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Pilot Survey of Levels of Polychlorinated Dibenzo-*p*-dioxins, Polychlorinated Dibenzofurans, Polychlorinated Biphenyls, and Mercury in Rural Soils of the United States

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Office of Research and Development
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Washington, DC 20460

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LIST OF ABBREVIATIONS AND ACRONYMS

ASE	Accelerated solvent extraction
BOD	Biological oxygen demand
CALUX	Chemical-Activated Luciferase Expression
CB	Chlorinated biphenyl
CDD	Chlorinated dibenzo-p-dioxin
CDDs/CDFs	Chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans
CDF	Chlorinated dibenzofuran
GC	Gas chromatography
GPC	Gel permeation chromatography
HpCDD	Heptachlorodibenzo-p-dioxin
HpCDF	Heptachlorodibenzofuran
HRMS	High-resolution mass spectrometry
HxCDD	Hexachlorodibenzo-p-dioxin
HxCDF	Hexachlorodibenzofuran
ND	Nondetect
NDAMN	National Dioxin Air Monitoring Network
NR	Not reported
OCDD	Octachlorodibenzo-p-dioxin
OCDF	Octachlorodibenzofuran
PCB	Polychlorinated biphenyl
PCD/PCDF	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PeCDD	Pentachlorodibenzo-p-dioxin
PeCDF	Pentachlorodibenzofuran
QA	Quality assurance
QC	Quality control
r	Regression coefficient
RL	Reporting limit
RPD	Relative percent difference
SD	Standard deviation
SE	Standard error
SOP	Standard operating procedure
TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzofuran
TEF	Toxicity equivalence factor

TEQ	Toxicity equivalent
TOC	Total organic carbon
WHO	World Health Organization
XDS	Xenobiotic Detection Systems, Inc.

UNITS

°C	degrees Centigrade
cm	centimeters
d	day
fg	femtograms
ft	feet
g	grams
kg	kilograms
L	liters
m	meters
mg	milligrams
mL	milliliters
mm	millimeters
ng	nanograms
oz	ounces
pg	picograms
µg	micrograms
µL	microliters

PREFACE

Many environmental contaminants accumulate in soils. Understanding the concentrations and spatial distribution of these chemicals is critical to determining how they may contribute to human exposure via direct contact or uptake through the food chain. The purpose of this document is to report the results of a pilot survey of the levels of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and mercury in rural soils of the United States. All samples were collected during 2003. The study was conducted by the National Center for Environmental Assessment with contract support provided by Battelle.

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EXECUTIVE SUMMARY

This report provides a national-scale pilot survey of the levels of the following chemicals in rural/remote soils of the United States: chlorinated dibenzo-*p*-dioxins (CDDs), chlorinated dibenzofurans (CDFs), polychlorinated biphenyls (PCBs), and mercury.

Soils can serve as long-term reservoirs for CDDs, CDFs, PCBs, and mercury, with releases to both terrestrial and aquatic systems (U.S. EPA, 2003, 1997; Brzuzy and Hites, 1996). Understanding their distribution in soil is important because they are taken up by plants and animals through soil pathways and bioaccumulate through the human food chain. The relative importance of soil as a potential source for these chemicals is increasing as their point source emissions are being reduced. The final reason for conducting this study is that relatively few soil surveys of these compounds have been conducted.

The soil samples were collected in 2003 at 27 monitoring stations of the National Dioxin Air Monitoring Network (NDAMN) (U.S. EPA, 2005a). These stations are located in rural/remote areas, matching the areas of interest for the soil survey. Also they are distributed across the continental United States and Alaska, providing the nation-wide perspective desired for this study. Use of these sites provided the opportunity to study air-soil relationships using historical air concentration data available from NDAMN to compare with soil data collected under this study. Finally, NDAMN sites were a practical choice because site operators were already in place, facilitating logistics and reducing the costs of gathering soil samples.

The results presented pertain to the 27 sites sampled and should not be more broadly interpreted as statistically representative of all rural soils in the United States. These results, however, may be a plausible basis for a preliminary characterization of soils in rural/remote areas. The primary measurement results are summarized below.

- Total CDDs averaged 1,585 pg/g (standard deviation (SD) = 2945). Total CDFs averaged 47 pg/g (SD = 68). Levels of the tetrachlorodibenzo-*p*-dioxin (TCDD) homologues were the lowest, with an average concentration of 0.2 pg/g. Levels of the octachlorodibenzo-*p*-dioxin (OCDD) homologue were the highest, with an average concentration of 1,482 pg/g. The range of concentrations found here is similar to the range across five published studies on CDD/CDF levels in soils from rural areas of North America.

- Total PCBs averaged 3,089 pg/g (SE = 1,009, SD = 5,241). Levels of the deca-chlorinated biphenyl homologues were the lowest, with an average concentration of 29 pg/g. Levels of the penta-chlorinated biphenyl homologues were the highest, with an average concentration of 1,013 pg/g. The range of concentrations found here is similar to the range across three published studies on PCB levels in soils from rural areas worldwide.

- Total toxicity equivalents (TEQs) averaged 1.76 pg/g (SD = 2.47). The PCBs generally were a small fraction of the total TEQs in soil. The mean for total TEQs from this study falls near the center of the range of values across 10 published studies.

- Mercury concentrations averaged 22 ng/g across all sites (SD = 15 ng/g). The mean from this study falls within the range of values from five published studies on mercury levels in soils from rural areas of North America.

This study also evaluated relationships between air concentrations and soil concentrations across sites. A general association between air and soil was observed for the CDDs, based on the significant air-soil correlations observed across sites for most homologue groups and the similarity in air and soil congener profiles observed at most sites. Little association between air and soil could be observed for the CDFs, based on the lack of significant air-soil correlations for homologue groups across sites and the lack of similarity in air and soil congener profiles for many sites. Some association between air and soil was observed for the PCBs. Data limitations restricted the air and soil comparisons to only six PCBs. One of these had a significant air-soil correlation across sites. The air and soil profiles based on these six chemicals were very similar at most sites.

The observations for CDDs and PCBs are consistent with the theory that air transport and deposition are the primary ways that these chemicals are distributed to soils, particularly those in rural areas. The lack of similar observations for the CDFs does not necessarily mean that they are not distributed in a similar manner, but it does suggest that different factors affect the environmental fate of these chemicals.

This study also evaluated relationships between chemical levels in soil and total organic carbon (TOC) levels in soil. The raw data analyses showed significant positive correlations for many of the CDD/CDF homologues and one PCB homologue. However, the correlations were

generally not very strong, indicating that other factors, such as grain size, may also be affecting sorption characteristics of the soil.

TEQ levels were estimated both on the basis of applying toxicity equivalence factors (TEFs) to the high-resolution mass spectrometry (HRMS) analyses and on the basis of a bioassay method called Chemical-Activated Luciferase Expression (CALUX). The CALUX results were higher—by varying amounts—than the HRMS total TEQs in almost all of the site composites. Significant positive correlations were found comparing the data on both a raw basis ($r = 0.82$) and on a log-transformed basis ($r = 0.78$). The likely reason for the high bias in the CALUX data relative to HRMS data is that CALUX responds to all compounds that activate the aryl hydrocarbon receptors, including a number of compounds other than CDDs, CDFs, and PCBs that may be present in soils.

1. INTRODUCTION

This report provides a national-scale pilot survey of the levels of the following chemicals in rural/remote soils of the United States: chlorinated dibenzo-*p*-dioxins (CDDs), chlorinated dibenzofurans (CDFs), polychlorinated biphenyls (PCBs), and mercury. All samples were collected during 2003 and analyzed at Battelle in Columbus, OH.

The term "dioxins" is used in this study to refer collectively to the 17 2,3,7,8-substituted CDDs and CDFs and the 12 co-planar PCBs (see complete listing in Table 1). Dioxin concentrations are expressed in terms of both total mass and toxicity equivalents (TEQs). TEQs allow concentrations of dioxin mixtures to be expressed as a single value computed by multiplying each congener concentration by a toxicity weight (toxicity equivalence factor [TEF]) and summing across congeners. TEFs are expressed as a fraction equal to or less than 1, with 1 corresponding to the most toxic dioxin congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). The TEQ data presented here are based on TEFs from the 1998 World Health Organization (WHO) recommendations, as shown in Table 1 (Van den Berg et al., 1998). This report adds subscripts to TEQs when necessary to clarify which chemicals have been included in the TEQ calculation: "D" for CDDs, "F" for CDFs, and "P" for PCBs.

Table 1. Congeners and TEFs used to calculate TEQs

CDDs		CDFs		PCBs	
Congener	**TEF**	**Congener**	**TEF**	**Congener**	**TEF**
2,3,7,8-TCDD	1.0	2,3,7,8-TCDF	0.1	PCB 77	0.0001
1,2,3,7,8-PeCDD	1.0	1,2,3,7,8-PeCDF	0.05	PCB 81	0.0001
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.5	PCB 105	0.0001
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1	PCB 114	0.0005
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1	PCB 118	0.0001
1,2,3,4,6,7,8-HpCDD	0.01	2,3,4,6,7,8-HxCDF	0.1	PCB 123	0.0001
OCDD	0.0001	1,2,3,7,8,9-HxCDF	0.1	PCB 126	0.1
		1,2,3,4,6,7,8-HpCDF	0.01	PCB 156	0.0005
		1,2,3,4,7,8,9-HpCDF	0.01	PCB 157	0.0005
		OCDF	0.0001	PCB 167	0.00001
				PCB 169	0.01
				PCB 189	0.0001

Source: Van den Berg et al. (1998).

TEF = toxicity equivalence factor
TEQ = toxicity equivalent

Soils can serve as long-term reservoirs for CDDs, CDFs, PCBs, and mercury, with releases to both terrestrial and aquatic systems (U.S. EPA, 2003, 1997; Brzuzy and Hites, 1996). Understanding their distribution in soil is important because they are taken up by plants and animals through soil pathways and bioaccumulate through the human food chain. More than 90% of the general population exposure to dioxin is via food ingestion; human exposure to mercury is similarly dominated by dietary exposure (U.S. EPA, 2003, 1997). The relative importance of soil as a potential source for these chemicals is increasing as their point source emissions are being reduced. The final reason for conducting this study is that relatively few soil surveys of these compounds have been conducted, and none had a national-scale perspective. Many were associated with Superfund sites or other contaminated areas and covered relatively small geographic areas (U.S. EPA, 2003).

1.1. SCOPE OF STUDY

A comprehensive national soil survey would represent all geographic regions of the country, the major land use categories (rural, suburban, urban, agricultural, commercial, and industrial), and a full range of climatic conditions, soil types, terrains, and vegetative covers (e.g., forest, grassland, cropland). As a pilot survey with limited resources, this study could address only a small subset of these lands. It was decided to focus on undisturbed soil in rural/remote areas because this would provide a baseline for evaluating soil levels in other areas. The soil samples were collected at the air monitoring stations of the National Dioxin Air Monitoring Network (NDAMN) (U.S. EPA, 2005a; Cleverly et al., 2006). These stations were located in rural/remote areas, matching the areas of interest for the soil survey. The 35 NDAMN stations were distributed across the continental United States and Alaska (Figure 1), providing the nation-wide perspective desired for this study. Use of these sites provided the opportunity to study air-soil relationships using historical air concentration data available from NDAMN to compare with soil data collected under this study. Finally, NDAMN sites were a practical choice because site operators were already in place, facilitating logistics and reducing the costs of gathering soil samples (see Section 2 for further information about NDAMN and the site selection process).

The original focus of this study was on CDDs, CDFs, and PCBs. Mercury was added to the study after the initial project planning had been completed. Like the CDDs/CDFs and PCBs, mercury is a persistent chemical that accumulates in soil. Also, relatively few soil surveys for mercury have been conducted in the United States and none had a national-scale perspective. Accordingly it was decided that this would be an appropriate addition to the study. Although much of the study design was specific to CDDs/CDFs and PCBs, the procedures were deemed

Figure 1. NDAMN air sampling stations. Circles indicate stations included in soil survey and triangles are excluded stations.

1. Penn Nursery, PA	11. Bennington, VT	20. Fond du Lac, MN	28. Rancho Seco, CA
2/3. Clinton Crops, NC	12. Jasper, NY	21. North Platte, NE	29. Marvel Ranch, OR
4. Everglades, FL	13. Beltsville, MD	22. Goodwell, OK	30. Ozette Lake, WA
5. Lake Dubay, WI	14. Caldwell, OH	23. Big Bend, TX	31. Fort Cronkhite, CA
6. Monmouth, IL	15. Oxford, OH	24. Grand Canyon, AZ	32. Newport, OR
7. McNay Farm, IA	16. Dixon Springs, IL	25. Theodore Roosevelt, ND	33. Craig, AK
8. Lake Scott, KS	17. Quincy, FL	26. Craters of the Moon, ID	34. Trapper Creek, AK
9. Keystone State Park, OK	18. Bay St. Louis, MS	27. Chiricahua, AZ	35. Yaquina Head, OR
10. Arkadelphia, AR	19. Padre Island, TX		

reasonable for mercury, and were similar to those used to collect samples for mercury analysis in a Washington State soil survey (Rogowski et al., 1999). Also, as discussed below, a brief investigation indicated that the NDAMN sites appeared unlikely to be impacted by local mercury sources.

Mercury is commonly found in more than 30 minerals, and natural deposits containing these minerals are found in many of the western states (Jasinski, 1994). Some of these deposits may be near the NDAMN sites in Arkansas, Texas, Arizona, California, Oregon, and Alaska. Historically, most mercury mining in the United States has occurred in California. The use of

mercury has declined significantly in recent years and recycling is increasing. As a result, demand for new mercury has decreased, and no mining has occurred in the United States since 1990 (Jasinski, 1994). Mercury can be released in the mining and processing of gold ores. About 99% of the gold currently produced in the United States comes from 30 mines (USGS, 2002), and none of them are near the NDAMN sites. Thus, it appears unlikely that the NDAMN sites were impacted by local mining operations.

1.2. STUDY OBJECTIVES

The primary objective of this study was to provide preliminary estimates of the levels of CDDs, CDFs, PCBs, and mercury in rural/remote soils. The data summaries presented here should be interpreted as summaries of the sites sampled and should not be interpreted as being statistically representative of all rural soils. However, the surveyed sites cover a wide range of climates, geographic areas, terrains, and soil types and thus provide a reasonable basis for a preliminary characterization of soil in rural/remote areas.

This study also evaluated relationships between chemical levels in air and soil and relationships between chemical levels in soil and the organic carbon content of soil. As discussed below, it is believed that CDDs/CDFs, PCBs, and mercury are distributed to the environment primarily via air transport and enter soils via deposition from the air (U.S. EPA, 2003, 1997). Understanding air-soil relationships may improve our understanding of these fate processes and ultimately lead to better models for predicting the fate of these chemicals in the environment.

1.3. ENVIRONMENTAL FATE OVERVIEW

CDDs and CDFs are released to the environment primarily as combustion by-products and are widely distributed through the environment via air transport. In the atmosphere, they are present in the vapor phase and sorbed to particles. Wet and dry deposition remove CDDs/CDFs from the atmosphere to soils, plants, or other environmental surfaces. CDDs/CDFs sorbed to plants are transferred to soils during leaf fall or when plants die and subsequently decay. Although these compounds are generally very persistent in soils, losses can occur via run-off, particle resuspension, volatilization, and biological degradation (U.S. EPA, 2003; ATSDR, 1998).

PCBs were produced in large quantities (571,000 metric tons) in this country from 1929 until their ban in 1978. Because PCBs are no longer manufactured or imported in large quantities, significant releases of newly manufactured or imported materials to the environment do not occur. PCBs have become distributed throughout the environment primarily via air transport. Like CDDs/CDFs, PCBs are present in the atmosphere, in both vapor phase and

sorbed to particles. Wet and dry deposition remove PCBs from the atmosphere to soil, surface water, plants, and other environmental surfaces. Volatilization is the primary mechanism by which they are released from soils and water back into the atmosphere (ATSDR, 2000).

Mercury occurs naturally as a mineral and in gaseous forms and is distributed throughout the environment by both natural and anthropogenic processes. It is emitted to the atmosphere from multiple types of combustion sources, primarily coal-fired utility boilers, municipal waste combustion, commercial/industrial boilers, and medical waste incinerators (U.S. EPA, 1997). The element has three valence states and is found in the environment in the metallic form and in the form of various inorganic and organic complexes. Most of the soil mercury is thought to be Hg(II). The major features of the bio-geochemical cycle of mercury include degassing of mineral mercury from the lithosphere and hydrosphere, long-range transport in the atmosphere, wet and dry deposition to land and surface water, sorption to soil and sediment particulates, and revolatilization from land and surface water (ATSDR, 1999; U.S. EPA, 1997).

2. SITE SELECTION

As discussed above, all soil samples were collected at NDAMN air sampling stations. The overall purposes of NDAMN were to determine background air concentrations of dioxin-like compounds in rural and remote areas of the United States and to investigate changes that might occur over time. The number of NDAMN sites increased from 9 in 1998 to a peak of 35 in 2002 (Figure 1). Operation was suspended in 2005. The selection of sites for the NDAMN program was not based on a statistical process, but rather judgements on a variety of considerations (U.S. EPA, 2005a; Cleverly et al., 2006):

- *Remoteness*. Sites could not be impacted by nearby industrial and municipal sources. Although no specific criteria were used to determine how far a site could be from an urban area, all were located in rural or remote areas (one exception was the Beltsville, MD, site located in the Washington Metropolitan Area, which was used early in the program for development of sampling protocols; air monitoring data from this site were not included in background estimates). Some sites were located in very remote locations (e.g., the Grand Canyon and Alaska) to explore impacts in pristine areas.

- *Agricultural importance*. Many of the sites were located on farms in agriculturally important areas to help better understand how dioxins enter the human food chain.

- *Air modeling needs*. Some sites were selected to help air modelers verify and calibrate their models.

- *Climate*. Sites were chosen to represent a wide range of climatic conditions.

- *Regions*. Sites were chosen to represent a variety of geographic regions.

- *Practicality*. Sites had to be accessible and secure. Many sites were co-located with existing air monitoring networks to minimize costs.

For purposes of this study, all sites were reviewed for suitability for soil testing. Eight sites were eliminated for the following reasons:

- Clinton Crops, NC (Site 3): a duplicate quality assurance/quality control (QA/QC) monitor at same location as Site 2.

- Beltsville, MD (Site 13): not a regular NDAMN station because it was located within the Washington Metropolitan Area.

- Oxford, OH (Site 15): used in the development of the soil sampling protocol, so not included in the final survey.

