3,4,7,8-HxCDD, 2,3,4,7,8-PCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-

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HxCDF, 2,3,4,6,7,8-HxCDF, and OCDF. There was also an improvement in OCDD. It was noted that the vapor fraction assumed for OCDD was 0.0 in the 1994 exercise, but

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| TABLE A-7 | | | | | | |
|---|-------------|-------------|----------------------------------|-------------------------------------|--------------------------------|------------------------------|
| Comparison of Predicted Leafy Vegetation Samples of the Current, Revised Validation Exercise with the Previous Predictions of Leafy Vegetation and Several Observations in the Literature (Units are pg/g dry weight) | | | | | | |
| Congener | Predicted | | U.S. Alfalfa ^a , 1994 | U.K. Grass ^b , 1979-1988 | U.K. Grass ^c , 1996 | U.S. Hay ^d , 1989 |
| | 1994 | 1996 | | | | |
| 2,3,7,8-TCDD | 0.1 | 0.05 | 0.11 | 0.03 | 0.12 | ND |
| 1,2,3,7,8-PCDD | 0.9 | 0.18 | 0.16 | 0.14 | 0.07 | ND |
| 1,2,3,4,7,8-HxCDD | 0.7 | 0.18 | 0.29 | 0.14 | 0.1 | ND |
| 1,2,3,6,7,8-HxCDD | 0.2 | 0.22 | 0.25 | 3 | 0.17 | 1.2 |
| 1,2,3,7,8,9-HxCDD | 0.2 | 0.32 | 0.23 | 1.4 | 0.08 | ND |
| 1,2,3,4,6,7,8-HpCDD | 21 | 4.12 | 0.85 | 7.1 | 2.8 | 30 |
| OCDD | 6 | 13.2 | 6.21 | 24 | 15.6 | 285 |
| 2,3,7,8-TCDF | 7.2 | 0.07 | 0.06 | 0.46 | 1.28 | ND |
| 1,2,3,7,8-PCDF | 1.4 | 0.19 | 0.21 | 0.18 | 0.29 | ND |
| 2,3,4,7,8-PCDF | 0.8 | 0.16 | 0.08 | 0.2 | 0.28 | ND |
| 1,2,3,4,7,8-HxCDF | 0.5 | 0.26 | 0.19 | 0.32 | 0.21 | ND |
| 1,2,3,6,7,8-HxCDF | 0.9 | 0.31 | 0.3 | 0.16 | 0.09 | ND |
| 1,2,3,7,8,9-HxCDF | 0.3 | 0.04 | 0.24 | 0.02 | 0.02 | ND |
| 2,3,4,6,7,8-HxCDF | 0.5 | 0.14 | 0.2 | 0.15 | 0.09 | ND |
| 1,2,3,4,6,7,8-HpCDF | 1.4 | 1.68 | 0.31 | 1.9 | 1.02 | 5.4 |
| 1,2,3,4,7,8,9-HpCDF | 0.1 | 0.25 | 0.45 | 0.14 | 0.13 | ND |
| OCDF | 0.4 | 0.96 | 0.96 | 2 | 0.98 | 7.5 |
| TOTAL | 42.6 | 22.3 | 11.1 | 41.34 | 32.2 | --- |
| TEQ | 3.2 | 0.46 | 0.44 | 0.89 | 0.57 | --- |

^a From an unpublished data set for alfalfa supplied by V. Fiel, United States Department of Agriculture, for a beef feeding study that is currently underway. For these results, all but the hepta dioxin and the two octa congeners were not detected; results above are ½ detection for the two alfalfa samples taken.

^b Kjeller et al. (1991)

^c Kjeller et al. (1996)

^d Reed et al. (1990) - detection limits not supplied for nondetects, but described as between 0.31 and 6.5 ppt

ND = Not detected

in a detailed examination in Lorber et al. (1994), use of a vapor fraction of 0.0002 for OCDD, which is what the V/P model calculated, actually resulted in grass concentration approaching the hay concentration found in Reed et al. (1990). Given the other leafy concentrations, it would appear that an OCDD grass concentration in the 10-30 ppt range is more appropriate than one greater than 100 ppt. As a final and simple test of the current model predictions for leafy vegetation, the two data sets from the U.K. were averaged with the one set from alfalfa in the United States and correlated against the two sets of model predictions. The best-fit regression line for the 1994 model predictions and this average of three observations had a slope of 0.26, an intercept of 0.84, and, importantly, a rather poor r^2 of 0.14. In contrast, the best fit regression line for the 1996 model predictions had a slope of 1.13, an intercept of 0.007, and a much improved r^2 of 0.98.

Table A-8 compares the final predicted and observed beef data sets from the 1994 and the current validation exercise. There are reductions in both the observed and predicted beef concentrations from the 1994 results to the current results. However, given the fact that the USDA/EPA beef data set is superior to the grab sample relied on previously for this validation exercise, it is most appropriate to compare the predictions made in 1994 and those made in the current exercise with the USDA/EPA beef data set. Just by visual inspection, it is seen that notable improvements in model predictions are seen for the following congeners: 1,2,3,7,8-PCDD, OCDD, and 2,3,7,8-TCDF. There are some congener predictions for which the 1994 validation exercise appears to result in a superior match, including 1,2,3,4,7,8-HxCDD, 1,2,3,7,8-PCDF, 1,2,3,7,8,9-HxCDF, and 2,3,4,6,7,8-HxCDF. Overall, the TEQ concentration in the current validation is closer to the observed TEQ concentration, although the total concentration appears more favorable for the 1994 validation exercise.

A simple correlation test suggests that the current model validation is superior to the 1994 model predictions. The following shows the results of linear regressions of

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the 1994 and 1996 model predictions with the EPA/USDA monitoring results, assuming ND = ½ detection limit and ND = 0.0:

| TABLE A-8 | | | | |
|---|-------------------------|----------------|----------------------------|----------------|
| Results of the 1994 Air-to-beef Model Validation Exercise Compared Against Results from the Current Air-to-beef Model Validation Exercises (all beef concentrations in terms of pg/g lipid; values in parentheses are observations calculated assuming nondetects equal 0.0; values not in parentheses assume nondetects equal ½ detection limit) | | | | |
| Congener | 1994 Validation Results | | Current Validation Results | |
| | Observed Beef | Predicted Beef | Observed Beef | Predicted Beef |
| 2,3,7,8-TCDD | 0.13 (0.06) | 0.16 | 0.05 (0.03) | 0.13 |
| 1,2,3,7,8-PCDD | 1.17 (0.13) | 1.42 | 0.35 (0.04) | 0.37 |
| 1,2,3,4,7,8-HxCDD | 1.38 (0.74) | 0.53 | 0.64 (0.18) | 0.19 |
| 1,2,3,6,7,8-HxCDD | 4.40 (4.40) | 0.16 | 1.42 (1.21) | 0.2 |
| 1,2,3,7,8,9-HxCDD | 1.08 (0.34) | 0.21 | 0.53 (0.26) | 0.38 |
| 1,2,3,4,6,7,8-HpCDD | 10.13 (9.99) | 1.53 | 4.48 (4.39) | 0.79 |
| OCDD | 15.32 (14.84) | 1.53 | 4.78 (3.21) | 4.54 |
| 2,3,7,8-TCDF | 0.30 (0.25) | 2.42 | 0.03 (0) | 0.04 |
| 1,2,3,7,8-PCDF | 0.23 (0.005) | 0.37 | 0.31 (0) | 0.07 |
| 2,3,4,7,8-PCDF | 1.11 (0.90) | 0.89 | 0.36 (0.06) | 0.25 |
| 1,2,3,4,7,8-HxCDF | 2.68 (2.44) | 0.42 | 0.55 (0.27) | 0.29 |
| 1,2,3,6,7,8-HxCDF | 0.33 (0.10) | 0.68 | 0.40 (0.12) | 0.28 |
| 1,2,3,7,8,9-HxCDF | 0.30 (0) | 0.21 | 0.31 (0) | 0.05 |
| 2,3,4,6,7,8-HxCDF | 0.38 (0.11) | 0.37 | 0.39 (0.10) | 0.14 |
| 1,2,3,4,6,7,8-HpCDF | 2.08 (1.74) | 0.21 | 1.00 (0.75) | 0.35 |
| 1,2,3,4,7,8,9-HpCDF | 0.68 (0.07) | 0.05 | 0.31 (0) | 0.11 |
| OCDF | 1.18 (0.55) | 0.05 | 1.88 (0) | 0.13 |
| TOTAL | 42.9 (36.7) | 11.21 | 17.8 (10.7) | 8.29 |
| TEQ | 2.51 (1.55) | 1.85 | 0.93 (0.35) | 0.61 |

| | <u>Slope</u> | <u>Intercept</u> | <u>r²</u> |
|-----------------------------|--------------|------------------|----------------------|
| 1994 model/ND = ½ detection | 0.70 | 0.58 | 0.11 |
| 1994 model/ND = 0 | 0.74 | 0.13 | 0.16 |
| 1996 model/ND = ½ detection | 1.02 | 0.55 | 0.57 |
| 1996 model/ND = 0 | 0.76 | 0.25 | 0.41 |

As seen, there is a better regression with the current modeling exercise as compared with the 1994 model exercise, with current r² of 0.57 and 0.41 compared against r² of 0.11 and 0.16.

A.4.6. Modeling the Vapor/Particle (V/P) Partitioning of Dioxins and Furans.

Chapter 3 describes how the Junge-Pankow model is used to estimate particulate percentages for airsheds characterized as clean continental background, average background, background plus local sources, and urban. Briefly, this model is described by this equation:

$$\phi = \frac{c \Theta}{P^{\circ}_L + c \Theta} \quad (\text{A-1})$$

where:

- ϕ = fraction of compound adsorbed to aerosol particles
- P°_L = saturation liquid-phase vapor pressure of pure compound at ambient temperature, Pa
- Θ = particle surface area per unit volume of air, cm² aerosol/cm³ air
- c = constant related to the difference between heat of desorption from the particle surface, Q_d , and heat of vaporization of compound, Q_v , estimated at 17.2 Pa/cm

The dioxin exposure document describes the derivation of the P°_L for the dioxin and furan congeners. The particle surface areas, Θ , for the four watersheds identified above are: $4.2 \cdot 10^{-7}$ for clean continental, $1.5 \cdot 10^{-6}$ for average background, $3.5 \cdot 10^{-6}$ for

background plus local sources, and 1.1×10^{-5} for urban. Table A-9 shows the particle fraction, ϕ , for all 17 dioxin and furan congeners for the four watershed conditions and

| TABLE A-9 | | | | |
|---|-------------------|--------------------|-------------------------------|-------|
| Particle Fractions, ϕ , in Four Airsheds at 20°C for the Dioxin-like Congeners | | | | |
| Congener | Clean Continental | Average Background | Background plus Local Sources | Urban |
| 2,3,7,8-TCDD | 0.1 | 0.29 | 0.49 | 0.75 |
| 1,2,3,7,8-PCDD | 0.44 | 0.74 | 0.87 | 0.95 |
| 1,2,3,4,7,8-HxCDD | 0.78 | 0.93 | 0.97 | 0.99 |
| 1,2,3,6,7,8-HxCDD | 0.78 | 0.93 | 0.97 | 0.99 |
| 1,2,3,7,8,9-HxCDD | 0.78 | 0.93 | 0.97 | 0.99 |
| 1,2,3,4,6,7,8-HpCDD | 0.93 | 0.98 | 0.99 | 0.997 |
| OCDD | 0.98 | 0.995 | 0.998 | 0.999 |
| 2,3,7,8-TCDF | 0.09 | 0.27 | 0.47 | 0.73 |
| 1,2,3,7,8-PCDF | 0.27 | 0.57 | 0.75 | 0.91 |
| 2,3,4,7,8-PCDF | 0.38 | 0.69 | 0.84 | 0.94 |
| 1,2,3,4,7,8-HxCDF | 0.63 | 0.86 | 0.93 | 0.98 |
| 1,2,3,6,7,8-HxCDF | 0.63 | 0.86 | 0.93 | 0.98 |
| 1,2,3,7,8,9-HxCDF | 0.74 | 0.91 | 0.96 | 0.99 |
| 2,3,4,6,7,8-HxCDF | 0.74 | 0.91 | 0.96 | 0.99 |
| 1,2,3,4,6,7,8-HpCDF | 0.86 | 0.96 | 0.98 | 0.99 |
| 1,2,3,4,7,8,9-HpCDF | 0.92 | 0.98 | 0.99 | 0.997 |
| OCDF | 0.98 | 0.995 | 0.998 | 0.999 |

at an ambient temperature of 20°C. The dioxin exposure document describes how the P°_L varies as a function of temperature, and how different particle fractions, ϕ , for the dioxins can be calculated at different temperatures.

Data on measured vapor/particle partitioning for dioxins (and other compounds) comes from hi-volume two-stage samplers consisting of a glass or quartz fiber filter followed by a sorbent trap such as polyurethane foam (PUF), XAD resins, or a combination of the two. The filter is assumed to capture particle-bound contaminants and the PUF (or XAD) is assumed to capture vapor-phase contaminants.

Measurements on the partitioning of dioxins were available from Eitzer and Hites (1989), Hunt and Maisel (1992), Hites (1991), and Welsch-Pausch et al. (1995). The airsheds in these four studies were generally assumed to be semirural and the airshed category of "background plus local sources" was assumed to apply. These measurements were taken at different ambient air temperatures, and therefore needed to be normalized to a common temperature. In order to normalize the data from the four references, the following procedure was followed:

Step 1. The gas phase concentrations, C_g , and the particle phase concentrations, C_p , were calculated from the original references. The ratio of C_p/C_g was defined to be " K_p ." The $\log K_p$ values of the various dioxin congeners were examined for outliers (only one point was omitted, from the Hites [1991] data set), then regressed against $\log P^{\circ}_L$ of the various congeners at the ambient sampling temperature listed for each site. The regression equation is:

$$\text{Log } K_p = m \text{ Log } P^{\circ}_L + b \tag{A-2}$$

where:

- K_p = particle/gas partition coefficient, $\text{m}^3/\mu\text{g}$, defined as: $C_p \text{ (ng}/\mu\text{g)}/C_g \text{ (ng}/\text{m}^3)$, where C_p is concentration associated with aerosols, and C_g is gas-phase concentration
- P°_L = liquid subcooled vapor pressure, Pa
- m, b = empirically derived slope and intercept from data set

Regression parameters of Equation A-2 are given in Table A-10 for the various field studies.

| TABLE A-10 | | | |
|--|----------|--------------|----------------|
| Regression Parameters Slope M and Intercept B for Equation A.2, $\log K_p = M \log P^{\circ}_L + B$, Based on Field Measurements of Particle/gas Distributions for Dioxins and Furans | | | |
| Reference | Slope, m | Intercept, b | r ² |
| Eitzer and Hites (1989) | -0.775 | -5.72 | 0.96 |
| Hites (1991) | -0.988 | -6.87 | 0.87 |
| Hunt and Maisel (1992) | -0.62 | -5 | 0.61 |
| Welsch-Pausch et al. (1995) | -0.707 | -5.73 | 0.99 |

Step 2. For each study, values of K_p for each dioxin and furan congener at 20°C were calculated from the liquid vapor pressures of each congener at 20°C, using Equation A-2 and the regression parameters in Table A-7.

Step 3. Although Equation A-1 describes the Junge-Pankow model that solves for the particulate fraction, ϕ , this quantity can also be expressed by:

$$\phi = \frac{C_p (TSP)}{C_g + C_p (TSP)} \quad (A-3)$$

where TSP is the total suspended particulate (in $\mu\text{g}/\text{m}^3$). Manipulation of this equation yields:

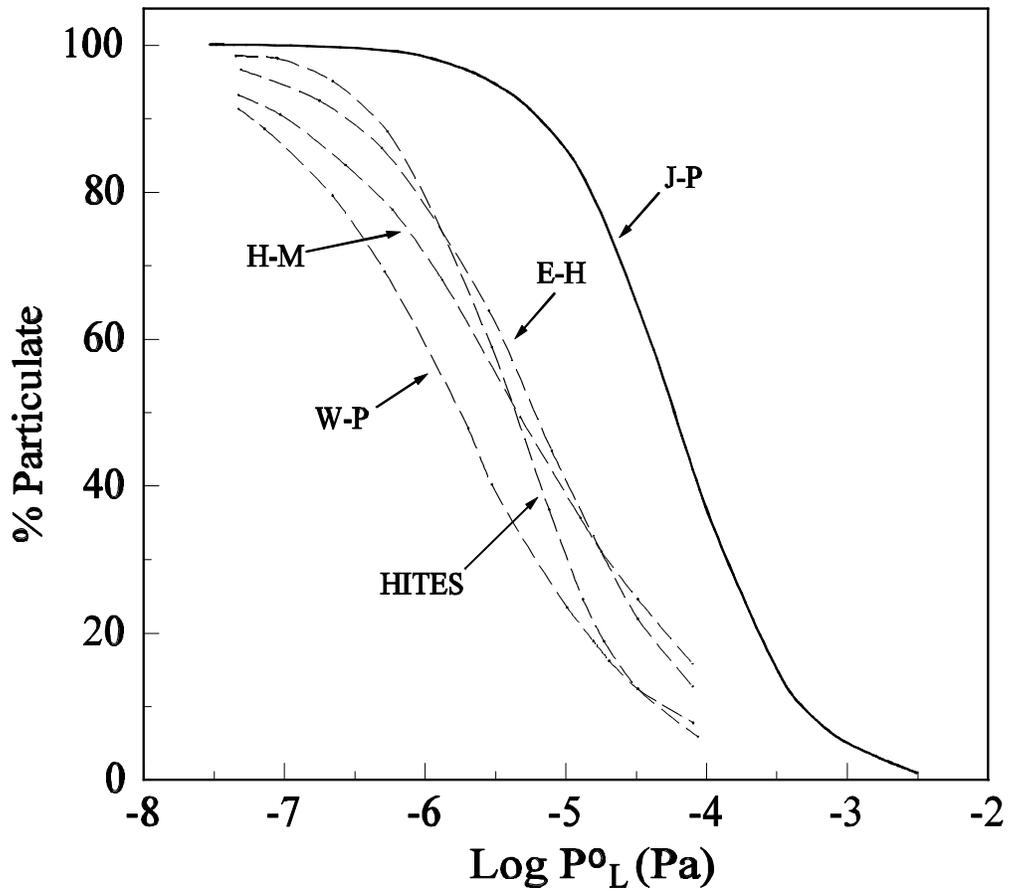
$$\phi = \frac{K_p (TSP)}{1 + K_p (TSP)} \quad (A-4)$$