- Craters of the Moon, ID (Site 26): sampling not feasible because site was located on a lava bed and operator was not available during testing period.

- Fort Cronkhite, CA (Site 31): soil may have been disturbed by past military operations.

- Newport, OR (Site 32): monitor on roof of building and surrounding soil was likely disturbed.

- Craig, AK (Site 33): sampling not feasible due to rocky soil and steep terrain.

- Yaquina Head, OR (Site 35): sampling not feasible due to rocky soil and steep terrain.

As a result of the review process, a total of 27 sites were included in the soil survey.

3. PROTOCOL DEVELOPMENT

A three-step process was used to develop a protocol for soil sample collection and handling.

Step 1. A literature search was conducted to identify published soil collection guidance. Guidance in *Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies* (U.S. EPA, 1992) was selected as the primary basis for developing the protocol. Other useful reports included soil sampling guidance by the U.S. Department of Housing and Urban Development (HUD, 1995); Rogowski et al. (1999), who conducted a dioxin soil survey in Washington state; and Vikelsoe (2002), who conducted a dioxin soil survey in Denmark.

Step 2. A surface soil sampling protocol and a standard operating procedure (SOP) for collecting soil samples were developed on the basis of information gathered in the literature survey. The surface soil sampling protocol recommends that an initial survey be carried out for each specific application to determine, e.g., an acceptable number of sampling points and sampling depth. For this project, the initial survey was conducted at the NDAMN site in Oxford, OH. The full report on the Oxford survey is presented in Appendix A. Three key issues were evaluated during this initial survey:

- *Grid size and number of samples*. A review of several soil sampling surveys indicated grid squares with sides ranging from 25 ft (7.6 m) to approximately 200 ft (61 m). For this initial survey a 100 ft × 100 ft (30.5 m × 30.5 m) grid was used. Twenty-one samples were collected within the grid. This sample number was selected as a reasonable starting point for making subsequent statistical calculations regarding variability. An additional 4 samples were collected approximately 1,000 ft (305 m) from the grid center. Based on CALUX analysis (described in Section 5.2 and Appendix B), no significant differences were seen between the averages of the grid samples and the distant samples. The CALUX analysis of all samples was used to conduct a statistical analysis that indicated that at least 5 samples were required to derive a mean with less than a 20% standard error. On this basis it was decided to collect 5 samples at each site over a 100 ft ×100 ft (30.5 m × 30.5 m) area (one at each corner and one at the center).

- *Sampling Depth.* EPA indicates that the surface layer of soil (0–15 cm) reflects the deposition of airborne pollutants, especially recently deposited pollutants and pollutants that do not move downward because of attachment to soil particles (U.S. EPA, 1992). Brzuzy and Hites (1995) studied dioxin concentrations in soil as a function of depth and found that more than 80% of total CDDs/CDFs were found in the upper 15 cm. Rogowski et al. (1999) used a sampling depth of 5 cm in a dioxin soil survey in Washington state, and Vikelsoe (2002) used a sampling depth of 10 cm in a dioxin soil survey in Denmark. EPA reports that nearly all mercury in soil is found in the top 20 cm (U.S. EPA, 1997). In the Oxford survey, 10 cm cores were collected and divided into the top 5 cm and bottom 5 cm. The composites for the top and bottom layers were analyzed for CDDs/CDFs, PCBs, and mercury. No significant differences in analyte concentrations were seen. The 5-cm cores were

frequently unstable and difficult to handle in the field. On this basis, 10-cm cores were selected for this study.

- *Sample Size.* 600 g of soil were collected at each sampling point. The soil was thoroughly mixed and 10 g subsamples were removed for chemical analysis. Because many of the CDD/CDF congeners were below detection limits, it was decided to double the subsample size to 20 g for the final multisite survey.

Step 3. The SOP was revised on the basis of sampling experience during the Oxford survey and sent to the field operators, who were asked to carefully read it and respond with any questions. The final SOP is presented in Appendix C.

4. SAMPLE COLLECTION, HANDLING, AND STORAGE

The soil samples were collected by the local operators at 26 of the sites. These operators had experience in collecting air samples for the NDAMN program, and at many of the locations they also collected samples for other national air monitoring networks. Some had specific environmental science background and others did not. The operator at the Everglades, FL, site (Site 4) was unable to collect samples because of time constraints, and a Battelle staff member was sent to the site to collect the soil samples. All samples from the 27 sites were collected between August 12, 2003, and October 20, 2003.

The SOP was distributed to the NDAMN operators, who were contacted by e-mail or phone to make sure they received it and understood the sampling procedures. Sampling supplies were purchased and assembled into individual sampling kits and sent to the operators approximately one week before sampling was scheduled to begin. Battelle staff was accessible by phone to the operators during the sampling period to answer any questions that might arise while in the field.

At each NDAMN site, a 100 ft ×100 ft (30.5 m × 30.5 m) sampling area was chosen as near the air monitor as possible and where the terrain was relatively flat and there was no visible evidence of soil disturbance from flooding, erosion, construction, digging, or plowing. Five sampling points were located in an "X" configuration over the area (one at each corner and one at the center). Ground cover and vegetation was removed over a 20 cm × 20 cm area at each sampling point. Core samples of 10 cm each were collected at each point using a metal "tulip bulb"-type planter that had a diameter of approximately 7.5 cm. A total of approximately 600 g of soil was collected at each sampling point, put into three precleaned jars, packed in ice, and shipped to Battelle.
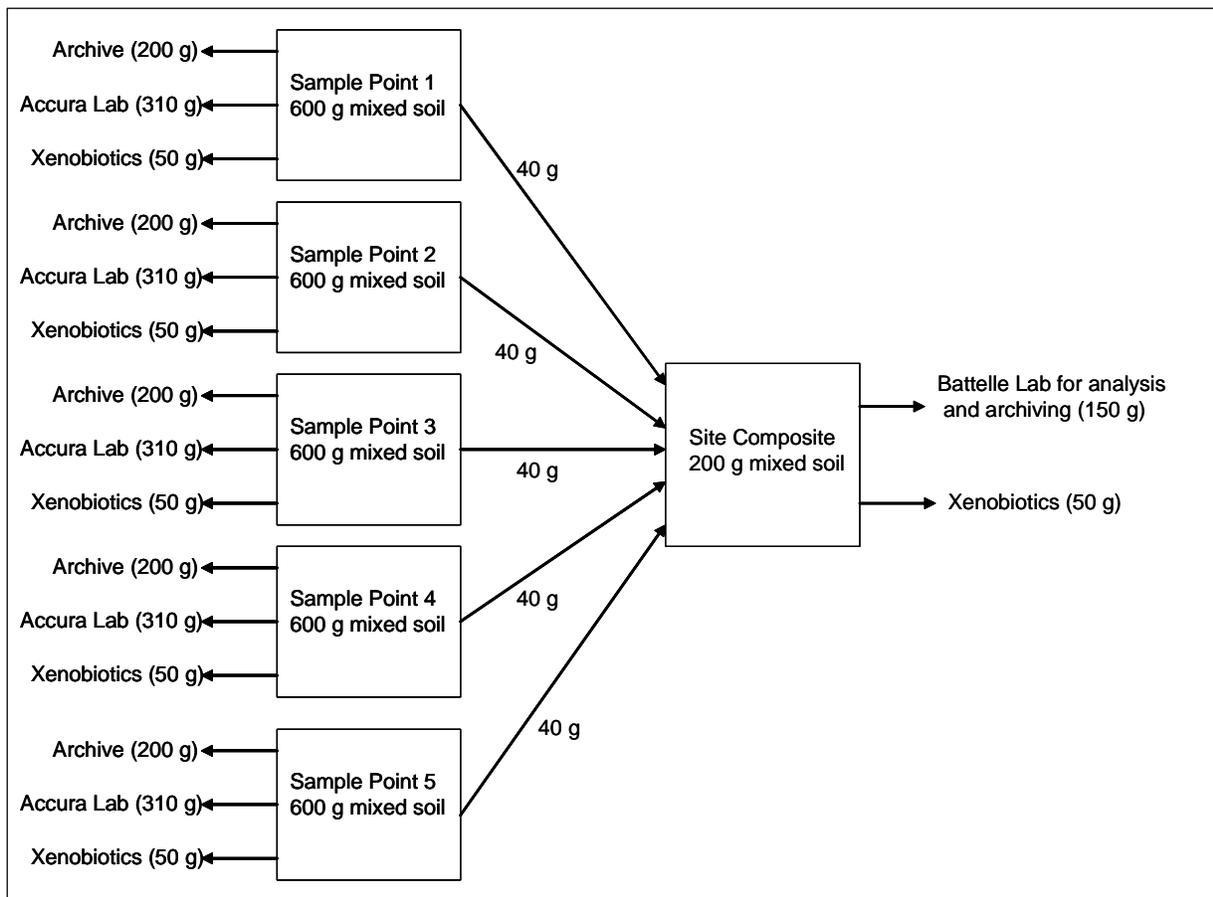
Figure 2. Sample handling diagram.

All of the soil samples were received at Battelle in good condition. As illustrated in Figure 2, the samples from each site were handled as follows:

- The soil from the three sample jars representing one sampling point were thoroughly mixed in a stainless steel bowl with a large stainless steel spoon. Fifty grams of this mixed soil were transferred to a new, pre-cleaned, labeled 4-oz (120-mL) jar. The jar was shipped to Xenobiotic Detection Systems, Inc. (XDS) (Durham, NC), for CALUX analysis. An additional 40 g of mixed soil were transferred to a stainless steel bowl for making a site composite. The remaining mixed soil was put back in the original sampling jars. Sample jar 1 of 3 was set aside for archiving (200 g). Sample jars 2 of 3 and 3 of 3 were sent to Accura Analytical Labs, Inc. (Atlanta, GA), for physical/ chemical parameter testing (containing a total of about 310 g). This process was repeated for the remaining four sampling points.

- The 40 g of soil that had been set aside for the site composite from each of the five sampling points were thoroughly mixed in a stainless steel bowl. Approximately 50 g of this composited soil were placed in a new, pre-cleaned, labeled 4-oz (120-mL) jar. The jar was shipped to XDS (Durham, NC) for CALUX analysis. The remaining 150 g were transferred to a new, precleaned, labeled 8-oz (240-mL) jar. The jar was

transferred to Battelle's analytical laboratories for analysis of CDDs, CDFs, PCBs, and mercury. The unused portion was archived.

This process was repeated with the samples from all 27 sites. Sample holding times and temperatures were as follows:

- CDDs/CDFs: all samples were frozen until extraction, extracted within 15 days of receipt, and analyzed within 5 weeks of extraction.

- PCBs: all samples were frozen until extraction, extracted within 15 days of receipt, and analyzed within 10 weeks of extraction.

- Mercury: all samples were refrigerated until extraction, extracted within 28 days of receipt, and analyzed same day (with three exceptions, as noted in Section 6.5).

- CALUX: all samples were held at room temperature, extracted within 30 days of receipt, and analyzed within 3 weeks of extraction.

5. ANALYTICAL METHODS

5.1. PHYSICAL/CHEMICAL PARAMETER TESTS

Physical/chemical parameter testing was performed on soils from 135 individual sampling points (27 sites, 5 sampling points per site). Two 8-oz (240-mL) jars from each of the five sampling points at the 27 sites were sent to Accura Analytical Labs, Inc. (Atlanta, GA), for analysis of pH, total organic carbon (TOC), grain size distribution, and moisture content according to the following methods:

- pH: EPA Method SW 9045C (U.S. EPA, 1995)
- TOC: Walkley-Black Method (Walkley and Black, 1934)
- Grain size distribution: ASTM D422 (ASTM, 2002a)
- Moisture content: ASTM D2216 (ASTM, 2002b)

5.2. CALUX BIOASSAY TEQ

Several biological methods are commercially available for measuring dioxin TEQs, and bids from several companies were received. The CALUX method by XDS was chosen, primarily because it provided the lowest detection limit.   XDS has patented a genetically engineered cell line that contains the firefly luciferase gene under trans-activational control of the aryl hydrocarbon receptor. This cell line can be used for the detection and relative quantification of aryl hydrocarbon receptor agonists and is referred to as Chemical-Activated Luciferase

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Expression (or CALUX) assay (Denison et al., 1998). The most widely studied class of compounds that activate this system is the polychlorinated diaromatic hydrocarbons (PCDH), which includes 2,3,7,8-TCDD. The CALUX assay can be used to provide a measure of dioxin TEQs in a sample. When the cells are exposed to dioxins and related chemicals, they produce the enzyme luciferase in a time-, dose-, and chemical-specific manner. Luciferase activity is determined by measuring light emitted and is directly proportional to the amount of dioxin-like chemicals within the test samples (see Appendix B for further details of the CALUX method).

CALUX testing was performed on soils from 135 individual sampling points (27 sites, 5 sampling points per site) plus 27 composites representing each site. When XDS received soil samples from Battelle, the samples were logged in and held at room temperature until processing and analysis. Samples were extracted with a bottle sonication method using organic solvents following XDS Method WL-2. Sample extracts were processed through a patent-pending procedure, XDS Method WL-3, which removes commonly interfering substances such as polyaromatic hydrocarbons. All samples were processed in duplicate along with a batch recovery sample for each set of samples in order to provide semi-quantitative results.

5.3. MERCURY ANALYSIS

Total mercury was determined on 27 composites (one from each site) using modified EPA SW846 Method 7471A (U.S. EPA, 1994a). All standards and samples were digested and analyzed by cold vapor atomic absorption. Approximately 2 g of sample were weighed into a biological oxygen demand (BOD) bottle and digested by adding nitric acid, sulfuric acid, and potassium permanganate and heating in a water bath at ~ 95°C. Samples were cooled and the excess permanganate reduced using sodium chloride hydroxylamine hydrochloride. Mercury hydride was generated by the addition of stannous chloride. The hydride was swept into an absorption cell.

5.4. HRMS ANALYSIS OF CDDs/CDFs, AND PCBs

CDD/CDF and PCB congeners were measured in 27 composites (one from each site) using gas chromatography/high-resolution mass spectrometry (referred to as HRMS in the remainder of this document). Soil composites were extracted and analyzed for the 17 2,3,7,8-substituted CDDs/CDFs following general procedures in EPA Method 1613, Revision B (U.S. EPA, 1994b) and Battelle SOPs ASAT.II-001-02 and ASAT.II-002-02. All 209 PCB congeners were determined following general procedures in EPA Method 1668, Revision A (U.S. EPA, 1999) and Battelle SOP ASAT.II-009-00. Specific steps were taken during sample preparation to enhance the detection limit. These steps included extracting nearly twice the standard amount of soil and concentrating the sample to half the standard final extract volume.

Overall, an aliquot of approximately 20 g wet weight of each composite was spiked with isotopically labeled analogs (internal standards) of 15 of the 17 2,3,7,8-substituted CDDs/CDFs and 27 PCBs. The composites were extracted with methylene chloride using accelerated solvent extraction (ASE) techniques. Extracts were processed through a gel permeation chromatography column, spiked with CDD/CDF and PCB cleanup standards, and processed through acid/base silica columns. The extracts were then processed into separate CDD/CDF and PCB fractions using carbon columns. The CDD/CDF fractions were spiked with CDD/CDF recovery standard and concentrated to a final volume of 10 µL. The PCB fractions were spiked with PCB recovery standard and concentrated to a final volume of 25 µL.

Sample extract fractions were analyzed for CDDs/CDFs and PCBs by HRMS in the selected ion monitoring mode at high resolution. Initial analysis for CDDs/CDFs was carried out on a DB-5 or equivalent column. Because 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is not completely separated from the other TCDF isomers on the DB-5 column, second column confirmation of 2,3,7,8-TCDF levels above the lowest calibration level in the initial analysis was carried out on a DB-225 column or equivalent column. PCBs were determined using an SPB-Octyl column. Approximately 110 of the PCBs were determined as individual congeners, and the remaining congeners adding up to 209 were determined as various sets of co-eluting congeners. All analytes were quantified by isotope dilution or by the internal standards method using the labeled internal standards for quantitation.

5.5. QUALITY ASSURANCE/QUALITY CONTROL

Data quality parameters assessed were accuracy, precision, representativeness, comparability, completeness, and sensitivity. Each of these is discussed below.

The QA/QC measurement quality objectives for accuracy and precision for all analytes are addressed in detail in Appendix D and summarized below:

- *Procedural blanks.* Mercury was nondetect in the blanks, and CDD/CDF blanks were low relative to the field samples. A number of PCBs were detected in the procedural blanks, with up to 16 PCBs exceeding 3 pg/g. In terms of total PCBs, most of the sites exceeded the blanks by a large margin. However, the sites with the lowest total PCBs approached the blank levels, i.e., the lowest site was 248 pg/g, as compared with an average level in blanks of 170 pg/g. Appendix E provides the congener-specific PCB levels in blanks, and these should be considered in interpreting individual congener values.

- *Recoveries.* Lab control spike recoveries and matrix spike recoveries were generally within QC goals.

- *Replicates.* The relative percent differences (RPDs) were generally within QC goals for mercury and CDDs/CDFs. The PCB duplicates had mixed results. Some of the duplicate pairs had excellent agreement, such as those for Theodore Roosevelt, ND (Site 25), where all congeners had an RPD of less than 18% and the RPD for total PCBs was just 2%. Others had poor agreement such as those for Lake Scott, KS (Site 8), where individual congeners had RPDs ranging from 21 to 161% and the RPD for total PCBs was 140%.

Representativeness was addressed through the sampling design and selection of sampling locations to accomplish the project goals. Samples were handled carefully following good laboratory practices to ensure that chain-of-custody and processing were carried out appropriately.

Comparability was addressed by having all samples collected within an approximate 2-month time frame using the same sampling protocol and procedures at each site. Samples were analyzed within holding times, with the exception of three mercury samples. These samples exceeded the specified 28 days and are flagged in Table 2. Due to the holding time exceedance, mercury results for these three samples should be considered minimum concentrations. However, the mean across sites was essentially the same with or without these samples.

The completeness goal for this project was to collect 100% of the planned samples and for 95% of the laboratory data be considered valid. Soil sample collection was planned at 30 NDAMN air sampling stations. Sampling actually took place at 27 stations, resulting in 90% of the planned samples being collected. Details of sample collection are included in Section 4. All laboratory data (100%) from the collected samples are included in the report.

All data were generated following accepted analytical methods, and the reporting units used are consistent with accepted conventions for environmental analyses. Sensitivity was ensured by meeting target reporting limits for each analysis.