The TSP can be solved for as a function of the total volume of particles per volume of air (cm^3 aerosol/ cm^3 air) and a particle density (g/cm^3). Assuming a density of $1.4 \text{ g}/\text{cm}^3$, the TSPs for the four airsheds are: clean continental background $9 \mu\text{g}/\text{m}^3$, average background $42 \mu\text{g}/\text{m}^3$, background plus local sources $60 \mu\text{g}/\text{m}^3$, and urban $98 \mu\text{g}/\text{m}^3$.

Step 4: As the final step, the particulate fractions at 20°C were calculated from K_p by Equation A-4, assuming $\text{TSP} = 60 \mu\text{g}/\text{m}^3$, which corresponds to the background plus local sources assumption made for the four data sources of V/P partitioning for the dioxins.

Thus, although the actual field measurements were done under a variety of temperatures, they were normalized to 20°C for comparison. Figure A-4 shows the particulate percentages from four field studies in comparison with those predicted by Junge-Pankow model for the background plus local sources air regime. All of the field data fall substantially below the model curve. For example, the particle-bound percentages of tetrachlorodioxins and furans, which are predicted to be 43-65%, averaged only 11-18% with the filter-sorbent sampler.

Reasons for these discrepancies may be related to both sampling artifacts and model uncertainties. Blow-off losses during collection are likely to reduce the filter-retained fraction (which is assumed to be equal to the particle-bound fraction). This artifact is expected to be the most serious for long sampling times, especially if the day-to-night temperature changes are large. However, the Welsch-Pausch samples, which were collected over 2-week integration times, show only slightly lower particulate values than those of other workers, which were obtained over 24- to 36-hour sampling periods. Aside from the Eitzer-Hites (1989) data, the data were from Whitby (1978). It is likely that Whitby's values of Θ do not reflect the true surface area distribution, since



they were based on the average size spectrum of aerosols and assumed spherical particles. Other limitations of the model are the inability to consider the kinetics of

Key: E-H = Eitzer and Hites (1989) HITES = Hites (1991)
H-M = Hunt and Maisel (1992) W-P = Welsch-Pausch et al. (1995)

FIGURE A-4

Comparison of Measured Particulate Percentages of Dioxins and Furans with Predictions of the Junge-Pankow Model as a Function of the Subcooled Liquid Vapor Pressure, P°_L , of the Dioxins and Furans.

adsorption/desorption (Kamens et al., 1995; Rounds et al., 1993) and humidity effects (Pankow et al., 1993).

In conclusion, neither the filter-sorbent sampler nor the Junge-Pankow model necessarily give the correct vapor/particle distributions. Evidence based on limited field data suggests that the model overestimates the particulate fraction of PCDD/Fs relative to the filtration sampler, but it can just as well be stated that the sampler underestimates the particulate fraction relative to the model. Further work needed to improve the state of knowledge of PCDD/F partitioning between the aerosol and gas phases includes:

- ! Comparative monitoring with filter-sorbent samplers and other speciating devices such as denuders (Coutant et al., 1992; Eatough et al., 1993; Krieger and Hites, 1994; Lane et al., 1988; Lewis et al., 1991; Gundel et al., 1995; Subramanyam et al., 1994; Tang et al., 1994) and diffusion separators (Turpin et al., 1993).
- ! Laboratory experiments to investigate the kinetics and thermodynamics of the sorption of PCDD/Fs and other semivolatile compounds and sorption aerosols.
- ! Improvements in modeling particle/gas distributions in ambient air.

Despite the differences in the monitored and modeled results, the Junge-Pankow model is the recommended approach for estimating the particle/gas distribution of PCDD/Fs at the present time. In addition to reproducing the general trend in partitioning with vapor pressure, the Junge-Pankow equation was used in the air-to-beef model validation described above. That exercise used the Junge-Pankow model for partitioning dioxins in the air. A key finding of that work was that the transfer of vapor-phase dioxins to plants and subsequently to animals dominated the terrestrial food chain. Also, and as described below, vapor/particle partition data on other semivolatile organic compounds are compared with model predictions, and the match

for these compounds is, in most cases (especially for PAHs), superior to that of the PCDD/Fs.

A.5. COMPARISON OF MEASURED AND MODELED VAPOR/PARTICLE DISTRIBUTIONS FOR SEMIVOLATILE COMPOUNDS OTHER THAN DIOXIN

The previous section described the use of the Junge-Pankow model to predict the vapor/particle partitioning of dioxin congeners in ambient air. It was shown that the model tended to predict more partitioning in the particle phase than had been measured. While the general trend of an increasing particle component as the chlorination increased was seen in measurements and in the modeled values, this overprediction of modeled versus measured was also consistent as the degree of chlorination increased. As described above, there is no general agreement as to which is the better measure of reality—the measured or the modeled vapor/particle partitioning for the dioxins.

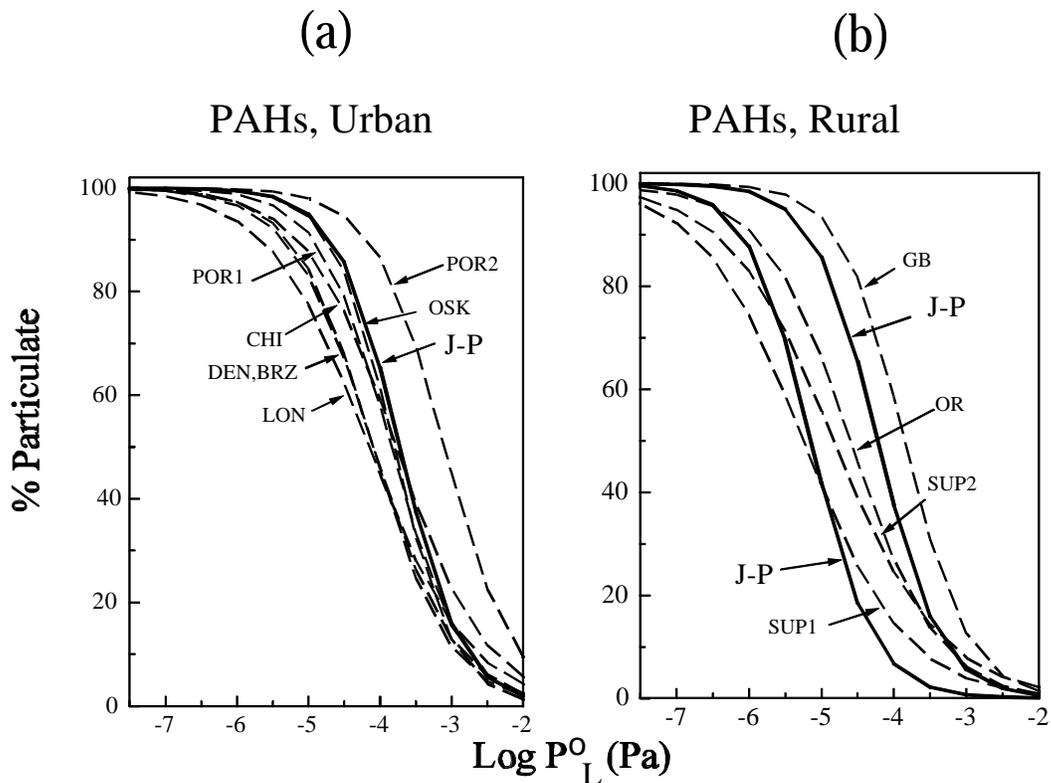
This section describes the application of the Junge-Pankow model to other semivolatile organic compounds. These include PAHs, PCBs, and organochlorine pesticides. The procedure for normalizing data from different literature sources was described in the previous section for dioxins and furans. The first step was the development of empirical relationships from the literature data. Table A-11 presents a summary of the m and b curve-fit parameters for this empirical relationship, which was shown in the previous section as Equation A-2. The subcooled liquid vapor pressures for the SOCs were taken from reports in the literature, including values for PAHs (MacKay et al., 1992; Yamasaki et al., 1984), PCBs (Falconer and Bidleman, 1994), and OC pesticides (Hinckley et al., 1990). The next step was to solve for the particle fraction, ϕ , as a function of K_p at a common temperature, 20°C, and the TSP (total suspended particulate) parameter. If TSP was not reported in the original paper (as in most cases), it was assumed that TSP = 98 $\mu\text{g}/\text{m}^3$ for urban air and 10-42 $\mu\text{g}/\text{m}^3$ for nonurban air of varying cleanliness.

This procedure was used to develop the dotted-line “observed” particle percentages shown in Figures A-5 and A-6. The modeled particle fractions were

determined for these sites using the Junge-Pankow model detailed in Chapter 3 and summarized in the section above on vapor/particle partitioning of dioxin.

| TABLE A-11 | | | | |
|--|--------------------|--------|-------|-----------|
| Parameters for the Empirical Relationship Relating the Subcooled Liquid Vapor Pressure, P°_L , to the Particle/Gas Partition Coefficient, K_p , of Semivolatile Organic Compounds (SOC) | | | | |
| Setting/SOC | Location | m | b | Reference |
| I. Urban | | | | |
| PAHs | Portland, Oregon | -0.882 | -5.38 | 1 |
| PAHs | Portland, Oregon | -0.89 | -4.75 | 2 |
| PAHs | Denver, Colorado | -0.76 | -5.1 | 3 |
| PCBs | Denver, Colorado | -0.946 | -5.86 | 3 |
| PAHs | Chicago, Illinois | -0.694 | -4.61 | 4 |
| PCBs | Chicago, Illinois | -0.726 | -5.18 | 4 |
| PAHs | London, U.K. | -0.631 | -4.61 | 5 |
| PAHs | Osaka, Japan | -1.04 | -5.95 | 6 |
| PAHs | Brazzaville, Congo | -0.81 | -5.31 | 7 |
| OC pesticides | Brazzaville, Congo | -0.74 | -5.76 | 7 |
| II. Rural | | | | |
| PAHs | Coastal Oregon | -0.724 | -4.94 | 1 |
| PAHs | Lake Superior | -0.586 | -3.83 | 8 |
| PAHs | Lake Superior | -0.614 | -4.25 | 9 |
| PAHs | Green Bay | -1 | -5.47 | 4 |
| PCBs, OC pesticides | Bayreuth, Germany | -0.61 | -4.74 | 10 |

- References:
- | | |
|--------------------------------|-------------------------------|
| 1. Ligocki and Pankow (1989) | 2. Hart (1989) |
| 3. Foreman and Bidleman (1990) | 4. Cotham and Bidleman (1995) |
| 5. Baek et al. (1991) | 6. Yamasaki et al. (1982) |
| 7. Ngabe and Bidleman (1992) | 8. McVeety and Hites (1988) |
| 9. Baker and Eisenreich (1990) | 10. Kaupp and Umlauf (1992) |



Key: J-P: Junge-Pankow model; the two solid lines in the rural setting represent clean continental background and background + local sources regimes
DEN = study in Denver (Foreman and Bidleman, 1990)
POR1 and POR2 = two studies in Portland (Ligocki and Pankow, 1989; Hart, 1989)
CHI = study in Chicago (Cotham and Bidleman, 1995)
SUP1 and SUP2 = two studies in Lake Superior (McVeety and Hites, 1988; Baker and Eisenreich, 1990)
BRZ = study in Brazzaville, Congo (Ngabe and Bidleman, 1992)
LON = study in London (Baek et al., 1991)
OSK = study in Osaka, Japan (Yamasaki et al., 1982)
GB = study in Green Bay (Cotham and Bidleman, 1995)

FIGURE A-5

Comparison of Measured and Predicted Particulate Percentages of PAHs in Urban and Rural Air.

The agreement between the measured and predicted aerosol-bound fractions of PAHs is remarkably good, as seen in Figure A-5. Two model curves are shown for rural air in Figure A-5b, representing clean continental background and background plus local sources regimes. Experimental PAH distributions fall reasonably close to the range of particulate values predicted by the model, although the fraction of aerosol-bound PAHs at rural sites (e.g., Lake Superior) is greater than expected for the more volatile compounds. This may be due to a portion of these PAHs being nonexchangeable (Pankow, 1988).

Fewer data are available for nondioxin organochlorine compounds. Figure A-6 shows the measured particulate percentages of PCB congeners and chlorinated pesticides in comparison to predictions. Again, the two depictions of model predictions for rural conditions (Figure A-6b) show a range from clean continental to background plus local sources. The monitored data fall below the model values, but the discrepancy is generally not as great as for the dioxins and furans.

Overall, it can be concluded the Junge-Pankow model appears to predict vapor/particle partitioning very similar to measurements for PAHs, but not as similar for PCBs and chlorinated pesticides, although the match there is still superior to that of dioxins and furans. This exercise does lend additional credibility, in general, to the Junge-Pankow model. However, the model and the measurements for PCDD/Fs do diverge, as described in the previous section, and the debate remains as to which is correct for the PCDD/Fs, the model or the measurements.

A.6. A VALIDATION EXERCISE FOR THE AIR-TO-PLANT ALGORITHMS FOR POLYCYCLIC AROMATIC HYDROCARBONS

Validation of the air-to-plant pathway was performed by utilizing PAH data collected in 1991-1992 in Bloomington, Indiana (Simonich and Hites, 1994). In this study, researchers collected air and vegetation samples during the growing season and analyzed them for 10 PAHs to suggest a link between plant lipids and resulting plant concentrations. The site-specific data were obtained from the researchers and used as input for this model validation exercise. Air concentrations of several PAHs became the source term input data, and the observed vegetation concentrations became the

dependent model result. Both sets of data (i.e., air and plant) were available temporally, and there was variation in both air and plant concentrations. For example, the pine needle concentration of anthracene varied from 26 to 10 to 21 ng/g dry weight from spring to summer to fall. Since the models of this assessment are steady state, both the air and plant data will be averaged over the growing season to give one independent air concentration and one dependent vegetation concentration for each contaminant/vegetation pair. This data set also provided another test for the Junge-Pankow model as the researchers provided measured vapor and particle fractions from the ambient air monitoring results.

Air concentrations were measured each sampling day and reported as total, particle-phase, and vapor-phase concentrations in ng/m³. Vegetation was sampled from two species of trees: *Acer saccharum* (sugar maple) and *Pinus strobus* (white pine). This exercise utilized the observed sugar maple leaf, sugar maple seed, and white pine needle data for comparisons with the predicted concentrations. Bark concentrations were also measured, but it was judged that this vegetation was not the type for which the air-to-plant models were developed. The pine needle samples were divided by the researchers into current-year growth and previous-year growth. An evaluation of the concentrations showed that the previous year's pine needles were consistently slightly higher than the current year's pine needles. This suggests that the previous year's pine needles, although not actively growing during the current season, still serve as passive collectors for airborne contaminants. Since the models were developed for actively growing vegetation, these previous-year pine needle concentrations will not be utilized in this exercise. Data were available for 10 PAHs. However, the appropriate fate parameters were not available for one of the PAHs, indeno[1,2,3-cd]pyrene, and results were not generated for it. In summary, then, there were three vegetations (sugar maple leaf, sugar maple seed, and white pine needle) and nine PAHs. Therefore, there were 9 independent source term concentrations and 27 dependent plant concentrations (9 PAHs · 3 vegetation).

The following describes the development of the model parameters for this exercise:

Particle fraction. These will be taken directly from Figure A-5, which shows the modeled particle fraction of PAHs as a function of airshed particle density and log of the subcooled liquid vapor pressure, P°_L (Pa), at 20°C. This is likely not a representative concentration for the spring/summer/fall of the full data set from Simonich and Hites (1994), but it is judged here to be sufficient for current purposes. The PAH data were taken from Bloomington, Illinois, which will be assumed to qualify as rural, specifically the background + local sources category of the two rural options (the other being continental background). The P°_L , taken from MacKay et al. (1992), is displayed in Table A-12 along with other fate parameters necessary for modeling PAHs in this exercise.

Other fate parameters. The other fate parameters that were used for calculating plant concentrations are listed in Table A-12 and include the Henry's Law Constant (H) and octanol-water partition coefficient (K_{ow}). The H and K_{ow} were used to calculate the volumetric air-to-leaf transfer factor, B_{vol} , using the Bacci empirical algorithm described in Chapter 6. It is noted that the recommendation in Chapter 6 is to calculate the B_v (which is calculated from the B_{vol}) and then divide the result by 100, based on evidence that the Bacci algorithm overestimates the transfer of dioxins from air to grass leaves by about a factor of 100.