6. SOIL MEASUREMENTS

This section presents the measurement results from the study. Averages and other descriptive statistics are generally presented assuming that nondetects were equal to half the detection limit. Wherever this assumption was made, the influence of the nondetects was

Table 2. Soil concentrations (dry weight) by site

Site	Total CDDs (tetras-octas) (pg/g)	Total CDFs (tetras - octas) (pg/g)	Total CDDs and CDFs (tetras - octas) (pg/g)	Total PCBs (pg/g)	Mercury (ng/g)
1. Penn Nursery, PA	6,602	29	6,631	1,366	26[a]
2. Clinton Crops, NC	1,361	5	1,367	475	69[a]
4. Everglades, FL	680	98	778	2,604	22
5. Lake Dubay, WI	96	13	110	15,700	4
6. Monmouth, IL	395	96	491	2,037	25
7. McNay Farm, IA	1,696	47	1,743	358	30
8. Lake Scott, KS	22	2	24	1,115	11
9. Keystone State Park, OK	65	22	87	2,464	9
10. Arkadelphia, AR	685	5	690	4,028	26
11. Bennington, VT	178	28	205	3,023	43
12. Jasper, NY	11,400	77	11,480	1,543	15
14. Caldwell, OH	2,307	16	2,322	1,019	26
16. Dixon Springs, IL	9,574	239	9,813	845	19
17. Quincy, FL	369	10	380	303	13[a]
18. Bay St. Louis, MS	1,686	51	1,738	4,930	24
19. Padre Island, TX	74	5	79	255	5
20. Fond du Lac, MN	130	63	193	1,308	19
21. North Platte, NE	50	14	64	493	13
22. Goodwell, OK	288	43	331	4,954	5
23. Big Bend, TX	22	3	25	24,570	18
24. Grand Canyon, AZ	25	7	32	713	9
25. Theodore Roosevelt, ND	107	21	127	570	0.5
27. Chiricahua, AZ	1,110	8	1,118	509	45
28. Rancho Seco, CA	203	50	253	3,274	37
29. Marvel Ranch, OR	3,534	284	3,817	1,300	24
30. Ozette Lake, WA	105	28	133	2,419	39
34. Trapper Creek, AK	15	4	19	1,224	22
Average	1,585	47	1,632	3,089	22
Standard deviation	2,946	68	2,982	5,241	15
Standard error	567	13	574	1,009	3

[a] Sample exceeded 28 day holding time for mercury analysis and should be considered a minimum value.

evaluated by computing the values assuming both nondetects were equal to zero and nondetects were equal to the full detection limit. For total CDDs/CDFs, total PCBs, and mercury, both calculations gave essentially the same values, and the full results are presented only on the basis of nondetects equal to half the detection limit. For some sites, the TEQ estimates have significant differences, depending on treatment of the nondetects, so these data are presented two ways: TEQ1 assumes nondetects equal zero, and TEQ2 assumes nondetects were equal to half the detection limit. All concentrations are presented on a dry-weight basis.

This section includes comparisons of the soil levels found in the study with those of similar studies found in the published literature. A detailed literature review of levels of CDDs/CDFs, PCBs, and mercury in rural soils is provided in Appendix F. The discussions in this section briefly summarize the key studies from Appendix F. The focus is generally on studies of North America. In the case of total PCBs, however, relatively few data on North America could be found, so studies from other areas are also discussed. It should be noted that the studies included in this review have a wide variety of design features (e.g., detection limits, treatment of nondetects in deriving statistics, congener inclusion, sampling procedures, analytical techniques), which makes it difficult to compare them on a completely equal basis. Information is provided in Appendix F to help readers consider these differences, but no adjustments were made to the values reported in the original studies.

6.1. PHYSICAL/CHEMICAL PARAMETER RESULTS

The complete set of physical/chemical parameter data for samples collected at all sites is presented in Appendix G and briefly summarized here. A wide range of soil types were collected in this study, with grain size distributions (based on criteria from the Unified Soil Classification System, ASTM D2487) as follows (SE is the standard error of the mean and SD is the standard deviation for all samples):

% finer than #4 sieve (4.75 mm): mean of 98.4 (SE = 0.3, SD = 23.9)
% finer than #200 sieve (0.075 mm): mean of 61.3 (SE = 2.2, SD = 25.6)
% finer than 0.005 mm: mean of 18.3 (SE = 0.9, SD = 10.8)

Moisture content averaged 22.2% (SE = 2.1, SD = 23.9). Soil pH averaged 6.0 (SE = 0.1, SD = 1.3). Total organic carbon averaged 34,900 mg/kg (SE = 2,400, SD = 27,800).

6.2. CDD AND CDF RESULTS

CDD/CDF total homologues (tetra and higher) and individual CDD/CDF congener (tetra and higher) results for each site are included in Appendix H. Table 2 shows the CDD and CDF

levels (tetra through octa) for the composite samples from each site. CDDs ranged from 15 to 11,400 pg/g, with an average of 1,585 pg/g (SE = 567, SD = 2,945). Total CDFs ranged from 2 to 284 pg/g, with an average of 47 pg/g (SE = 13, SD = 68). Total CDDs/CDFs ranged from 19 to 11,480 pg/g, with an average of 1,632 pg/g (SE = 574, SD = 2,982). These values were calculated assuming that nondetects were equal to half the detection limit. Treatment of the nondetects, however, had a negligible impact on these homologue sums because they were generally very low when compared with the detected levels. For example, at Trapper Creek, AK (site 34), which had the lowest levels, total CDDs/CDFs were 18.71 pg/g assuming that nondetects were equal to zero and 19.03 pg/g assuming that nondetects were equal to the full reporting limit.

Table 3 shows all of the CDD/CDF homologue concentrations for all sites. TCDD homologue concentrations were the lowest, with an average of 0.2 pg/g. The octachlorodibenzo-*p*-dioxin (OCDD) homologue concentrations were the highest, with an average of 1,482 pg/g.

Table 4 summarizes information from four studies on CDD/CDF levels in soils from rural areas of North America. This table shows that the total CDD/CDF concentration ranged from nondetect to 10,000 pg/g, which is similar to the range of 19 to 11,480 pg/g found in the current study.

Total CDDs/CDFs in procedural blanks averaged 2 pg/g. All sites exceeded this value by a wide margin, i.e., the concentration at the lowest site was 19 pg/g. The blank levels are listed in Appendix H along with the homologue levels and should be considered when interpreting these values individually.

6.3. PCB RESULTS

PCB individual congener results for each site are provided in Appendix E. Approximately 110 of the 209 PCB congeners co-eluted with other congeners, preventing resolution of individual levels. In Appendix E, all the congeners that co-eluted are marked with a "C" followed by the PCB compound number with which each one co-eluted. Table 2 provides total PCB levels for the composite samples from each site; concentrations ranged from 255 to 24,570 pg/g, with an average of 3,089 pg/g (SE = 1,009, SD = 5,241). These values were calculated assuming that nondetects were equal to half the detection limit. Treatment of the nondetects, however, had a negligible impact on these sums because they were generally very low when compared with the detected levels. For example, at Dixon Hills, IL (site 19), which had the lowest levels, the total PCBs were 248 pg/g assuming that nondetects were equal to zero and 262 pg/g assuming that nondetects were equal to the full reporting limit.

Table 5 summarizes the PCB homologue concentrations for all sites. Deca-chlorinated biphenyl homologue concentrations were the lowest, with an average of 29 pg/g. Penta-

Table 3. Soil concentrations (pg/g dry weight) of CDD and CDF homologues

Site	Total TCDFs	Total TCDDs	Total PeCDFs	Total PeCDDs	Total HxCDFs	Total HxCDDs	Total HpCDFs	Total HpCDDs	OCDF	OCDD
1. Penn Nursery, PA	1.4	0.2	4.7	1.8	5.9	12.5	7.9	119.3	8.7	6,468
2. Clinton Crops, NC	0.3	0.1	0.8	0.6	0.9	6.7	1.6	55.9	1.3	1,299
4. Everglades, FL	1.3	0.0	19.4	0.2	19.8	12.5	25.8	89.2	31.9	578
5. Lake Dubay, WI	0.9	0.1	1.2	0.5	2.2	2.6	5.0	11.0	3.8	82
6. Monmouth, IL	1.3	0.5	3.0	2.6	9.9	19.6	51.5	64.0	30.1	308
7. McNay Farm, IA	0.5	0.8	1.7	3.1	6.0	17.9	18.4	107.0	20.1	1,568
8. Lake Scott, KS	0.1	0.0	0.4	0.1	0.6	0.6	0.7	2.6	0.6	19
9. Keystone State Park, OK	5.7	0.0	5.2	0.4	3.3	2.3	4.3	11.2	3.3	51
10. Arkadelphia, AR	0.7	0.0	0.6	0.3	0.9	3.7	1.3	31.3	1.1	650
11. Bennington, VT	1.2	0.1	4.4	1.0	5.4	6.1	8.6	30.4	7.9	140
12. Jasper, NY	3.2	0.4	5.4	3.9	11.6	42.3	31.7	442.9	25.5	10,910
14. Caldwell, OH	0.2	0.1	1.0	0.7	2.6	5.4	5.8	48.8	6.2	2,252
16. Dixon Springs, IL	0.5	0.3	3.8	4.3	26.7	41.9	100.1	412.3	108.0	9,116
17. Quincy, FL	0.0	0.0	0.2	0.1	1.1	1.7	4.0	15.5	5.1	352
18. Bay St. Louis, MS	0.6	0.2	1.7	2.0	7.9	17.8	22.4	136.1	18.7	1,530
19. Padre Island, TX	0.0	0.0	0.1	0.1	1.2	1.4	1.2	3.5	2.3	69
20. Fond du Lac, MN	0.5	0.0	1.9	0.6	6.8	4.5	24.7	28.7	28.7	97
21. North Platte, NE	2.3	0.2	2.1	0.1	2.4	2.2	3.5	9.7	3.4	38
22. Goodwell, OK	0.3	0.0	2.6	0.4	7.5	7.0	17.1	80.1	15.5	201
23. Big Bend, TX	0.2	0.0	0.2	0.1	0.6	0.3	0.7	1.5	1.4	20
24. Grand Canyon, AZ	0.0	0.0	0.3	0.0	1.5	0.9	3.2	6.1	2.4	18
25. Theodore Roosevelt, ND	0.4	0.1	4.2	0.4	5.2	2.8	7.0	16.6	4.0	87
27. Chiricahua, AZ	0.3	0.1	1.0	1.5	1.4	10.8	2.4	58.1	2.8	1,040
28. Rancho Seco, CA	0.6	0.0	1.1	0.9	3.9	7.2	21.8	36.2	22.7	159
29. Marvel Ranch, OR	2.1	0.1	4.1	1.2	31.9	77.5	158.4	583.0	87.1	2,872
30. Ozette Lake, WA	5.1	0.6	1.9	13.6	3.5	10.5	11.5	11.8	6.0	69
34. Trapper Creek, AK	1.0	0.0	0.1	0.1	0.3	0.4	1.8	2.3	0.5	12
Mean	1.1	0.2	2.7	1.5	6.3	11.8	20.1	89.4	16.6	1,482
Standard deviation	1.5	0.2	3.7	2.7	7.9	17.1	34.7	147.6	25.6	2,820
Standard error	0.3	0.0	0.7	0.5	1.5	3.3	6.7	28.4	4.9	543

Table 4. Literature summary for CDDs/CDFs in rural soils of North America

Concentration (pg/g)	Location	Site		Reference
		Description	n	
Range: ~990–3100	Elk River, MN	Semi-rural, untilled area	2	Reed et al. (1990)
Range: ND–810 Mean: 73	Ontario, Canada, and U.S. Midwest	Rural	30	Birmingham (1990)
Range: 60–10,000	Michigan and Indiana	Undisturbed	4	Brzuzy and Hites (1995)
Range: 9–258 Mean: 94	Washington	Open, nongrazed	4	Rogowski et al. (1999, 2005)
Range: 79–426 Mean: 267	Washington	Forest, noncommercial	4	Rogowski et al. (1999); Rogowski and Yake (2005)
Range: 19–11,483 Mean: 1,632	United States	Rural/remote	27	Current study

chlorinated biphenyl homologue concentrations were the highest, with an average concentration of 1,013 pg/g.

Only a few studies were found that reported total PCB levels in rural soils (Table 6). The only U.S. study (Vorhees et al., 1999) measured PCBs in residential soils near New Bedford Harbor, MA. The sediments in that area are contaminated with PCBs and may have affected nearby residential soils. The study reported a maximum concentration of 1,800,000 pg/g, which far exceeds the maximums seen in rural areas in other countries and is not likely to be representative of rural areas in the United States. The other three studies summarized in Table 6 show concentrations in rural areas at a variety of locations world-wide, with a range of 26 to 97,000 pg/g. This range is wider but similar to that observed in the current study (255–24,600 pg/g). The average from the large (n = 191) world-wide study by Meijer et al. (2003) was 5,400 pg/g, which is similar to the mean in the current study of 3,087 pg/g.

Total PCBs in procedural blanks averaged 170 pg/g. Although most of the sites exceeded this value by a large margin, the sites with the lowest total PCBs approached this value, i.e., the concentration at the lowest site was 255 pg/g. All congener values and associated blanks are listed in Appendix E. Up to 16 PCBs were detected at >3 pg/g in each blank. The blanks should be considered when interpreting individual congener values, especially those at the low-level sites.

Table 5. PCB homologue concentrations (pg/g dry weight)[a]

Site	Mono-CBs (1–3)	Di-CBs (4–15)	Tri-CBs (16–39)	Tetra-CBs (40–81)	Penta-CBs (82–127)	Hexa-CBs 128–169)	Hepta-CBs (170–193)	Octa-CBs (194–205)	Nona-CBs (206–208)	Deca-CBs (209)
1. Penn Nursery, PA	6	16	33	83	241	391	277	193	82	45
2. Clinton Crops, NC	7	25	26	41	67	100	86	62	39	21
4. Everglades, FL	34	92	164	281	408	596	599	271	100	57
5. Lake Dubay, WI	646	4,472	5,036	3,043	1,229	900	279	55	23	20
6. Monmouth, IL	11	41	115	237	580	646	281	54	32	41
7. McNay Farm, IA	3	10	21	36	78	94	57	32	16	12
8. Lake Scott, KS	12	50	112	155	342	269	126	37	7	4
9. Keystone State Park, OK	121	466	441	341	364	397	234	72	17	10
10. Arkadelphia, AR	24	72	168	371	1,788	1,201	328	59	11	5
11. Bennington, VT	8	38	83	110	277	797	1,068	525	89	29
12. Jasper, NY	7	23	56	118	336	482	307	134	52	28
14. Caldwell, OH	3	12	34	125	451	250	93	41	8	3
16. Dixon Springs, IL	2	10	25	57	132	146	70	45	52	306
17. Quincy, FL	5	11	28	46	71	47	26	19	13	38
18. Bay St. Louis, MS	7	22	155	829	1,756	1,311	566	218	54	12
19. Padre Island, TX	3	9	20	38	88	57	22	11	4	2
20. Fond du Lac, MN	15	29	94	193	390	378	150	36	13	9
21. North Platte, NE	4	10	26	63	144	123	68	30	14	12
22. Goodwell, OK	140	335	460	803	681	1,328	914	245	42	8
23. Big Bend, TX	5	21	52	1,655	15,170	6,755	800	95	13	4
24. Grand Canyon, AZ	6	13	60	149	181	210	76	13	3	2
25. Theodore Roosevelt, ND	3	5	22	47	137	174	125	44	10	4
27. Chiricahua, AZ	3	9	22	49	130	114	81	51	30	21
28. Rancho Seco, CA	9	43	130	518	1,163	996	288	90	30	6
29. Marvel Ranch, OR	14	41	44	149	343	385	183	87	41	13
30. Ozette Lake, WA	56	90	203	390	517	643	303	83	69	64
34. Trapper Creek, AK	14	35	83	233	299	389	141	25	3	2
Mean	43	222	286	376	1,013	710	279	97	32	29
Standard deviation	125	856	956	637	2,868	1,268	277	111	28	58
Standard error	24	165	184	123	552	244	53	21	5	11

[a] Values in parenthesis in the header indicate which PCBs are included in the homologue groups.

Table 6. Literature summary for PCBs in rural soils world-wide

Concentration (pg/g)	Location	Site Description	n	Reference
Range: 15,000–1,800,000[a]	New Bedford Harbor, MA	Residential	34	Vorhees et al. (1999)
Range: ND–45,000	Canadian Arctic	Remote, but near radar stations	21	Bright et al. (1995)
Range: 26–97,000 Mean: 5,400	World-wide	Background	191	Meijer et al. (2003)
Mean: 15,000	Poland	Forest soils	4	Masahide et al. (1998)
Range: 255–24,600 Mean: 3,087	United States	Rural/remote	27	Current study

[a] This site was included in this table because it was the only US study found which came close to meeting the criteria of reporting total PCBs in rural areas. However, it should be noted that the site is more suburban than rural and has probably been affected by nearby contaminated sediments.

6.4. TEQ RESULTS

CALUX bioassay TEQ testing was performed on soils from 135 individual sampling points (27 sites, 5 sampling points per site), 27 composites (1 per site), and 16 related field blanks. The complete set of CALUX analysis is presented in Appendix I.

The TEFs listed in Table 1 were used to calculate TEQs for the HRMS data. The TEQ estimates for the composite samples from all sites are shown in Table 7. This table shows both the CALUX-derived and the HRMS-derived estimates and the HRMS estimates on a TEQ1 basis (nondetects equal to zero) and a TEQ2 basis (nondetects equal to one-half the detection limit). The treatment of nondetects made a difference at many of the sites, particularly those with lower concentrations. For the HRMS CDD/CDF concentrations, TEQ2 values exceeded TEQ1 values by more than 50% at 3 sites. For the HRMS PCB concentrations, TEQ2 values exceeded TEQ1 values by more than 50% at 18 sites.