Volume adjustment factor for vapor transfers. This adjustment factor, VG_{ag} (the subscript *ag* is for "above ground"), was incorporated into the vapor-to-plant algorithms to account for the differences in the plants for which the air-to-plant transfer factor (B_v) was developed (azalea and grass leaves) and bulky above-ground vegetation to which it might be applied, such as tomatoes or apples. A VG_{ag} of 1.0 was used for pine needles and maple leaves, which assumes they are reasonably analogous to the thin azalea and grass leaves, whereas a VG_{ag} of 0.1 was used for maple seeds. In this case, the VG_{ag} would account for the dilution of vapor-phase contaminants dispersing through the seed covering and into the seed.

| TABLE A-12 | | | |
|---|---|---------------------|--|
| Physical Chemical Properties of the Polycyclic Aromatic Hydrocarbons Assigned for this Exercise | | | |
| PAH | Henry's Law Constant atm·m ³ ·mole ⁻¹ ·@25°C | Low K _{ow} | P ^o _L , pascals |
| Anthracene | 3.83·10 ⁻⁵ | 4.54 | 7.78·10 ⁻² |
| Phenanthrene | 3.13·10 ⁻⁵ | 4.57 | 1.13·10 ⁻¹ |
| Benz[a]anthracene | 5.62·10 ⁻⁶ | 5.91 | 6.06·10 ⁻⁴ |
| Chrysene/triphenylene | 6.29·10 ⁻⁷ | 5.86 | 1.07·10 ⁻⁴ |
| Fluoranthene | 1.00·10 ⁻⁵ | 5.22 | 8.72·10 ⁻³ |
| Pyrene | 8.91·10 ⁻⁶ | 5.18 | 1.19·10 ⁻² |
| Benzo[a]pyrene | 4.45·10 ⁻⁷ | 6.04 | 2.13·10 ⁻⁵ |
| Benzo[e]pyrene | 1.93·10 ⁻⁷ | 6.04 | 2.41·10 ⁻⁵ |
| Benzo[ghi]perylene | 7.26·10 ⁻⁷ | 6.5 | 2.25·10 ⁻⁵ |

Data from: MacKay et al. (1992)

Surface loss/weathering constant. The 14-day weathering half-life of particle-bound contaminants depositing onto vegetation that was discussed in Chapter 6 for general use was used in this exercise; this equates to a loss constant (k_p) of 18.02/year.

Deposition velocity and rates. The wet and dry deposition velocities are used to calculate respective particle-bound contaminant deposition rates: an ambient air concentration of particle-bound contaminant times the deposition velocity gives the rate of deposition in appropriate units of mass/area/time. A dry deposition velocity (V_d) of 0.37 cm/s for PAHs (McVeety and Hites, 1988) was used in this exercise. The McVeety and Hites (1988) study also derived a ratio of 6:1 for dry to wet fluxes; therefore, the wet deposition rate (D_{yw}) was calculated by dividing the dry deposition rate (D_{yd}) by 6. This ratio of 6:1 contrasts with the ratio of about 1:1 that Koester and Hites (1992)

found for dioxins and furans, and which was used in the air-to-beef model validation exercise above.

Dry matter yield. Belcher and Travis (1989) specified crop yields (Y_{p_i}) for many crops, including animal forage, animal grain, potatoes, leafy vegetables, root vegetables, garden fruits, and legumes. The most reasonable match for maple leaves and pine needles appeared to be the dry matter yield for leafy vegetables, 0.18 kg/m^2 ; for maple seeds, the dry matter yield for legumes, 0.10 kg/m^2 , was chosen.

Plant density, moisture content, surface retention, and interception. These are plant properties required for various aspects of the air-to-plant model. The plant density and plant moisture content are required to convert the parameter volume-based air-to-leaf transfer factor, B_{vol} , to the mass-based transfer factor, B_v (see Chapter 6). This information was not provided in Simonich and Hites (1994), but these data were presented for other vegetation in McCrady (1994). Specifically, McCrady lists densities of 800 to 1000 g/L for various vegetation, including grass, pepper, azalea, and kale leaves; spruce needle; and the fruits of tomato, pepper, and apple. For this exercise, it will be simplistically assumed that the plant density for the leaves, needles, and seeds will be 900 g/L. Simonich and Hites (1994) list moisture fractions of between 0.25 and 0.6 for all vegetation, without providing any more detail. It will be assumed that all the vegetations have a moisture fraction of 0.5. A value of 0.6 is given to the surface retention parameter, F_w , based on the recommendation made in Chapter 6. This fraction is defined as the fraction of the wet deposition that is retained on the surfaces of the vegetation after the rainfall is over; since the value of F_w is 0.6, this means 0.4 (or 40%) of the particle-bound contaminants depositing during rainfall wash off the plant. An interception fraction reflects the amount of depositing contaminant that is intercepted before it reaches the ground. Since these studies are for trees, which will be assumed to be dense vegetation, in general an interception fraction of 1.0 is appropriate. This will be assumed for the pine needles. However, the maple leaves will intercept some of the depositions that might have reached maple seeds, and vice

versa. For this reason, the interception fraction of 1.0 for the maple tree in general will be split between the leaves, at 0.7, and seeds, at 0.3.

As a final note, the plant impact pathway of soil-to-plant, discussed in Chapter 6, is not considered in this exercise. Because of the physical structure of the tree canopy that restricts deposition to soil, the depth of tree root systems, and the relatively short half-lives of PAHs in soil (Howard et al., 1991), the contribution of root uptake and translocation was assumed to be negligible. Therefore, this exercise assumes that the primary source of contamination to the vegetation is from the air. This is similar to the assumption made above in the air-to-beef validation exercise for dioxins.

The results for this exercise are shown in Tables A-13 and A-14, which compare observed and predicted vapor fractions and vegetation concentrations, respectively. The model is generally consistent and accurate in predicting vapor fractions: the observed was very near the predicted except for benz[a]anthracene and benzo[e]pyrene, where the predicted vapor fraction was about 3 times as high as the observed vapor fraction. These results are consistent with the tests of the vapor/particle partitioning model for PAHs discussed in the section above. However, the model consistently underpredicts the final concentration in the vegetation. This underprediction was greater than a factor of 10 nearly half the time. The model and the data do show reduced concentrations in seeds. This result lends some credibility to the assignment of 0.1 for the VG_{ag} for seeds, in contrast to values of 1.0 for leaves and needles.

The question to ask, obviously, is why the model did so poorly. One possibility, of course, is that the basic assumptions and structure of the model are flawed. An evaluation of whether this is the case is beyond the scope of this document, but there is no immediate reason to negate the simple steady-state construct of this model for PAHs. There is evidence of a varying PAH concentration in the pine and maple vegetation in these experiments, which may question the use of a steady-state model. However, these variations in plant concentrations are not by orders of magnitude.

Another possibility is that the input air concentrations data or the observed vegetation concentrations are flawed, but again there is no reason to believe this to be the case.

| PAH | Observed Air Concentrations, ng/m ³ | | Observed Vapor Fraction | Predicted Vapor Fraction | Ratio Pred/Obs |
|-----------------------|--|-------------|-------------------------|--------------------------|----------------|
| | Particle Phase | Vapor Phase | | | |
| Anthracene | 0.03 | 2.257 | 0.99 | 0.99 | 1 |
| Phenanthrene | 0.172 | 28.577 | 0.99 | 0.99 | 1 |
| Benz[a]anthracene | 0.15 | 0.069 | 0.32 | 0.9 | 2.8 |
| Chrysene/triphenylene | 0.254 | 0.28 | 0.53 | 0.58 | 1.1 |
| Fluoranthene | 0.295 | 5.357 | 0.95 | 0.99 | 1 |
| Pyrene | 0.221 | 3.194 | 0.94 | 0.99 | 1 |
| Benzo[a]pyrene | 0.18 | 0.047 | 0.21 | 0.25 | 1.2 |
| Benzo[e]pyrene | 0.275 | 0.055 | 0.17 | 0.25 | 1.5 |
| Benzo[ghi]perylene | 0.413 | 0.04 | 0.09 | 0.25 | 2.8 |

Appendix A
Model Validation

| TABLE A-14 Observed and Predicted Pine Needle, Maple Leaf, and Maple Seed Concentrations | | | | |
|---|-----------------------|------------------------------------|-----------|----------|
| Vegetation Type | PAH | Observed conc., ng/g dry weight | Predicted | |
| | | | ng/g dw | Pred/Obs |
| Pine needles | Anthracene | 18.1 | 0.9 | 0.05 |
| | Phenanthrene | 345.85 | 12 | 0.03 |
| | Benz[a]anthracene | 16.7 | 1.7 | 0.1 |
| | Chrysene/triphenylene | 61.41 | 19.1 | 0.31 |
| | Fluoranthene | 136.11 | 4.7 | 0.03 |
| | Pyrene | 78.31 | 2.8 | 0.04 |
| | Benzo[a]pyrene | 16.81 | 7.1 | 0.42 |
| | Benzo[e]pyrene | 24.93 | 11 | 0.44 |
| | Benzo[ghi]perylene | 21.12 | 14.8 | 0.7 |
| Maple leaves | Anthracene | 10.88 | 1 | 0.09 |
| | Phenanthrene | 142.2 | 12.2 | 0.09 |
| | Benz[a]anthracene | 18.51 | 1.7 | 0.09 |
| | Chrysene/triphenylene | 56.36 | 19.2 | 0.34 |
| | Fluoranthene | 179.92 | 4.7 | 0.03 |
| | Pyrene | 104.53 | 2.8 | 0.03 |
| | Benzo[a]pyrene | 18.62 | 7.2 | 0.39 |
| | Benzo[e]pyrene | 24.79 | 11.2 | 0.45 |
| | Benzo[ghi]perylene | 19.15 | 15 | 0.78 |
| Maple seeds | Anthracene | 4.15 | 0.9 | 0.22 |
| | Phenanthrene | 55.09 | 11.4 | 0.21 |
| | Benz[a]anthracene | 6.53 | 1 | 0.15 |
| | Chrysene/triphenylene | 18.03 | 9.9 | 0.55 |
| | Fluoranthene | 51.09 | 2.5 | 0.05 |
| | Pyrene | 37.53 | 1.5 | 0.04 |
| | Benzo[a]pyrene | 10.69 | 6.8 | 0.64 |
| | Benzo[e]pyrene | 11.88 | 9.9 | 0.83 |
| | Benzo[ghi]perylene | 4.98 | 13.6 | 2.73 |