The composite range and averages across sites are summarized below:

HRMS CDD/CDF TEQ2: 0.21 to 11.42 pg/g, average of 1.69 pg/g (SE = 0.48, SD = 2.47)

HRMS PCB TEQ2: 0.017 to 0.38 pg/g, average of 0.072 pg/g (SE = 0.02, SD = 0.082)

HRMS Total TEQ2: 0.24 to 11.49 pg/g, average of 1.76 pg/g (SE = 0.48, SD = 2.47)

CALUX TEQ: 0.62 to 23.01 pg/g, average of 5.11 pg/g (SE = 1.04, SD = 5.38)

Table 7. TEQ soil concentrations by site (pg TEQ/g dry)[a]

		HRMS						CALUX Bioassay
		CDD/CDF		PCB		Total TEQ1	Total TEQ2	
	Site	TEQ1	TEQ2	TEQ1	TEQ2			
1.	Penn Nursery, PA	2.40	2.40	0.013	0.029	2.41	2.43	9.19±1.84
2.	Clinton Crops, NC	0.68	0.69	0.010	0.023	0.69	0.71	2.10±0.33
4.	Everglades, FL	1.23	1.48	0.020	0.045	1.25	1.53	2.16±0.89
5.	Lake Dubay, WI	0.34	0.35	0.018	0.033	0.36	0.38	3.68±0.21
6.	Monmouth, IL	2.42	2.43	0.034	0.049	2.45	2.48	4.97±0.43
7.	McNay Farm, IA	2.05	2.05	0.011	0.027	2.06	2.08	11.04±0.30
8.	Lake Scott, KS	0.08	0.21	0.013	0.031	0.09	0.24	1.58±0.76
9.	Keystone State Park, OK	1.16	1.18	0.009	0.023	1.17	1.20	1.88±0.50
10.	Arkadelphia, AR	0.53	0.53	0.047	0.062	0.58	0.59	2.92±0.35
11.	Bennington, VT	0.97	0.98	0.210	0.210	1.18	1.19	5.86±0.64
12.	Jasper, NY	5.97	5.97	0.012	0.031	5.98	6.00	7.04±1.74
14.	Caldwell, OH	0.82	0.84	0.012	0.029	0.83	0.87	4.60±1.81
16.	Dixon Springs, IL	6.24	6.24	0.049	0.049	6.29	6.29	12.61±0.00
17.	Quincy, FL	0.22	0.41	0.005	0.022	0.23	0.43	1.54±0.11
18.	Bay St. Louis, MS	2.08	2.08	0.236	0.236	2.32	2.32	17.06±1.01
19.	Padre Island, TX	0.23	0.33	0.004	0.017	0.23	0.35	0.62±0.24
20.	Fond du Lac, MN	0.67	0.70	0.015	0.029	0.69	0.73	2.87±0.11
21.	North Platte, NE	0.50	0.50	0.083	0.083	0.58	0.58	6.33±0.21
22.	Goodwell, OK	0.91	0.94	0.014	0.061	0.92	1.00	3.61±0.46
23.	Big Bend, TX	0.13	0.23	0.363	0.379	0.49	0.61	0.62±0.69
24.	Grand Canyon, AZ	0.12	0.25	0.004	0.062	0.12	0.31	0.82±0.84
25.	Theodore Roosevelt, ND	0.44	0.44	0.004	0.019	0.44	0.46	1.05±0.47
27.	Chiricahua, AZ	0.88	0.90	0.006	0.019	0.89	0.92	5.17±1.57
28.	Rancho Seco, CA	1.05	1.05	0.046	0.132	1.10	1.18	2.69±0.35
29.	Marvel Ranch, OR	11.37	11.42	0.010	0.070	11.38	11.49	23.01±3.19
30.	Ozette Lake, WA	0.43	0.63	0.011	0.094	0.44	0.72	1.14±0.59
34.	Trapper Creek, AK	0.11	0.29	0.007	0.078	0.12	0.37	1.79±0.58
	Mean	1.63	1.69	0.047	0.072	1.68	1.76	5.11
	Standard deviation	2.49	2.47	0.09	0.082	2.49	2.47	5.38
	Standard error	0.48	0.48	0.02	0.02	0.48	0.48	1.04

[a]TEQ1 values based on nondetects equal to zero. TEQ2 values based on nondetects equal to one-half the detection limit.

HRMS = high-resolution mass spectrometry

EPA's draft report *Exposure and Human Health Reassessment of 2,3,7,8-Tetra-Chlorodibenzo-p-Dioxin (TCDD) and Related Compounds* (U.S. EPA, 2003) presents a preliminary mean CDD/CDF TEQ in North America soil of 2.8 pg TEQ_{DF}/g in rural soils and 9.4 pg TEQ_{DF}/g in urban soils. These estimates were derived setting nondetects equal to zero, so they were compared with the TEQ1 values from this study. This study found an average CDD/CDF TEQ1 of 1.63 pg TEQ/g, which is about 40% lower than the rural soil average reported in EPA's draft report (U.S. EPA, 2003). A summary of CDD/CDF TEQ values from nine studies of rural areas of North America is shown in Table 8. The overall range across the studies is 0 to 22.9 pg TEQ/g, which encompasses the TEQ2 range from the current study (0.21–11.42 pg TEQ/g). The means across studies ranged from 0.4 to 5 pg TEQ/g, which bracket the TEQ2 mean from this study (1.69 pg TEQ/g).

Table 8. Literature summary for CDD/CDF TEQs in rural soils of North America

TEQ Concentration (pg/g)	Location	Site Description	n	Reference
Range: 0.16–2.2 Mean: 0.4	Ontario, Canada, and U.S. Midwest	Rural	30	Birmingham (1990)
Range: 0–57 Mean: 5	British Columbia, Canada	Background	53	BC Environment (1995)
Range: 0.2–0.9	Canadian Arctic	Remote	4	Grundy et al. (1995); Bright et al. (1995)
Range: 0.16–22.9 Mean: 3.1	Southern Mississippi	Rural	36	Rappe et al. (1995); Fiedler et al. (1995)
Mean: 1.4	Columbus, OH	Rural background	3	Lorber et al. (1998)
Range: 0.046–2.4 Mean: 0.71	Washington	Open, nongrazed	4	Rogowski et al. (1999, 2005)
Range: 0.45–5.2 Mean: 3.3	Washington	Forest, noncommercial	4	Rogowski et al. (1999); Rogowski and Yake (2005)
Mean: 5.74	Connecticut	Rural background	34	MRI (1992)
Range: 0.1–9.6 Mean: 1.6	Colorado	Open space background	36	U.S. EPA (2001)
Range: 0.21–11.42 Mean: 1.69	United States	Rural/remote	27	Current study

TEQ = toxicity equivalent

Only one study was found that reported PCB TEQs in rural North America soils (U.S. EPA, 2001). Thirty-six soil samples were collected from areas defined as "open space background" in the Front Range area near Denver, CO. The PCB TEQs averaged 1.2 pg/g, which is higher than the average from the current study of 0.07 pg/g. In fact, this mean exceeds the maximum value of this study (0.379 pg/g). The proximity of these sites to Denver may account for the difference. A rural soil survey was conducted in Poland in 2002 (Wyrzykowska et al., 2005). This study sampled soils in 13 agricultural areas and found a range of 0.054 to 0.42 pg TEQ/g and an average of 0.18 pg TEQ/g. Buckland et al. (1998) evaluated soils collected in New Zealand. The PCB concentrations ranged from 0.067 to 2.3 pg TEQ/g for provincial centers. The PCB TEQ average from the current study falls within the ranges reported for the studies in Poland and New Zealand.

PCBs are generally a small fraction of the total TEQs in soil. The only exception was Big Bend, TX (Site 23), where PCBs contributed 62% of the total TEQ2s.

The distribution of CDD/CDF and PCB TEQ values across sites is displayed graphically in Figures 3 and 4, respectively. Figure 5 compares the total TEQs by CALUX, HRMS TEQ1, and HRMS TEQ2. Figures 6 and 7 show frequency diagrams for levels of CDD/CDF TEQs and PCB TEQs, respectively, across all sites. These diagrams show the number of sites with levels within various ranges. For example, in Figure 6, the first bar shows the number of sites with concentrations between 0 and 1 pg TEQ2/g, the second bar shows the number of sites with concentrations between 1 and 2 pg TEQ2/g, and so on. These results show how the concentrations were distributed across sites. Section 7.3 discusses how the TEQ results derived from CALUX compare with those derived from the HRMS analysis.

CDD/CDF TEQs in procedural blanks had an average TEQ1 of 0.05 and an average TEQ2 of 0.21 pg/g. PCB TEQs in procedural blanks have an average TEQ1 of 0.0056 pg/g and an average TEQ2 of 0.020 pg/g. A few sites had TEQ levels near the blank levels, suggesting that TEQs were very low to nondetect at these sites.

6.5. MERCURY RESULTS

Table 2 provides mercury concentrations for each site composite. The complete set of mercury data is provided in Appendix J. Mercury concentrations ranged from 0.5 to 69 ng/g and averaged 22 ng/g across all sites (SE = 2.9, SD = 15 ng/g). The mean was calculated setting nondetects equal to half the detection limit; however, it was essentially the same whether nondetects were set to zero or to their full detection limit. As indicated in Table 2, three samples had holding times beyond the specified 28 days. Results for these three samples should be considered minimum values based on the holding time exceedance. Recomputing the mean without these samples reduced it to 21 ng/g. A summary of mercury concentrations from rural
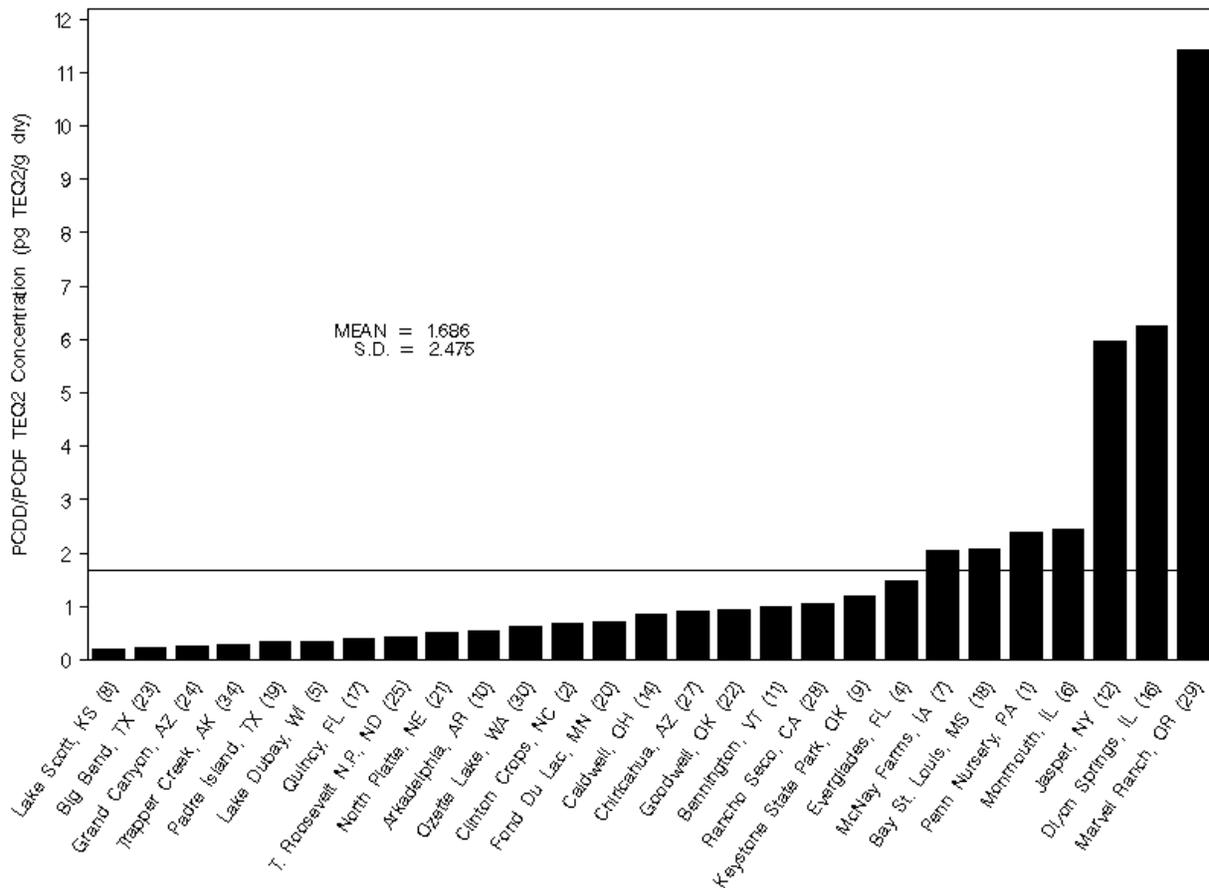
Figure 3. HRMS CDD/CDF TEQ2s for all 27 sites.

areas of North America is shown in Table 9. The five studies from the literature reported concentrations ranging from 10 to 600 ng/g. The mean from the current study (22 ng/g) falls within this range but near the lower end. Mercury was below detection limits in the procedural blanks.

The distribution of mercury concentrations across sites is displayed graphically in Figure 8. Figure 9 shows the frequency diagram for levels of mercury in soil across all sites. This diagram shows the number of sites with concentrations within various ranges. For example, the first bar shows the number of sites with concentrations between 0 and 0.01 mg/kg (0 and 10 ng/g), the second bar shows the number of sites with concentrations between 0.01 and 0.02 mg/kg (10 and 20 ng/g), and so on. These results show how the concentrations were distributed across sites.
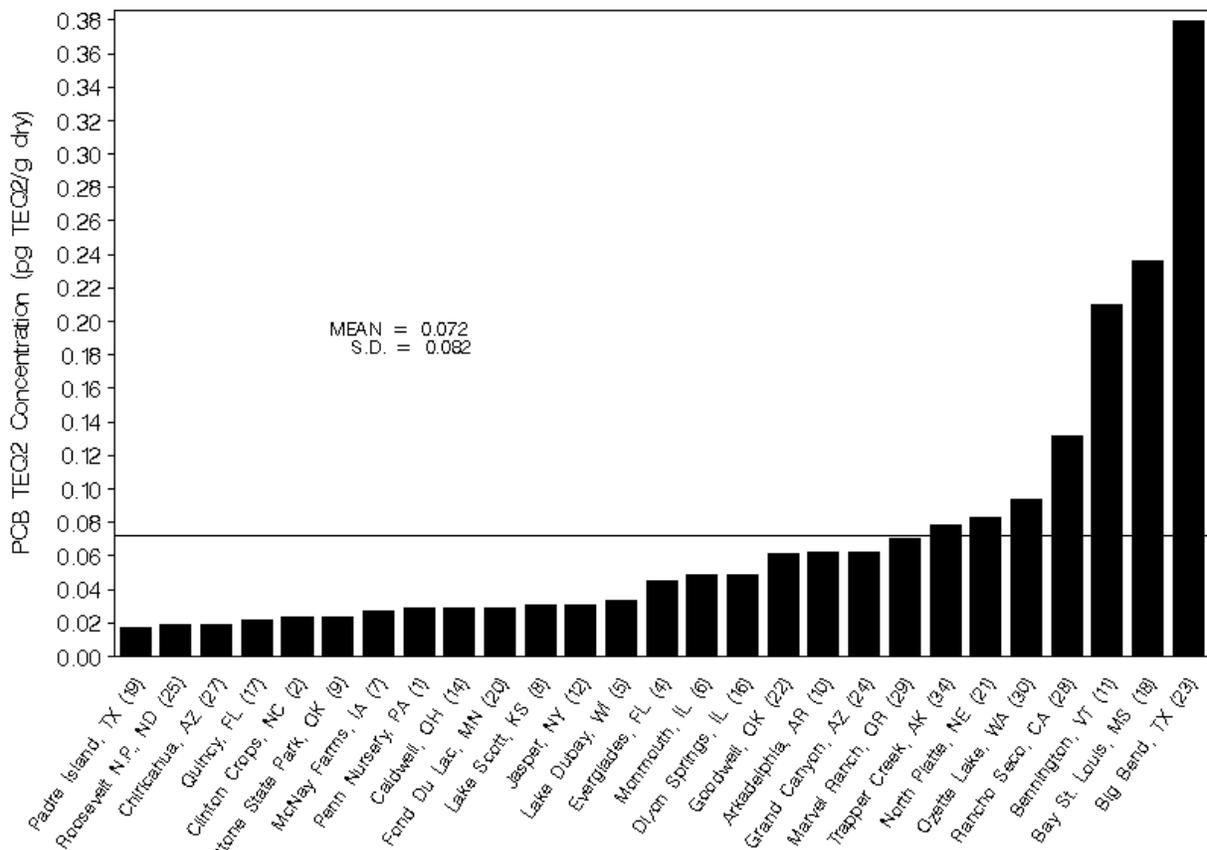
Figure 4. HRMS PCB TEQ2s for all 27 sites.

6.6. CONGENER PROFILES

Appendix K shows four congener profiles for each site: CDDs/CDFs, PCBs, CDD/CDF TEQs, and PCB TEQs. Each of the profiles is discussed below.

- *CDDs/CDFs.* These profiles are very similar across sites, with concentrations of OCDD being the highest at all sites. Heptachlorodibenzo-*p*-dioxins (HpCDDs) were second highest at all sites except three, where octachlorodibenzofuran (OCDF) was second highest. This pattern compares well with the Worldwide Deposition Profile presented by Brzuzy and Hites (1996).

- *PCBs.* These profiles are very similar across sites, with concentrations of PCB 118 being the highest at all sites. PCB 105 was second highest at all sites except one, where PCB 156/157 was second highest.
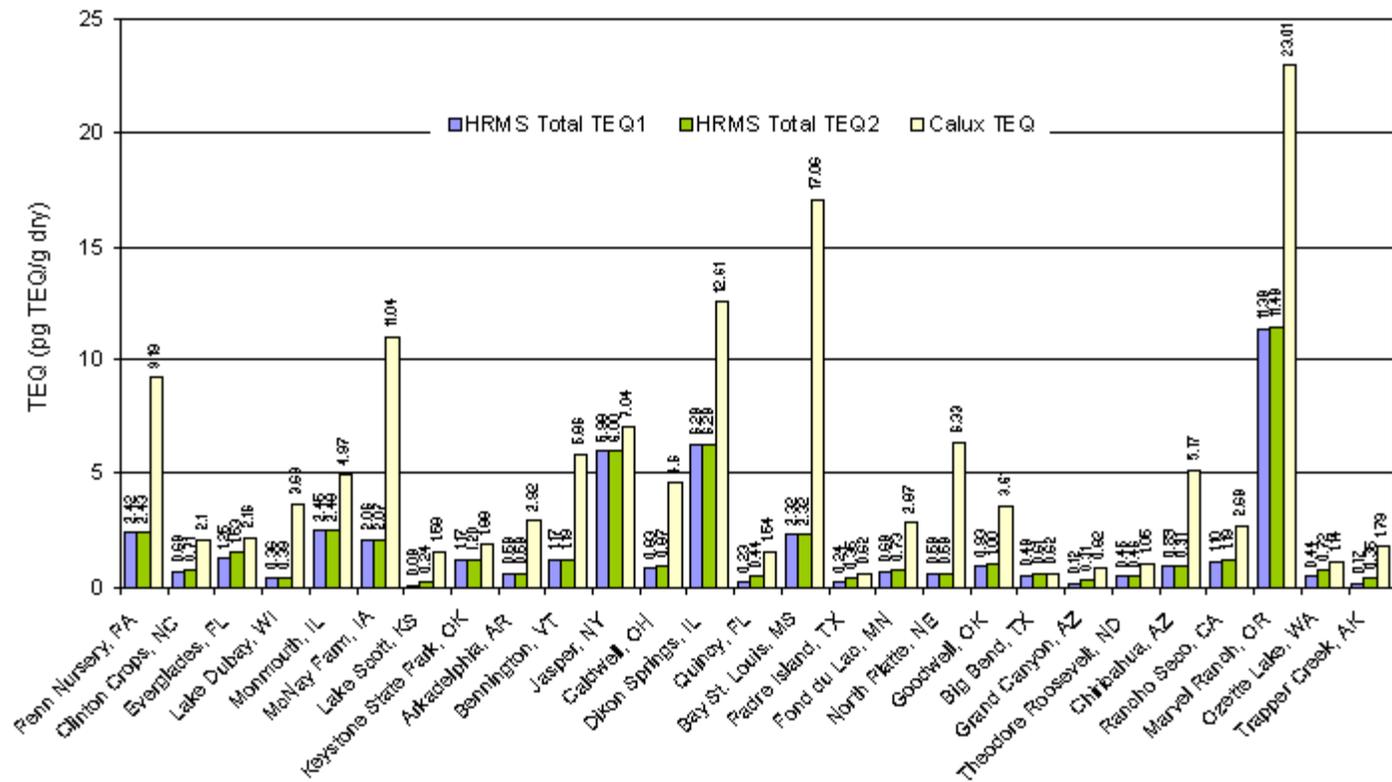
Figure 5. HRMS total TEQ1s, HRMS total TEQ2s, and CALUX TEQs for all 27 sites.
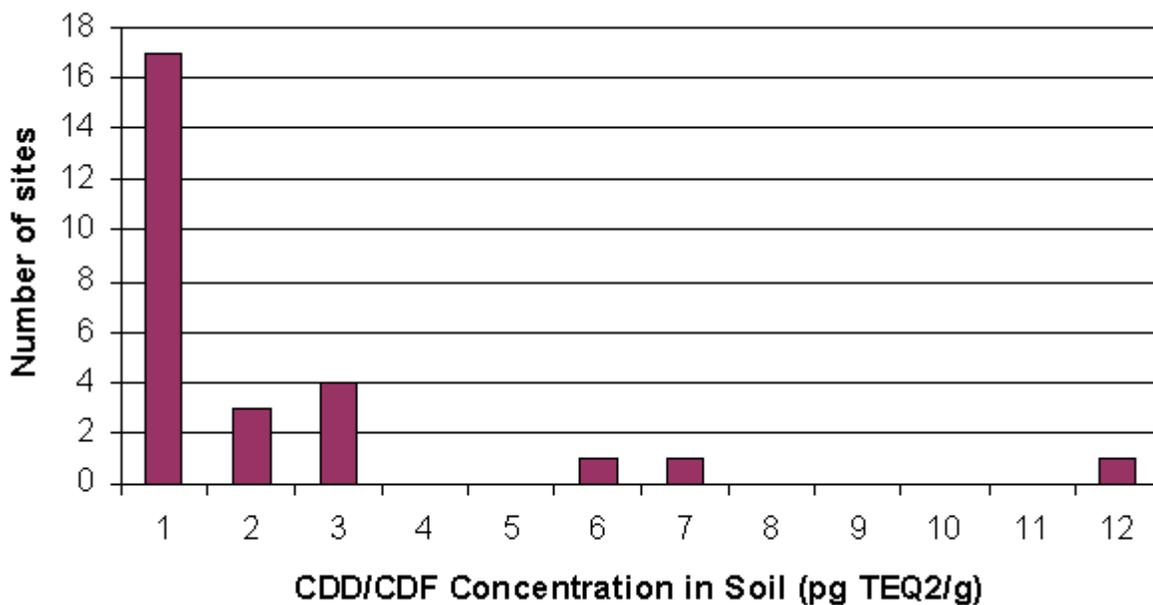
Figure 6. Frequency diagram for CDD/CDF TEQ2 concentrations among 27 sites.

26
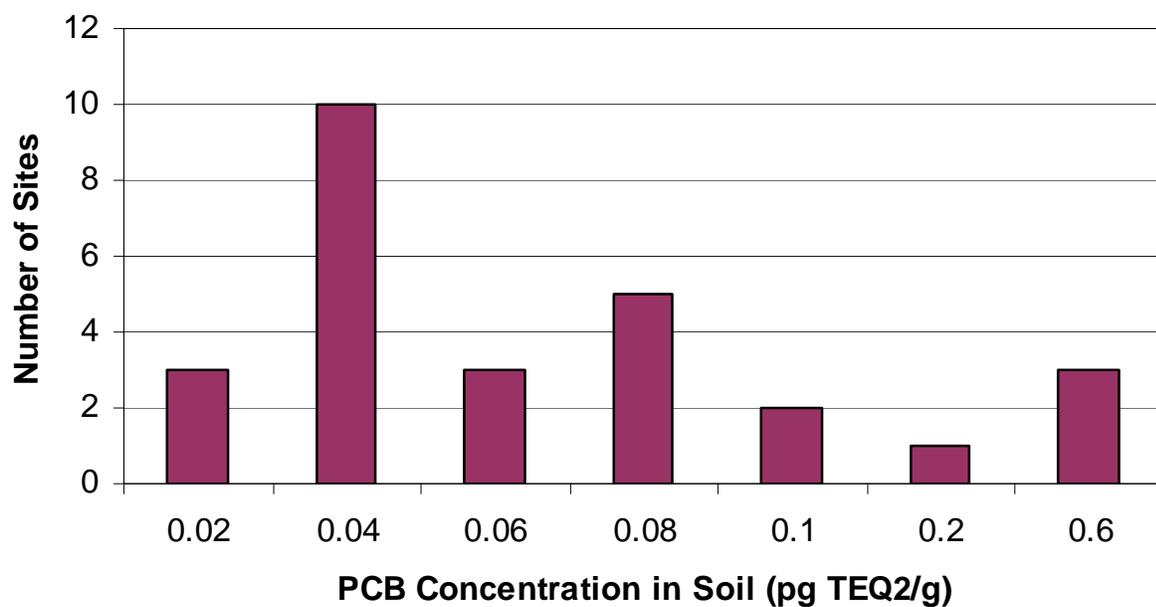
Figure 7. Frequency diagram for PCB TEQ2 concentrations among 27 sites.

Table 9. Literature summary for mercury in rural soils of North America

Concentration (ng/g)	Location	Site Description	n	Reference
Range: <10–260	New Jersey	Rural	35	NJDEP (2001)
Range: 10–550	New York	Orchards	13	Merwin et al. (1994)
Range: 12–220	Minnesota	Wilderness	NR	Glass et al. (1990)
Range: <3.2–66 Mean: 11	Washington	Background	13	Rogowski et al. (1999)
Median: <100 Range: <25–600	Michigan	Background	431	MDEQ (2005)
Range: 0.5–69 Mean: 22	United States	Rural/remote	27	Current study

NR = not reported

Mercury Concentration in Soil
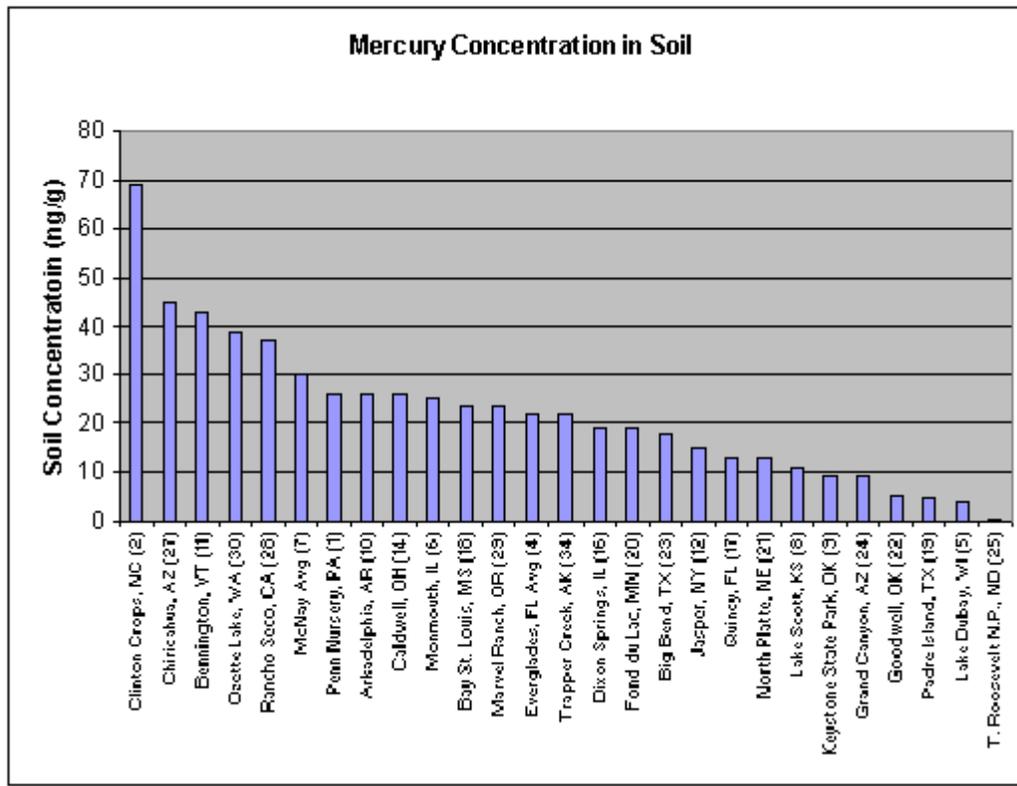
Figure 8. **Mercury concentrations at all 27 sites.**

- *CDD/CDF TEQs.* These profiles vary considerably across sites. The congeners with the highest concentrations were usually OCDD, HpCDDs, pentachlorodibenzo-*p*-dioxins (PeCDDs), or 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-PeCDF). For TEQ1 and TEQ2 values, in general the HpCDDs and OCDD were significant contributors to TEQ. 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF also contributed significantly in instances where these congeners were detected.

- *PCB TEQs.* These profiles are very similar across sites, with concentrations of PCB 126 (on a TEQ2 basis) being the highest at all sites except two, where PCB 118 was highest. Because of its large TEF, PCB 126 was also a significant contributor to TEQ1 when detected. PCBs 118, 105, 156/157, and 169 were important contributors to TEQ1 and TEQ2 for many sites.
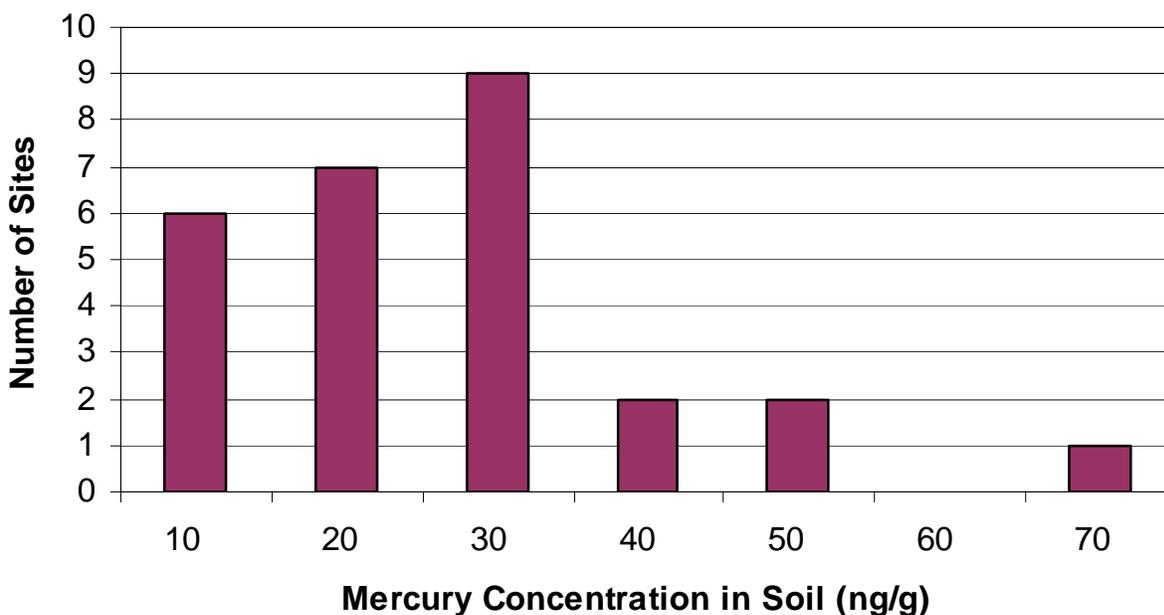
Figure 9. Frequency diagram for mercury concentrations among 27 sites.

7. COMPARATIVE ANALYSES

This chapter presents analyses that compare (1) chemical concentration levels in air with those in soil, (2) chemical concentration levels in soil with those of TOC in soil, and (3) HRMS-derived TEQs with CALUX-derived TEQs. For all analyses, the criteria for statistical significance is $p \leq 0.05$.

7.1. COMPARISON OF AIR AND SOIL CONCENTRATIONS

Air samples have been collected at NDAMN sites across the United States since 1998 and analyzed for concentrations of CDDs/CDFs and certain PCBs. NDAMN used high-volume air samplers that operated for 30 days, four times per year. The NDAMN data for the years 1998 to 2001 are presented in Cleverly et al., 2006 and U.S. EPA, 2005a,b. The comparisons were made using air data that most closely matched the date that the soil samples were collected (2003). Because the peer review of the 2001 air data had not yet been completed when this document was prepared, the 2000 air data were selected for this analysis. NDAMN collected air samples in 2003 so future studies could compare air and soil samples collected in the same year.

Note that Site 29 was located at Hyslop Farms, OR, in 2000 and was moved a few miles to Marvel Ranch, OR, in 2003 because Hyslop Farms is near a major transportation route and

Marvel Ranch is located in a more remote area away from transportation. The air sample was collected at Hyslop Farms and the soil sample at Marvel Ranch. Also, the NDAMN stations Site 28 (Rancho Seco, CA) and Site 34 (Trapper Creek, AK) were not in operation in 2000, so these sites were not included in the analysis.

7.1.1. Air and Soil Concentrations

This section evaluates reationships between the chemical levels in the soil and air across sites. Scatter plots of the raw data generally showed no obvious correlation as many concentrations are clustered close to zero and become more widely dispersed as concentration increases. Often when scatter plots have this form, it is useful to evaluate the correlation based on the natural log of the data. This is illustrated in Figure 10, which shows paired scatter plots for a number of the homologues on the basis of both the raw data and the natural log transform of the data. Table 10 summarizes the natural log linear correlations between air and soil levels across sites for PCBs, CDD/CDFs, and TEQs. The following observations can be made:

- *PCBs.* The PCB air data included only six congeners, limiting the analyses that could be done. Only PCB 77 showed a significant correlation with r = 0.47. The PCB TEQs did not yield a significant correlation.

- *CDDs/CDFs*. The analyses of the CDD/CDF data showed that correlations were significant for four homologues: PeCDDs (r = 0.40), HxCDDs (r = 0.42), HpCDDs (r = 0.48), and OCDD (r = 0.52). Additionally, significant correlations were found for total CDDs (r = 0.51) and total CDDs/CDFs (r = 0.53). None of the furan homologues showed significant correlations.

- *TEQs.* The analyses of the TEQ data showed that the correlations were significant for TEQ_{DF} (r = 0.58) and TEQ_{DFP} (r = 0.54).