Assuming then that the model and the air/plant concentrations are appropriate for this exercise, the logical next step is to examine the input data. The particle impact parameters are uncertain. Changing the assumption that wet deposition was one-sixth dry deposition to the assumption that wet and dry depositions were equal was tested and found not to impact the results. Decreasing the rate of blowoff/washoff of particle-bound contaminants, even by a great amount (assuming that particle-bound contaminants do not dissipate from the plants) would still not bring predicted concentrations in line with observations (and assuming no washoff or blowoff appears unreasonable anyway).

This leaves the vapor impact algorithm, which is a logical place to consider variations in the assignment of model parameters. Simonich and Hites (1994) concluded that the concentrations in tree vegetation (leaves, bark, needles, and seeds) were primarily a function of the gas-phase concentrations of the PAHs (not the particle phase), the temperature, and the plant lipid fractions. All these factors underscore the importance of the vapor phase. The vapor phase dioxins were also found to be of principal importance in explaining grass concentrations of dioxins both in experiments (Welsch-Pausch et al., 1995) and in modeling (Lorber et al., 1994; Lorber, 1995). Changing the vapor/particle modeling does not seem the best place to start, since both the modeling and the monitoring showed reasonably similar vapor fractions. This leaves the important air-to-leaf transfer factor, B_v , as a parameter to consider varying.

The first assignment of the B_v for the indirect methodologies of this document (U.S. EPA, 1990b) was based on the empirical algorithm developed by Bacci and colleagues (Bacci et al., 1992). They conducted chamber experiments with several organic contaminants transferring to azalea leaves. However, this algorithm was found to greatly overestimate the transfer of vapor-phase 2,3,7,8-TCDD to grass in similarly designed chamber experiments by McCrady and Maggard (1993). These researchers showed that 2,3,7,8-TCDD would volatilize out of grass at a rate about 20 times greater than out of azalea leaves. Also, by exposing the grass to natural sunlight, they demonstrated an additional twofold increase in the overall rate of disappearance of

dioxins from grass as compared to azalea leaves (which had not been exposed to sunlight in the Bacci experiments). Subsequently, U.S. EPA (1994) assigned values of B_v for each of the dioxin congeners by first deriving a Bacci B_v and dividing it by a factor of 40. Even this assignment was found to overestimate grass concentrations for the dioxins, and a later calibration by Lorber (1995) reduced the dioxin B_v by an additional factor of around 2 to 4 for all the dioxin congeners. This led to the approach recommended in Chapter 5 of this document, which was to assign B_v for organic contaminants by first using the Bacci algorithm and then dividing the final results by a factor of 100. However, the evidence presented in this section suggests that this leads to a B_v that is much too low for the PAH, at least for the tree vegetation in this exercise.

As just described, McCrady and Maggard (1993) found much less net transfer of 2,3,7,8-TCDD into grass than would be predicted using the Bacci algorithm. They attributed that to differences in plant species between the azalea leaves of the Bacci experiments and their grass leaves, and the fact that the Bacci experiments did not consider photodegradation. McCrady and Maggard (1993) did not identify or speculate on what they meant about plant species differences. McCrady (1994) later provided data that might lend some insight into this species difference. First, the lipid fractions listed in McCrady (1994) for azalea and grass leaves were quite comparable, so the amount of plant lipid may not explain the difference between the net transfer rates of 2,3,7,8-TCDD into azalea and grass leaves. However, the wax contents of grass and azalea leaves were very different. McCrady (1994) lists the wax content of the grass leaf as 0.046 g/cm^2 , whereas for azalea leaves the wax content is an order of magnitude higher at 0.48 g/cm^2 . This plant characteristic may have been critical in slowing the volatile release of organic contaminants (one of which was a dioxin) in the Bacci experiments, as compared to the McCrady experiments with grass and 2,3,7,8-TCDD.

(Interestingly, McCrady (1994) found that the uptake of 2,3,7,8-TCDD into various vegetations was not a function of the wax content; the uptake was very similar for the eight vegetations he tested, which ranged in wax content from 0.046 g/cm^2 for grass to

4.9 g/cm² for apple. However, he did not conduct a follow-up phase of his experiments, which is the release phase, where he might have seen a difference. The air-to-leaf transfer factors are experimentally determined as the ratio of the rate of uptake divided by the rate of release.)

In any case, if a plant species difference is important in the uptake and (maybe more importantly) release of vapor-phase organic contaminants transferring from the air to plants, then it seems possible that the guidance for assignment of B_v in Chapter 6 might be reasonable for grass and similar vegetation of low wax content, but maybe not for vegetation of higher wax content. Simonich and Hites (1994) do not provide wax content data for their vegetation, but they do provide lipid fractions, which are very similar to the lipid fractions for azalea and grass leaves listed in McCrady (1994). However, McCrady (1994) does list the wax content of a spruce needle as 2.5 g/cm², which perhaps is similar to the pine needles of these PAH experiments, and also a kale leaf wax content of 0.50 g/cm² which, along with the azalea leaf, may be closer in wax content to the maple leaves of the PAH experiments.

The Simonich and Hites (1994) data and the analysis in this section imply that there is an important difference in plant species when values are assigned for the air-to-plant vapor transfer factor, B_v . This can be stated only as a hypothesis and not a conclusion. It may also be true that the Simonich and Hites (1994) data suggest something else, such as an important difference in organic contaminants and the transfer of their vapor-phase fractions into vegetation. Regardless of which of these two hypotheses (or both to some extent) is true, this exercise suggests that the Simonich and Hites (1994) data may more appropriate as a data set for calibration rather than validation. The calibrated parameter could be the air-to-leaf transfer factor, B_v , for the PAHs. Recall that the general recommendation for assigning B_v is to first calculate it using the Bacci algorithm and then divide the final result by 100. Instead of dividing by 100, this exercise suggests that the calibrated B_v for the PAHs and the (waxy) vegetation can be calculated as the Bacci B_v for each PAH with the following adjustments: anthracene (Bacci) B_v times a factor of 3, phenanthrene B_v times a factor

of 4, benz[a]anthracene B_v divided by 5, chrysene/triphenylene divided by 20, fluoranthene B_v divided by 2, pyrene B_v divided by 2, benzo[a]pyrene divided by 5, benzo[e]pyrene B_v divided by 10, and benzo[e]pyrene B_v divided by 20.

In summary, this exercise has demonstrated the importance of applying site-specific data to test this methodology. The available data were sufficient to validate the model; that is, appropriate source-term as well as dependent data were available. Gaps in site-specific data were filled by using judgment and information provided in this document and other references. When the model was fully parameterized, it was found to consistently underpredict the vegetation concentration. This suggested, therefore, that one or more of the model parameters were improperly assigned (assuming, of course, that the source term and observed vegetation concentrations, and the model in general, were appropriate). An examination of the possibilities further suggested that it was the air-to-leaf transfer factor for vapor-phase PAHs, the B_v , that was the most likely candidate for reassignment. An examination of the literature on vapor transfers of semivolatile organic contaminants such as PAHs and dioxins suggested that plant characteristics may be important in the uptake and release of these contaminants from air. Further, the data suggested that the high wax content of vegetation such as azalea leaves or pine needles may lead to greater net uptake as compared to less waxy vegetation such as grass. If this is the case, it may be most appropriate to use the calibrated B_v for PAHs in this section when modeling the transfer of these compounds to vegetation of high wax content, but to still use the recommended approach (i.e., the Bacci-derived B_v divided by 100) when developing B_v for terrestrial animal food chain vegetation such as grasses or fodder, which have lower wax content.

In any case, users of this methodology are encouraged to use any data available to test its models. While the exercises in this chapter may have demonstrated that the fate and transport models generally bring predictions in line with observations, exercises such as the one in this last section should alert users that uncertainties continue to exist and that model validation continues to be an issue to address.