The air sample and soil sample TEQs were calculated using the same TEFs; however, the PCB TEQ calculation for soils included additional PCB compounds: PCBs 81, 114, 123, 167, and 189. Figure 11 illustrates the annual average of quarterly air sample TEQ concentrations collected in 2000, and Figure 12 illustrates the soil sample TEQ concentrations collected during one sampling event in 2003. When visually comparing the total TEQ levels in air and soil shown in Figures 11 and 12, some similarities and some differences can be seen:

- Marvel Ranch, OR (Site 29), had the highest air level and the highest soil level. Two other sites had relatively high soil levels: Jasper, NY (Site 12), and Dixon Springs, IL (Site 16). Site 16 had a relatively high air level, but Site 12 did not. Grand Canyon, AZ (Site 24), had the lowest air level and the lowest soil level.
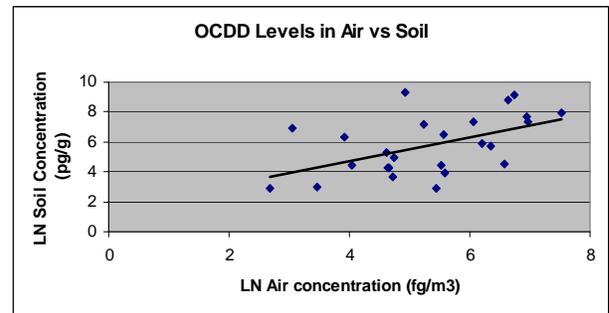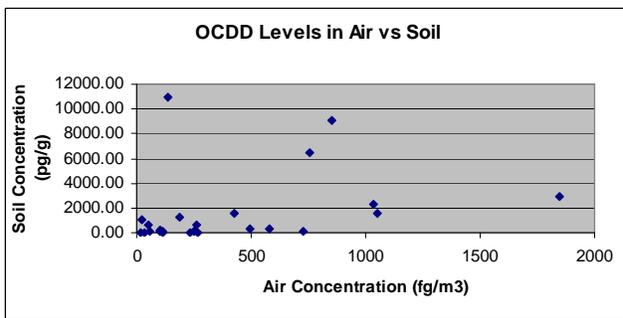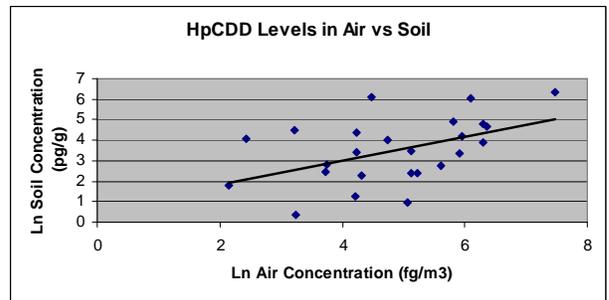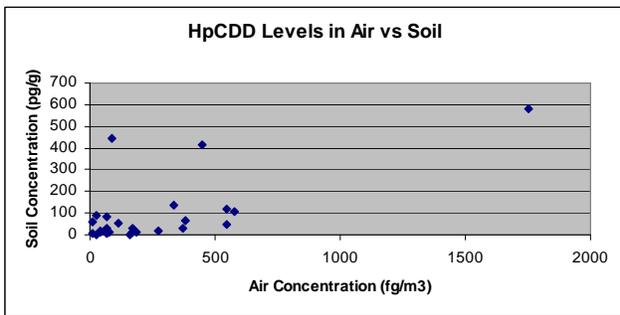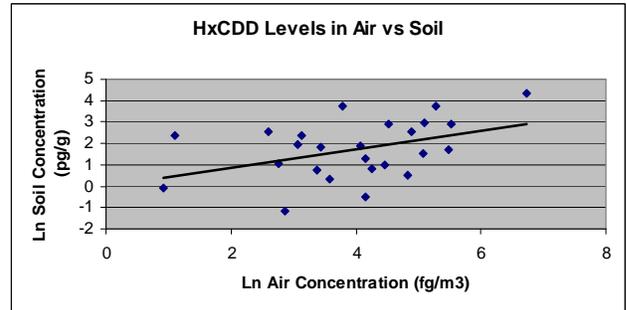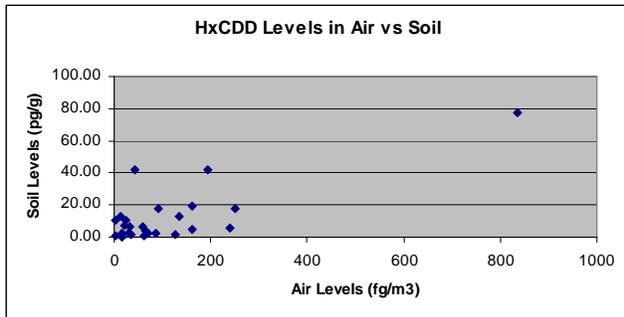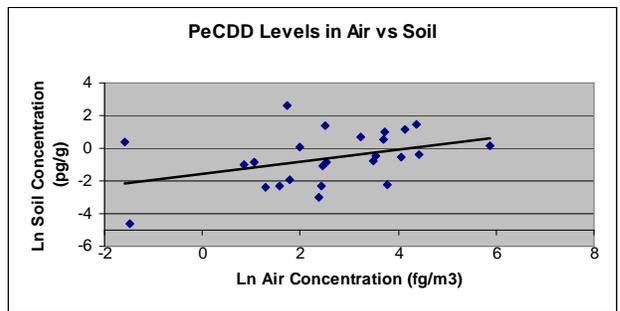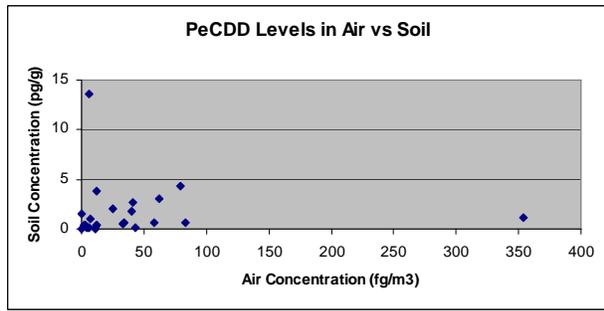
Figure 10. Scatter plots of homologue levels in air versus soil.

Table 10. Correlations across sites between soil concentrations and air concentrations[a,b]

Compound	Correlation coefficient	p-value
Total TCDFs	0.11	0.61
Total TCDDs	0.25	0.24
Total PeCDFs	0.15	0.49
Total PeCDDs	**0.40**	**0.05**
Total HxCDFs	0.24	0.26
Total HxCDDs	**0.42**	**0.03**
Total HpCDFs	0.37	0.07
Total HpCDDs	**0.48**	**0.01**
OCDF	0.36	0.07
OCDD	**0.52**	**0.01**
Total CDDs	**0.51**	**0.01**
Total CDFs	0.32	0.11
Total CDDs/CDFs	**0.53**	**0.01**
PCB 77	**0.47**	**0.02**
PCB 105	0.33	0.11
PCB 118	0.31	0.14
PCB126	-0.02	0.94
PCB 156/157	-0.02	0.94
PCB 169	0.16	0.43
TEQ$_{DF}$	**0.58**	**0.00**
TEQ$_{PCB}$	0.21	0.32
TEQ$_{DFP}$	**0.54**	**0.01**

[a] All correlations are based on natural log transforms of the data.
[b] Correlations where $p \leq 0.05$ are shown in bold

- In general, the percent of PCB TEQ contribution to the total TEQ is similar for air samples and soil samples. Notably, Grand Canyon, AZ (Site 24), had a high percentage of PCB relative to the total TEQ in both air and soil. Two sites had a higher percentage of PCB to total TEQ in soil samples than in the air samples: Big Bend, TX (Site 23), and Bennington, VT (Site 11). Bay St. Louis, MS (Site 18), had the highest percentage of PCB TEQs in the air, but a moderate percentage of PCBs in the soil.
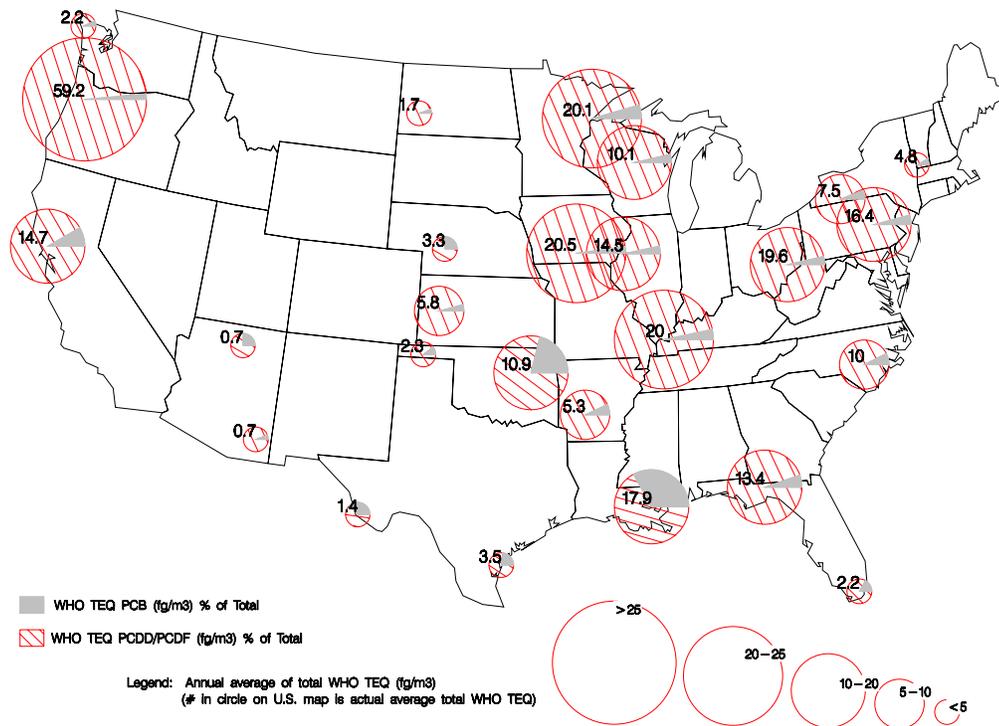
Figure 11. Annual average total TEQs for air samples obtained at NDAMN sites in 2000.
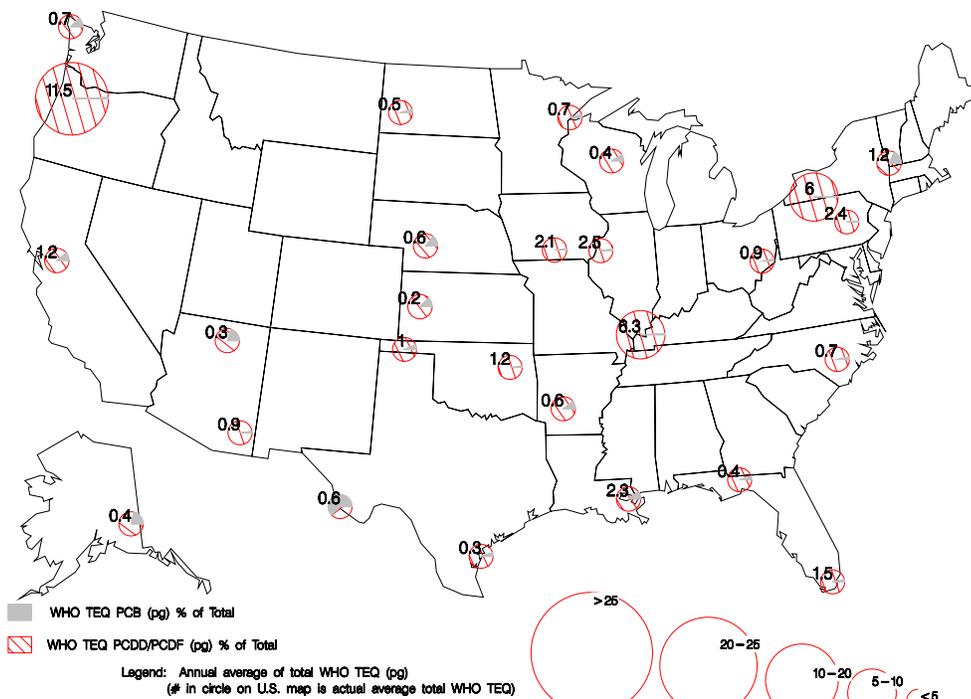
Figure 12. Total TEQ2 for soil samples taken at NDAMN sites in 2003.

Figures 13 and 14 show the scatter plots for the TEQ data on the basis of the raw data and the natural log-transformed data, respectively. The regression line for the log-scale version is:

$$\text{Ln(soil concentration)} = -0.749 + 0.455 \, \text{Ln(air concentration)}$$

The standard error on the intercept is 0.304. The standard error on the slope is 0.144. The closeness of the slope of the regression line to 0.5 indicates a relationship between the soil concentration and the square root of the air concentration. This relationship is not particularly strong (r = 0.54), but it should not be discounted.

Two facts should be considered while evaluating these air-soil correlations. First, dioxin levels in soil result from accumulation over many years, but the air samples used in this comparison were collected over just one year. Second, dioxin levels in the environment have changed over time. Dioxin levels began to rise in the 1930s and peaked in the early 1970s (U.S. EPA, 2003). Also, emissions in the United States decreased approximately 90% from 1987 to 2000 (U.S. EPA, 2006). Accordingly, soil levels may better reflect past air levels than current levels.

7.1.2. Air and Soil Congener Profiles

Appendix L shows paired air and soil congener profiles for all the sites except Rancho Seco, CA (Site 28), and Trapper Creek, AK (Site 34), which had no air data in 2000. These comparisons are presented for the 2,3,7,8-substituted CDD/CDF congeners and six PCB congeners. The PCB congeners included in this analysis were limited to the ones measured in both air and soil (PCBs 77, 118, 106, 126, 156/157, and 169). The air data used to derive these profiles were from samples collected in 2000, but the draft NDAMN report for 2001 suggests that the air congener profiles are similar to those in 2000 (U.S. EPA, 2005b). Observations from these profiles are described below.

- *CDDs.* The two prominent congeners in air and soil were the same at all sites (1,2,3,4,6,7,8-HpCDD and OCDD). The order of congeners in the air and soil was generally the same at most sites: from low to high, tetra, penta, hexas, heptas, and octa. At most sites, the relative proportion of octa to the other congeners was higher in the soil than in the air.

- *CDFs.* The two prominent congeners in air and soil were the same at all sites (1,2,3,4,6,7,8-heptachlorodibenzofuran [1,2,3,4,6,7,8-HpCDF] and OCDF). The order of congeners in the air and soil was somewhat variable across sites. The similarity in relative proportions of the congeners in air and soil was difficult to judge visually.
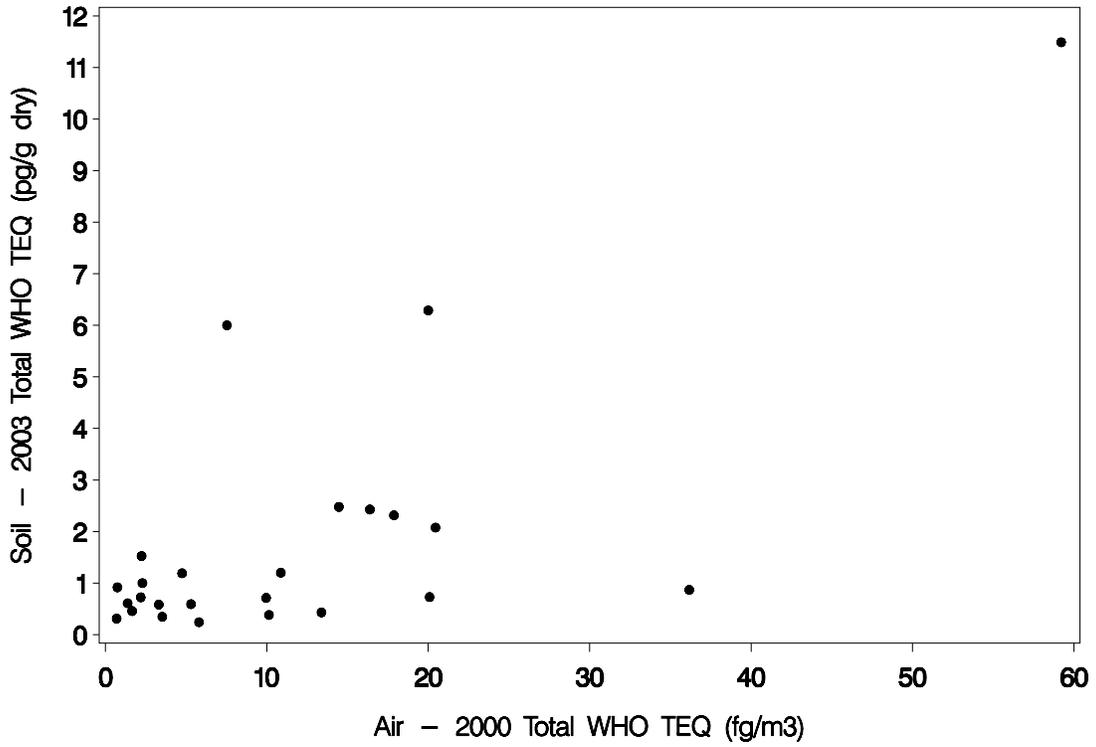
Figure 13. Annual average air total TEQs versus soil total TEQ2s (raw data).

$$\ln(Soil) = -0.749 + 0.455 \cdot \ln(Air)$$
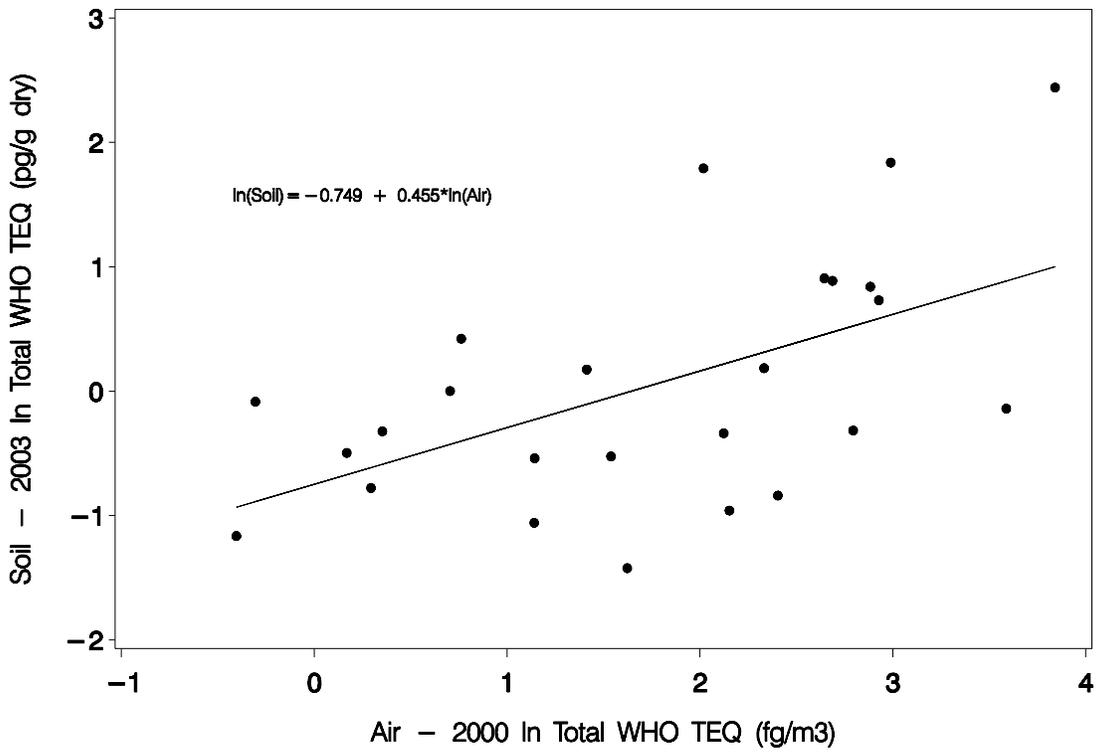
Figure 14. Annual average air total TEQs versus soil total TEQ2s (log transformed data).

- *PCBs.* The two prominent congeners in air and soil were the same at all sites (PCBs 118 and 105). The order of congeners in the air and soil was generally the same at most sites: from low to high, PCBs 169, 126, 77, 156/157, 105, and 118. At most sites, the relative congener proportions in air appeared similar to the proportions in soil.

7.2. COMPARISON OF SOIL CONCENTRATION WITH TOTAL ORGANIC CARBON CONCENTRATION

The tendency for persistent chemicals to bind to organic carbon suggests that CDD/CDF, PCB, and mercury levels in soil may correlate with TOC levels in soil. Other researchers have reported mixed results on this issue. Brzuzy and Hites (1995) observed a strong correlation between organic carbon and total CDDs/CDFs at some sites. At sites where this was not observed, they theorized that deposition exceeded the sorption capacity of the soil. Wilcke and Amelung (2000) studied PCBs in North American grasslands and found no correlation between organic carbon and 14 PCBs. EPA reported that mercury levels in soil are positively correlated with organic matter (U.S. EPA, 1997).

Scatter plots were used to investigate relationships between chemical levels in the soil and TOC levels in the soil across sites. As illustrated in Figure 15, the plots for a number of homologues suggested positive correlations. Correlation analyses were conducted for mercury, TEQs, and all homologue groups (Table 11). Based on these analyses, the following observations can be made:

- *Mercury.* The correlation was not significant.

- *PCBs.* The only significant correlation was for nonachlorobiphenyls (r = 0.47).

- *CDDs/CDFs.* The correlations were significant for seven homologues: TCDFs (r = 0.43), PeCDFs (r = 0.51), PeCDDs (r = 0.44), hexachlorodibenzofurans (HxCDFs) (r = 0.47), HxCDDs (r = 0.46), HpCDFs (r = 0.38), and HpCDDs (r = 0.38). Also, total CDFs had a significant correlation (r = 0.39).

- *TEQs.* The TEQ correlation was significant (r = 0.43). The scatter plot for these data are shown in Figure 16.
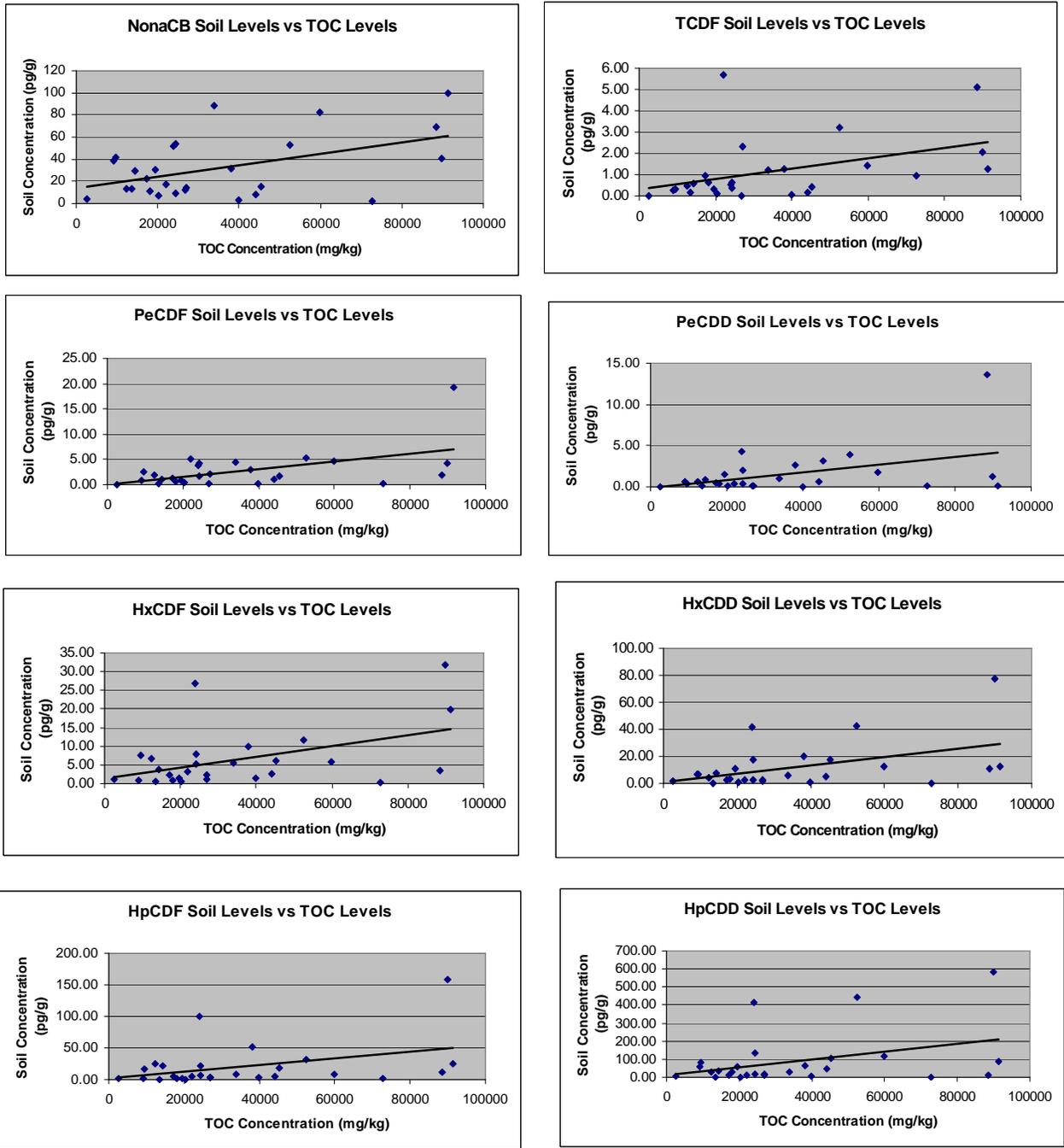
Figure 15. Scatter plots of chemical levels in soil vs TOC levels in soil.

Table 11. Correlation across sites between soil concentration and total organic carbon concentration[a]

Chemical	Correlation coefficient	*p*-value
Mercury	0.11	0.59
Mono-CBs	-0.14	0.49
Di-CBs	-0.15	0.46
Tri-CBs	-0.15	0.47
Tetra-CBs	-0.21	0.28
Penta-CBS	-0.19	0.34
Hexa-CBs	-0.18	0.38
Hepta-CBs	0.01	0.97
Octa-CBs	0.17	0.41
Nona-CBs	**0.47**	**0.01**
Deca-CBs	0.08	0.68
Total PCBs	-0.22	0.27
Total TCDFs	**0.43**	**0.03**
Total TCDDs	0.32	0.10
Total PeCDFs	**0.51**	**0.01**
Total PeCDDs	**0.44**	**0.02**
Total HxCDFs	**0.47**	**0.01**
Total HxCDDs	**0.46**	**0.02**
Total HpCDFs	**0.38**	**0.05**
Total HpCDDs	**0.38**	**0.05**
OCDD	0.21	0.30
OCDF	0.27	0.17
Total CDDs	0.22	0.27
Total CDFs	**0.39**	**0.04**
Total CDDs/CDFs	0.23	0.25
Total TEQ2	**0.43**	**0.02**

[a] Correlations where $p \leq 0.05$ are shown in bold
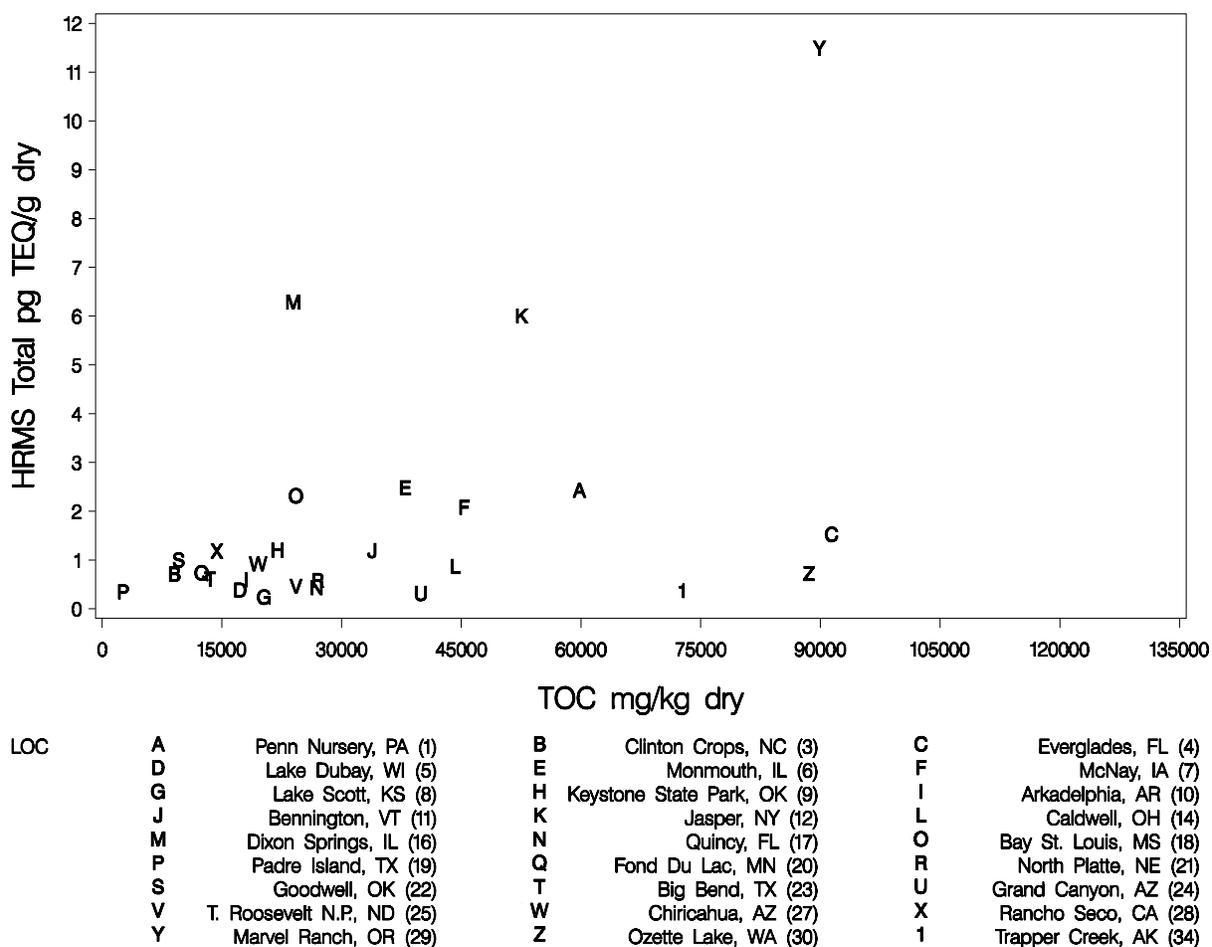
Figure 16. HRMS-based total TEQ2 versus total organic carbon (TOC) concentration of soil.

Although a number of homologue groups showed statistically significant correlations, none were particularly strong (maximum r was 0.51). This could indicate that other factors were also affecting sorption characteristics of the soil. Grain size may also correlate with dioxin levels in soil because organic carbon is sometimes associated with smaller particles and because smaller particles have a higher surface area-to-mass ratio, increasing sorption capacity. The other two soil properties measured in this study, pH and moisture content, do not have clear mechanistic reasons to correlate with dioxin levels in soil.

7.3. COMPARISON OF HRMS TEQs WITH CALUX BIOASSAY TEQs

HRMS and the CALUX bioassay method were used to analyze soils. This study was not intended to provide a detailed evaluation of the CALUX bioassay method; however, as

discussed below, a few observations can be made about its performance. For a more detailed analysis of bioassay methods, readers are referred to EPA's Superfund Innovative Technology Evaluation (SITE) Program. Under this program, EPA has evaluated a variety of technologies (including CALUX) for determining the presence of dioxin and dioxin-like compounds in soil and sediment (U.S. EPA, 2005c).

As shown in Table 7, the CALUX results were higher than the HRMS total TEQs in almost all of the site composites. The ratios of CALUX TEQs to HRMS total TEQ2s ranged from 1 to 11. The ratios were about 2 or less at 11 sites and 10 or more at 2 sites. These data are shown as scatter plots in Figures 17 (raw data) and 18 (log transformed data). Both data sets had a significant correlation, with $r = 0.82$ for the raw data and $r = 0.78$ for the log-transformed data.

LOC								
	A	Penn Nursery, PA (1)	B	Clinton Crops, NC (3)	C	Everglades, FL (4)		
	D	Lake Dubay, WI (5)	E	Monmouth, IL (6)	F	McNay, IA (7)		
	G	Lake Scott, KS (8)	H	Keystone State Park, OK (9)	I	Arkadelphia, AR (10)		
	J	Bennington, VT (11)	K	Jasper, NY (12)	L	Caldwell, OH (14)		
	M	Dixon Springs, IL (16)	N	Quincy, FL (17)	O	Bay St. Louis, MS (18)		
	P	Padre Island, TX (19)	Q	Fond Du Lac, MN (20)	R	North Platte, NE (21)		
	S	Goodwell, OK (22)	T	Big Bend, TX (23)	U	Grand Canyon, AZ (24)		
	V	T. Roosevelt N.P., ND (25)	W	Chiricahua, AZ (27)	X	Rancho Seco, CA (28)		
	Y	Marvel Ranch, OR (29)	Z	Ozette Lake, WA (30)	1	Trapper Creek, AK (34)		

Figure 17. HRMS total TEQ2s versus CALUX bioassay TEQs by site (raw data).
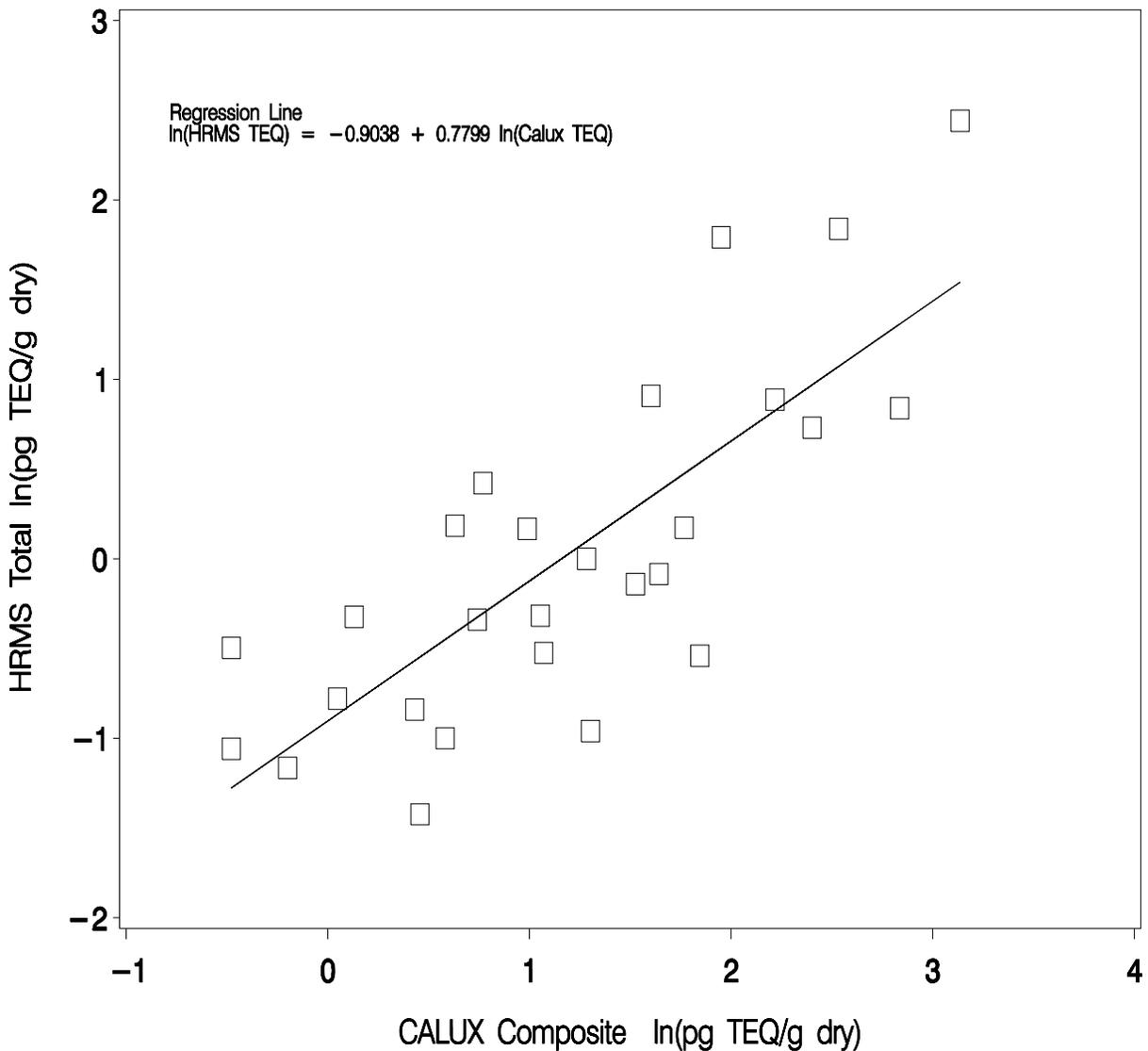
Figure 18. Scatter plot of HRMS total TEQ2 versus Calux bioassay TEQs on natural log-scale with natural log-linear regression line (r = 0.78).

The likely reason for the high bias in the CALUX data relative to the HRMS results is that CALUX responds to all compounds that activate the aryl hydrocarbon receptors, including a number of compounds other than CDDs, CDFs, and PCBs that may be present in soils, such as brominated and fluorinated dibenzo-*p*-dioxins/furans and biphenyls and halogenated napthlenes. Brown et al. (2004) showed that CALUX responds more to the hepta- and octa-chlorinated dioxins/furans and the tetrachlorinated biphenyls than would be expected on the basis of WHO TEF values and that this could lead to overestimation of the TEQ for samples that are contaminated primarily by these compounds. Although the two methods used different sample

extraction procedures, it is unlikely that the ASE extraction used for the HRMS analysis was less efficient than the bottle sonication extraction procedures used for the CALUX analysis.

Clark et al. (2003) compared CALUX bioassays with traditional HRMS techniques applied to soil samples. Their data also show a high bias in the CALUX data, but a much stronger correlation (r = 0.98). This stronger correlation may have resulted from the fact that the study was conducted with soil concentrations ranging from 100 to 100,000 pg/g, which are much higher than those measured here. The TEQs in these more highly contaminated samples are probably dominated by the CDDs, CDFs, and PCBs, reducing the influence of the other compounds that activate the aryl hydrocarbon receptors.