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**DERIVATION OF KINETIC BREAST MILK EXPOSURE MODEL
INCORPORATING BREAST FEEDING LOSSES**

B.1. Maternal Whole-Body Concentration at time t after start of Exposure

Scenario. The general formula for the rate of change of the maternal whole-body concentration of a pollutant is given in Equation B-1:

$$\frac{dM_t}{dt} = I_m - kM_t$$

(B-1)

where:

M_t = maternal whole-body concentration of pollutant after t days of exposure (mg/kg)

I_m = maternal intake of pollutant (mg/kg-day)

k = whole-body elimination constant (day^{-1})

Dividing Equation B-1 through by k and rearranging yields Equation B-2.

$$\frac{1}{\frac{I_m}{k} - M_t} dM_t = k dt$$

(B-2)

Integrating both sides of Equation B-2 with respect to time (t) gives Equation B-3.

$$-\ln \left(\frac{I_m}{k} - M_t \right) = kt + C_a$$

(B-3)

where C_a is the aggregate constant of integration.

Exponentiating both sides of Equation B-3 gives Equation B-4.

Appendix B
Derivation of Kinetic Breast Milk Exposure Model Incorporating
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$$\frac{I_m}{k} - M_t = e^{-kt - C_a}$$

(B-4)

Substituting C for $-C_a$ in Equation B-4 and solving for M_t yields Equation B-5.

$$M_t = \frac{I_m}{k} - e^C e^{-kt}$$

(B-5)

At $t = 0$, Equation B-5 becomes:

$$M_0 = \frac{I_m}{k} - e^C$$

(B-6)

where M_0 is the maternal whole-body concentration at the start of the exposure period.

Solving for e^C gives Equation B-7.

$$e^C = \frac{I_m}{k} - M_0$$

(B-7)

Substituting for e^C in Equation B-5 yields Equation B-8.

$$M_t = \frac{I_m}{k} (1 - e^{-kt}) + M_0 e^{-kt}$$

(B-8)

Equation B-8 is the general formula for calculating non-steady-state whole-body concentrations at time t following the start of the exposure, given a constant intake. For $M_0 = 0$, the equation simplifies to Equation B-9:

Appendix B

Derivation of Kinetic Breast Milk Exposure Model Incorporating Breast Feeding Losses

$$M_t = \frac{I_m}{k} (1 - e^{-kt})$$

(B-9)

where I_m/k represents the theoretical steady-state whole-body concentration. A more intuitive description of Equation B-8 is that it represents the sum of the fraction of the steady-state level reached at time t with constant intake and constant elimination, and the fraction of the initial concentration remaining after time t , given constant elimination.

B.2. Average Whole-body Concentration over Duration of Exposure Scenario.

The average body-burden concentration over time period T ($T > 0$) is given in Equation B-10:

$$M_{avg} = \frac{1}{T} \int_0^T M_t dt$$

(B-10)

Substituting for M_t from Equation B-8 yields Equation B-11a.

$$M_{avg} = \frac{1}{T} \int_0^T \left[\frac{I_m}{k} (1 - e^{-kt}) + M_0 e^{-kt} \right] dt$$

(B-11a)

The integral is simplified in Equations B-11b through B-11c.

$$M_{avg} = \frac{1}{T} \int_0^T \left(\frac{I_m}{k} - \frac{I_m}{k} e^{-kt} + M_0 e^{-kt} \right) dt$$

(B-11b)

$$M_{avg} = \frac{1}{T} \left[\int_0^T \frac{I_m}{k} dt + \left(M_0 - \frac{I_m}{k} \right) \int_0^T e^{-kt} dt \right]$$

(B-11c)

Appendix B
 Derivation of Kinetic Breast Milk Exposure Model Incorporating
 Breast Feeding Losses

Solving the integral yields Equation B-12, which is algebraically expanded to give Equation B-13.

$$M_{avg} = \frac{1}{T} \left[\frac{I_m}{k} T + \frac{1}{k} \left(M_0 - \frac{I_m}{k} \right) (1 - e^{-kT}) \right] \quad (\text{B-12})$$

$$M_{avg} = \frac{I_m}{k} + \frac{1}{kT} \left(M_0 - \frac{I_m}{k} \right) (1 - e^{-kT}) \quad (\text{B-13})$$

From Equation B-9, the expression for maternal whole-body concentration prior to breast feeding is:

$$M_0 = \frac{I_m}{k_m} (1 - e^{-k_m t_m}) \quad (\text{B-14})$$

where I_m , k_m , and t_m are equivalent to hDI_{MAT} (Eq. 9-2), k_{elim} (Eq. 9-5), and t_{pn} (Eq. 9-3), respectively.

Substituting for M_0 in Equation B-13, the average maternal whole-body concentration over the period of breast feeding is given by Equation B-15:

$$M_{avg} = \frac{I_m}{k} + \frac{1}{kT} \left(\frac{I_m}{k_m} (1 - e^{-k_m t_m}) - \frac{I_m}{k} \right) (1 - e^{-kT}) \quad (\text{B-15})$$

where k is now equivalent to k_{elac} (Eq. 9-6) and T is equivalent to t_{bf} (Eq. 9-4).

Equation B-15 can be algebraically manipulated to give Equation B-16:

$$M_{avg} = \frac{I_m}{k_m} \left[\frac{k_m}{k} + \frac{1}{kT} (1 - e^{-k_m t_m} - \frac{k_m}{k}) (1 - e^{-kT}) \right] \quad (\text{B-16})$$

B.3. Average Breast Milk Concentration over Duration of Breast Feeding. As the concentration of the pollutant in milkfat is assumed to be the same as in body fat and the fraction of ingested pollutant in body fat is assumed to be a constant, the average concentration in milkfat can be related to M_{avg} as in Equation B-17.

$$C_{milkfat} = M_{avg} \frac{f_f}{f_{fm}} \quad (B-17)$$

where:

$C_{milkfat}$ = contaminant concentration in maternal milk fat (mg/kg)

f_f = fraction of contaminant that is stored in maternal fat (dimensionless)

f_{fm} = fraction of mother's weight that is fat (kg maternal fat/kg total body weight)

Substituting from Equation B-16 and converting to the notation used in the body of the Chapter yields Equation B-18, which is identical to Equation 9-4.

$$C_{milkfat} = \frac{hDI_{MAT} f_f}{k_{elim} f_{fm}} \left[\frac{k_{elim}}{k_{elac}} + \frac{1}{k_{elac} t_{bf}} (1 - e^{-k_{elim} t_{pn}} - \frac{k_{elim}}{k_{elac}} (1 - e^{-k_{elac} t_{bf}})) \right] \quad (B-18)$$

GLOSSARY

Absorption: The process of a chemical crossing the boundary and entering the body of the organism.

Aerometric Information Retrieval System (AIRS): A computer-based repository of US air pollution information administered by the EPA Office of Air Quality Planning and Standards AIRWeb Air Resources Web, a US National Park-focused air quality information retrieval system developed by the Air Resources Division of the National Park Service.

Aerosol: A suspension of microscopic solid or liquid particles in air. See also haze, particulate matter.

Air Pollutant: An unwanted chemical or other material found in the air. See also air pollution.

Air Pollution: Degradation of air quality resulting from unwanted chemicals or other materials occurring in the air. See also air pollutant.

Air Quality: (in context of the national parks) The properties and degree of purity of air to which people and natural and heritage resources are exposed.

Air Pollution Control Permitting Process: Process by which facilities are permitted to emit specified types and quantities of air pollutants.

Air Quality Related Values (Aqrvs): Values including visibility, flora, fauna, cultural and historical resources, odor, soil, water, and virtually all resources that are dependent upon and affected by air quality. "These values include visibility and those scenic, cultural, biological, and recreation resources of an area that are affected by air quality" (43 Fed. Reg. 15016).

Air Quality: Ambient pollutant concentrations and their temporal and spatial distribution.

Algorithm: A specific mathematical calculation procedure. A model may contain several algorithms.

Ambient Air: Air that is accessible to the public.

Attainment Area: A geographic area in which levels of a criteria air pollutant meet the health-based National Ambient Air Quality Standard for that specific pollutant.

Background: Ambient pollutant concentrations due to:

- (1) natural sources;
- (2) nearby sources other than the one(s) currently under consideration; and
- (3) unidentified sources.

Best Available Control Technology (BACT): An emission limitation based on the maximum degree of reduction for each pollutant, that must be applied by sources subject to the Prevention of Significant Deterioration program.

Bioaccumulation: The accumulation of a substance by an organism as a result of all environmental sources.

Bioconcentration Factor (BCF): The equilibrium concentration of a chemical in a biological medium divided by the equilibrium concentration of a chemical in the environmental medium through which the exposure directly occurs.

Bioaccumulation Factor (BAF): The equilibrium concentration of a chemical in a biological medium divided by the equilibrium concentration of a chemical in the environmental medium where both the organism and its food were exposed.

Biological Effects: Ecological studies to determine the nature or extent of air pollution injury to biological systems. See also biological effects pages.

Bulk Density: A common soil parameter, which is the mass of a unit of dry soil (includes pore and solids)

Calibrate: An objective adjustment using measured air quality data (e.g., an adjustment based on least-squares linear regression).

Calm: For purposes of air quality modeling, calm is used to define the situation when the wind is indeterminate with regard to speed or direction.

Carbon Monoxide: A criteria air pollutant that is a colorless, odorless, poisonous gas produced by incomplete combustion; particularly, incomplete burning of carbon-based fuels e.g. gasoline, oil, and wood.

CD-144 Format: Card Deck-144 data format available from NCDC for National Weather Service surface observations commonly used for dispersion models. Each record represents an 80-column "card image".

Clean Air Act: Originally passed in 1963, our current national air pollution control program is based on the 1970 version of the law. Substantial revisions were made by the 1990 Clean Air Act Amendments. See also Clean Air Act pages.

Complex Terrain: Terrain exceeding the height of the stack being modeled.

Contact Medium: The contaminated material that comes into contact with the outer boundary of the body through a specific route of exposure. For example, with methylmercury-contaminated fish, fish is the contact medium; with benzene contaminated air, the air is the contact medium when the exposure occurs.

Criteria: (in the context of criteria pollutants) Information on health and/or environmental effects of pollution.

Dispersion Model: A group of related mathematical algorithms used to estimate (model) the dispersion of pollutants in the atmosphere due to transport by the mean (average) wind and small scale turbulence.

Dose: The amount of a substance available for interaction with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism.

Dose-response: The relationship between the dose of a pollutant and its effect on a biological system.

Emissions: Release of pollutants into the air from a source.

Erosivity: Represents the influence of precipitation on soil erosion.

Exposure: The condition of a chemical contacting the outer boundary of an organism.

Exposure Duration: The amount of time individuals are exposed.

Exposure Route: The way a chemical enters an organism after contact. Routes of human exposure include dermal, oral and respiratory.

Fine Particle: Particulate matter less than 2.5 microns in diameter.

Flow Vector: The direction towards which the wind is blowing.

Fluid Modeling: Modeling conducted in a wind tunnel or water channel to quantitatively evaluate the influence of buildings and/or terrain on pollutant concentrations.

Fugitive Dust: Dust discharged to the atmosphere in an unconfined flow stream such as that from unpaved roads, storage piles and heavy construction operations.

Hazardous Air Pollutants (HAP): Airborne chemicals that cause serious health and environmental effects.

Henry's Law Constant: The ratio at equilibrium of the gas phase concentration to the liquid phase concentration of the gas.

Meteorological Data File: Any file containing meteorological data, whether it be mixing heights, surface observations or on-site data.

Mixing Height: The depth through which atmospheric pollutants are typically mixed by dispersive processes.

Mobile Sources: Moving objects that release regulated air pollutants, e.g. cars, trucks, buses, planes, trains, motorcycles, and gas-powered lawn mowers. See also source; stationary source.

Model: A quantitative or mathematical representation or simulation which attempts to describe the characteristics or relationships of physical events.

Monin Obukhov Length: A constant, characteristic length scale for a particular example of flow. It is negative in unstable conditions (upward heat flux), positive for stable conditions, and approach infinity as the actual lapse rate for the ambient air reaches the dry adiabatic lapse rate.

Monitoring: Measurement of air pollution. See also continuous sampling device, integrated sampling device.

MPRM: Meteorological Processor for Regulatory Models, a program designed for the purpose of processing on-site meteorological data to prepare them for input to the regulatory models, such as ISC. Produces a file comparable to the RAMMET pre-processor output, and also capable of producing STAR summaries.

National Ambient Air Quality Standards (NAAQS): Permissible levels of criteria air pollutants established to protect public health and welfare. See also EPA's NAAQS page.

NCDC: National Climatic Data Center, the federal agency responsible for distribution of the National Weather Service upper air, mixing height and surface observation data.

Nitrogen Oxides: A criteria air pollutant, compounds NO, NO₂, NO₃, N₂O₅, alkyl nitrates, etc. See also NO_x and Noy.

NO_x: The sum of NO + NO₂. See also nitrogen oxides, Noy.

Octanol-water Partition Coefficient (K_{ow}): The ratio of the concentration of a substance in the octanol phase to its concentration in the aqueous phase in an equilibrated two-phase octanol-water system.

On-Site Data: Data collected from a meteorological measurement program operated in the vicinity of the site to be modeled in the dispersion analysis.

Organic Compounds: Chemicals that contain the element carbon.

Ozone: A gas similar to oxygen that is a criteria air pollutant and a major constituent of smog. See also reactive organic compounds; volatile organic compounds.

Particle Bulk Density: The mass of a volume of soil solids. (See bulk density)

Particle Sampler: An instrument to measure particulate matter in ambient air.

Particulate Matter: Dust, soot, other tiny bits of solid materials that are released into and move around in the air. See also fine particle, PM10, Visibility Research Program pages.

Pasquill Stability Categories: A classification of the dispersive capacity of the atmosphere, originally defined using surface wind speed, solar insolation (daytime) and cloudiness (nighttime). They have since been reinterpreted using various other meteorological variables.

PM10: A criteria air pollutant that is particulate matter in ambient air exceeding 10 microns in diameter.

Prevention of Significant Deterioration (PSD): A program established by the Clean Air Act that limits the amount of additional air pollution that is allowed in Class I and Class II areas.

Primary Standard. A pollution standard based on human health effects. Primary standards are set for criteria air pollutants. See also secondary standard.

Quality Assessment Check: Determining if the reported value of a variable is reasonable (see also Range Check).

Range Check: Determining if a variable falls within predefined upper and lower bounds.

Reactive Organic Compounds: (in the context of photochemically produced air pollution) Organic compounds that produce ozone in the presence of nitrogen oxides and sunlight. See also Volatile Organic Compounds.

Receptor: A location at which ambient air quality is measured or estimated.

Receptor Models: Procedures that examine an ambient monitor sample of particulate matter and the conditions of its collection to infer the types or relative mix of sources impacting on it during collection.

Refined Model: An analytical technique that provides a detailed treatment of physical and chemical atmospheric processes and requires detailed and precise input data. Specialized estimates are calculated that are useful for evaluating source impact relative to air quality standards and allowable increments. The estimates are more accurate than those obtained from conservative screening techniques.

Reformulated Gasoline: Specially-refined gasoline with low levels of smog-forming volatile organic compounds and low levels of hazardous air pollutants.

Regulatory Applications: Dispersion modeling involving regulatory decision-making as described in the Guideline on Air Quality Models (Revised), (U.S. EPA, 1987b).

Regulatory Model: A dispersion model that has been approved for use by the regulatory offices of the U.S. EPA, specifically one that is included in Appendix A of the Guideline on Air Quality Models (Revised), (U.S. EPA, 1987b), such as the ISC model.

Screening Technique: A relatively simple analysis technique to determine if a given source is likely to pose a threat to air quality. Concentration estimates from screening techniques are conservative.

Secondary Standard: An air pollution limit based on environmental effects, e.g. damage to property, plants, visibility, etc. Secondary standards are set for criteria air pollutants. See also primary standard.

Simple Terrain: An area where terrain features are all lower in elevation than the top of the stack of the source.

Smog: A mixture of air pollutants, principally ground-level ozone, produced by chemical reactions involving smog-forming chemicals. See also haze.

Soil Erodibility Factor: This factor reflects the influence of soil properties on erosion.

Source: Any place or object from which air pollutants are released. Sources that are fixed in space are stationary sources; sources that move are mobile sources. See also major source.

Sulfur Dioxide (SO₂): A criteria air pollutant that is a gas produced by burning coal and some industrial processes. See also acid deposition, sulfur dioxide park topics.

Surface Weather Observations: A collection of atmospheric data on the state of the atmosphere as observed from the earth's surface. In the U.S. the National Weather Service collect these data on a regular basis at selected locations.

Surface Roughness Length: Height at which the wind speed extrapolated from a near-surface wind speed profile becomes zero.

Temperature Inversion: Weather condition in which warm air sits atop cooler air, promoting stagnation and increased concentrations of air pollutants.

Toxic Air Pollutants: See hazardous air pollutants.

Total Suspended Particulates (TSP): Total particulate matter in a sample of ambient air.

Upper Air Data (or soundings): Meteorological data obtained from balloon- borne instrumentation that provides information on pressure, temperature, humidity, and wind away from the surface of the earth.

Vertical Potential Temperature Gradient: The change of potential temperature with height, used in modeling the plume rise through a stable layer, and indicates the strength of the stable temperature inversion. A positive value means that potential temperature increases with height above ground and indicates a stable atmosphere.

Visual Air Quality: Air quality evaluated in terms of pollutant particles and gases that affect how well one can see through the atmosphere.

Volatile Organic Compounds (VOC): Organic compounds that vaporize readily and contribute to the development of ozone. Many VOCs are also hazardous air pollutants. See also reactive organic compounds.

Watershed: The land area that contributes water to a river system.