Figure 19 shows results of a rank order analysis of the HRMS total TEQ2 versus CALUX TEQ data. This figure illustrates that the CALUX TEQ values are reasonable indicators of the relative TEQs among the sites as the lowest HRMS total TEQ2 values correspond to lowest CALUX TEQ values and as HRMS TEQ values increase CALUX values increase in a similarly corresponding manner.
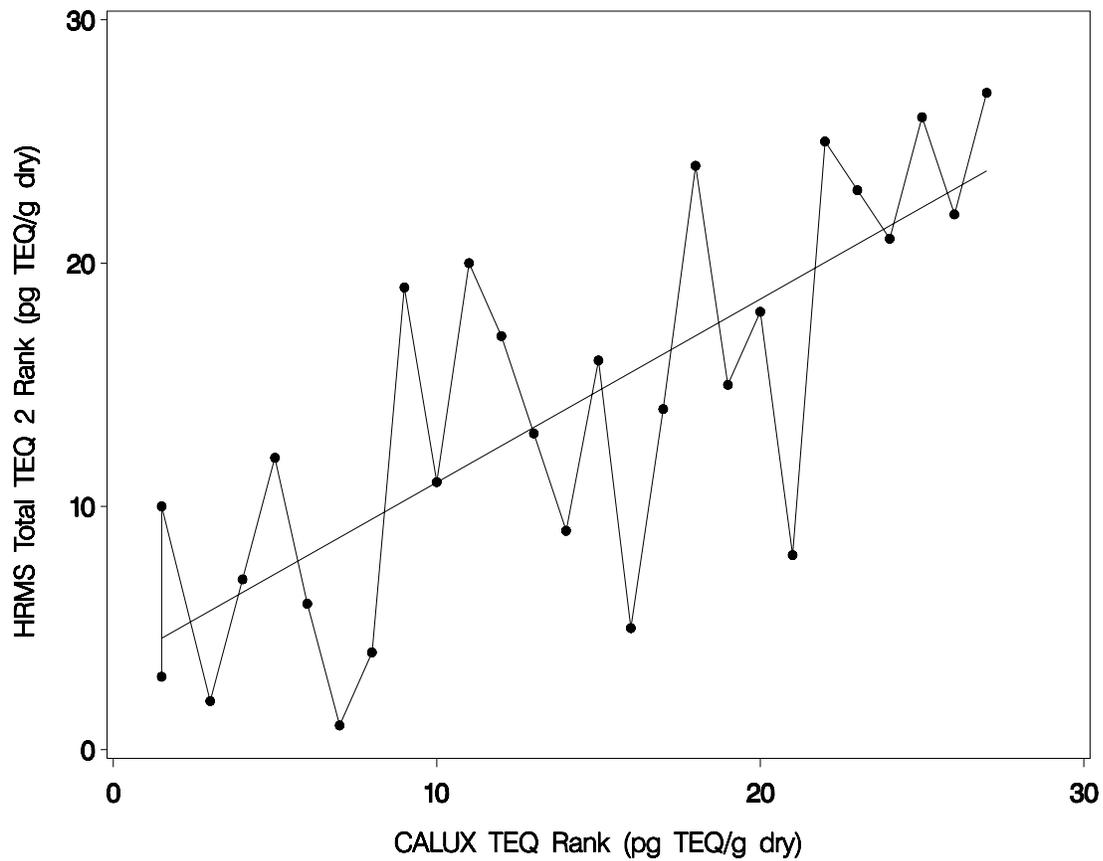
Figure 19. Rank order comparison of CALUX TEQs to HRMS total TEQ2s.

8. UNCERTAINTY

This chapter discusses the factors that contribute to the uncertainty in this study, including site selection, sampling protocol, analytical methods, and treatment of detection limits.

8.1. SITE SELECTION

The NDAMN sites were chosen as sampling locations because they are in rural/remote areas, they are well distributed nationally, they provide an opportunity to examine air-soil relationships, and they offered a cost-effective means for gathering soil samples. A statistically based random sampling design would have reduced bias in the site selection. However, the NDAMN study and the present soil survey were pilot studies and not meant to provide statistically unbiased results. Nonetheless, the results of the present study were consistent with other rural soil surveys.

8.2. SAMPLING PROTOCOL

A key uncertainty issue for a sampling protocol is the number of samples needed to represent a site. The number of samples per site used in this study was based on the coefficient of variation determined from the Oxford, OH, preliminary sample protocol evaluation (Appendix A). This initial study indicated that five samples within a 100 ft $\times$ 100 ft area would be sufficient to represent a site. Two aspects of this approach introduce uncertainty. First, it is unknown how representative the Oxford site is of the other sites in terms of spatial variability. Second, the Oxford exercise relied on CALUX analysis, which measures TEQs only. It is uncertain how well these results translate to specific chemicals. This uncertainty is greatest for mercury because it is unrelated to the dioxin-like chemicals detected by CALUX.

This study relied on composite soil samples (made by combining equal portions of five individual soil samples at each site) as the primary basis for chemical analysis. An important uncertainty issue is how well the composites represented the individual samples. The individual samples and the composites were analyzed for TEQs by the CALUX bioassay method, so the resulting data can be used to evaluate representativeness. Figure 20 shows, for each site, the average of the individual samples, the 95% confidence interval on the mean of the individual samples, and the composite sample TEQ value. Two observations from this figure suggest that
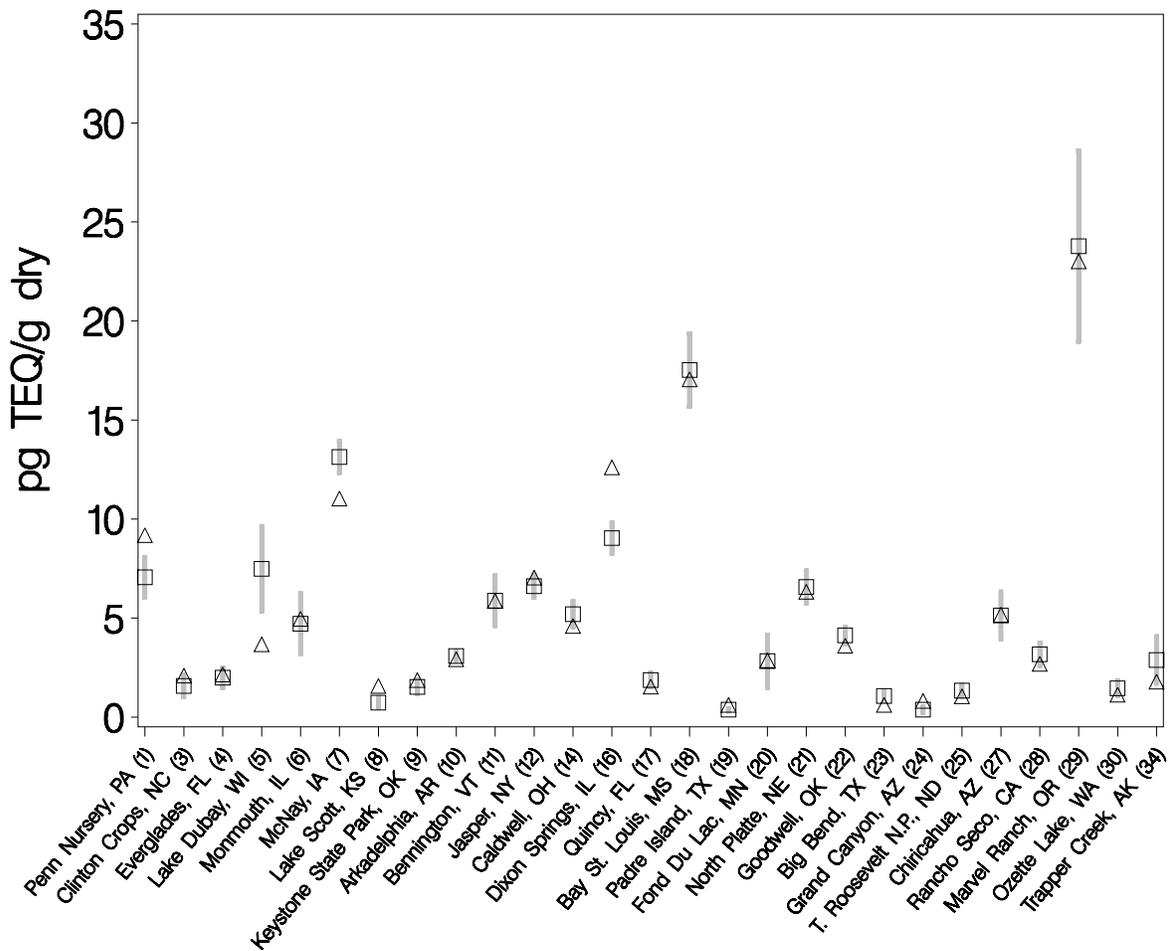
Figure 20. Comparison of five-point mean CALUX bioassay (□) and assay of composite soil sample (▵). Vertical line shows the 95% confidence interval about the mean.

the five-sample composite was adequate for characterizing TEQs at a site. First, most of the individual sampling point concentrations within a single site span a relatively small range, as evidenced by the short vertical bars. This means relatively little information was lost by analyzing the composite only. Second, the average of the individual sampling points was very near the composite concentration at almost all sites. The composite average fell outside the confidence interval at only four sites (1, 5, 7 and 16). A statistical analysis was performed to assess whether there was a statistically significant difference across sites between the average of the individual soil sample CALUX TEQ concentrations and the composite CALUX TEQ concentration. The analysis indicated that there was no statistical difference (at the 0.05 level) between the average and the composite.

Figure 21 shows a scatter plot of the paired values with the y = x line and the results of regressing the composite measurements on the five-point means. Statistical tests (F-tests) showed that the regression intercept was not significantly different from zero and the slope was not significantly different from one. Results from the site composite can therefore be considered to be representative of the five individual samples.
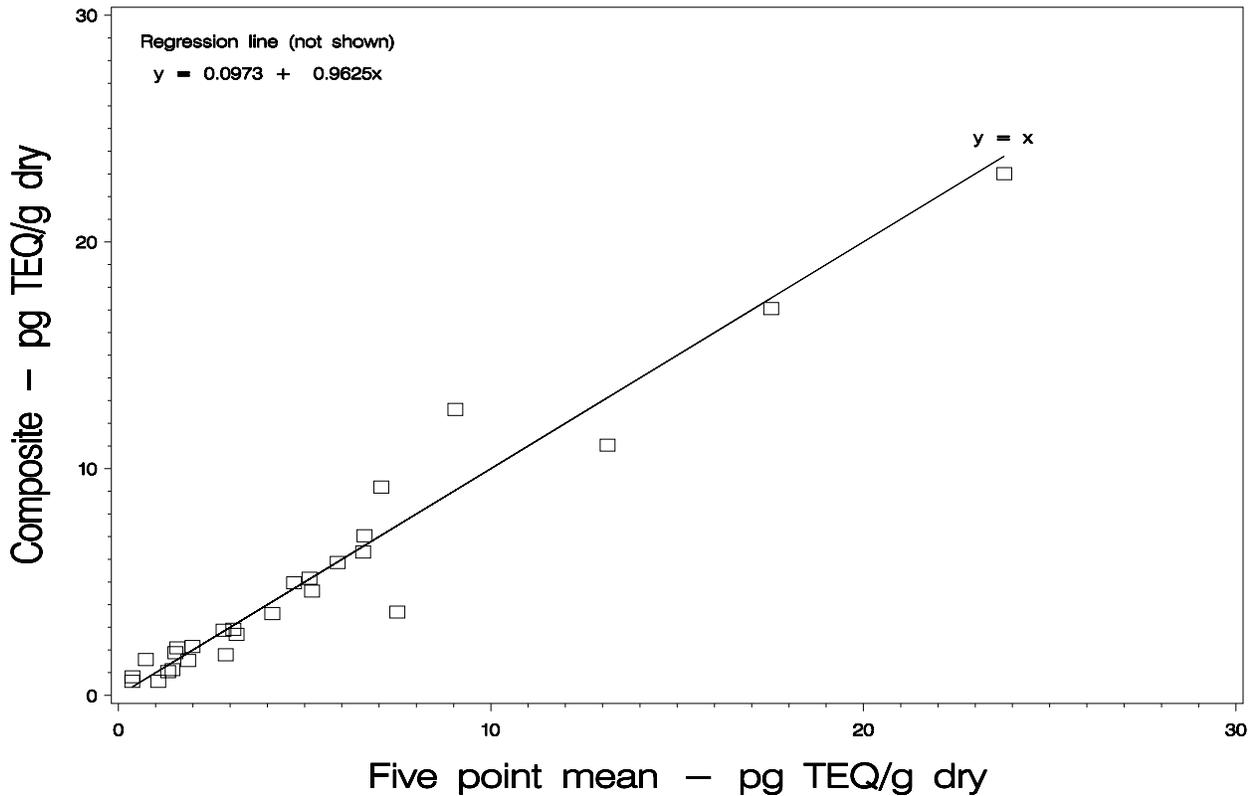
Figure 21. Scatter plot of five-point mean CALUX TEQs versus CALUX TEQs of soil composite (r = 0.97).

The similarity in the composites and averages of the individual samples at each site, as shown in Figure 20, also indicates an internal consistency in sample handling and compositing procedures.

Although more difficult to quantify, some between-site and within-site variation can be attributed to sampling technique because samples were collected by 27 different people with different experience levels. Attempts to control this variable were made by providing training and discussing sampling technique with each sampler, contacting the samplers by phone during

collection, conducting quality assurance audits at two sites during sampling, and documenting with photographs the sampling at each site.

Other sources of sampling variability, such as seasonality, temperature, soil conditions, and type and quantity of vegetation, may have contributed to the uncertainty and were not evaluated as part of this study.

8.3. ANALYTICAL METHODS

For a single sampling point, the relative percent difference between duplicate analyses gives some insight into within-sample variation. Within-sample variation is primarily affected by the sample homogenization and the analytical method. Section 5.5 and Appendix D present duplicate analysis results. In general, the relative percent difference between duplicates was within target limits for mercury and CDDs/CDFs, but it was more variable for PCBs.

Analytical protocols and equipment also have inherent uncertainties. Although there is a "true" measure of a concentration, even the best of analytical methods will only approximate the true measure and thereby introduce uncertainty. For this study, HRMS was selected to provide the final congener concentration levels for CDDs/CDFs and PCBs. HRMS analysis methods are the most accurate, sensitive methods currently available for detecting CDDs/CDFs and PCBs. The HRMS data were supported by CALUX analysis to ensure that the site composite analyzed by HRMS was representative of the five individual points that made up the composite. Ideally, all samples would be analyzed by HRMS; however, all studies are constrained by a finite budget and must make use of the best methods and protocols available given that budget.

8.4. TREATMENT OF DATA

In addition to the analytical protocol used, treatment of data can contribute to uncertainty, particularly when the study is concentrating on levels very near the detection limits. Various ways of treating missing data and data below the detection limit can change the mean concentration standard error, introducing uncertainty. In addition, evaluating data on a TEQ basis versus individual congener concentrations can potentially minimize the contribution of a highly variable congener should it have a low TEF, resulting in a small contribution to TEQ, or overestimate the contribution of a highly variable congener with a high TEF, resulting in a large contribution to TEQ.

9. CONCLUSIONS

This study conducted a national-scale pilot survey of levels of CDDs, CDF's, PCB's and mercury in rural/remote soils of the United States. The results presented pertain to the 27 sites sampled and should not be more broadly interpreted as statistically representative of all rural soils in the United States. These results, however, may be a plausible basis for a preliminary characterization of soils in rural/remote areas. The primary measurement results are summarized below.

- Total CDDs averaged 1,585 pg/g (SE = 567, SD = 2945). Total CDFs averaged 47 pg/g (SE = 13, SD = 68). Levels of the TCDD homologues were the lowest, with an average concentration of 0.2 pg/g. Levels of the OCDD homologue were the highest, with an average concentration of 1,482 pg/g. The range of concentrations found here is similar to the range across five published studies on CDD/CDF levels in soils from rural areas of North America.

- Total PCBs averaged 3,089 pg/g (SE = 1,009, SD = 5,241). Levels of the deca-chlorinated biphenyl homologues were the lowest, with an average concentration of 29 pg/g. Levels of the penta-chlorinated biphenyl homologues were the highest, with an average concentration of 1,013 pg/g. The range of concentrations found here is similar to the range across three published studies on PCB levels in soils from rural areas worldwide.

- Total TEQ2s averaged 1.76 pg/g (SE = 0.48, SD = 2.47). The PCBs generally were a small fraction of the total TEQs in soil. The mean for total TEQs from this study falls near the center of the range of values across 10 published studies.

- Mercury concentrations averaged 22 ng/g across all sites (SE = 2.9, SD = 15 ng/g). The mean from this study falls within the range of values from five published studies on mercury levels in soils from rural areas of North America.

Further details on ranges and distributions are provided in Chapter 6.

This study also evaluated relationships between air concentrations and soil concentrations across sites. Based on the log-transformed data, significant positive correlations were observed for TEQs (r = 0.54), PeCDDs (r = 0.40), HxCDDs (r = 0.42), HpCDDs (r = 0.48), OCDD (r = 0.52), PCB 77 (r = 0.47), total CDDs (r = 0.51), and total CDDs/CDFs (r = 0.53). None of the CDFs showed significant correlations. TEQ levels in soil and air were also compared visually using national maps (Figures 11 and 12). Although some correspondence could be seen in the lowest and the highest sites, many sites appeared inconsistent. The congener profiles of the air and soil were compared for the 2,3,7,8-substituted CDDs/CDFs and six PCB congeners. The

CDD and PCB profiles in air and soil were generally similar at all sites. The CDF profiles for air and soil were different at most sites.

The overall conclusions about the air-soil relationships for the three groups of chemicals are as follows:

- *CDDs.* A general association between air and soil was observed, based on the significant air-soil correlations observed across sites for most homologue groups and the similarity in air and soil congener profiles observed at most sites.

- *CDFs.* Little association between air and soil could be observed, based on the lack of significant air-soil correlations for homologue groups across sites and the lack of similarity in air and soil congener profiles for many sites.

- *PCBs.* Some association between air and soil was observed. Data limitations restricted the air and soil comparisons to only six PCBs. One of these had a significant air-soil correlation across sites. The air and soil profiles based on these six chemicals were very similar at most sites.

The observations for CDDs and PCBs are consistent with the theory that air transport and deposition are the primary ways that these chemicals are distributed to soils, particularly those in rural areas. The lack of similar observations for the CDFs does not necessarily mean that they are not distributed in a similar manner, but it does suggest that different factors affect the environmental fate of these chemicals.

This study also evaluated relationships between chemical levels in soil and TOC levels in soil. The raw data analyses showed significant positive correlations for TCDFs ($r = 0.43$), PeCDFs ($r = 0.51$), PeCDDs ($r = 0.44$), HxCDFs ($r = 0.47$), HxCDDs ($r = 0.46$), HpCDFs ($r = 0.38$), HpCDDs ($r = 0.38$), total CDFs ($r = 0.39$), total TEQs ($r = 0.43$), and nonachlorobiphenyls ($r = 0.47$). The correlations were generally not very strong, indicating that other factors, such as grain size, may also be affecting sorption characteristics of the soil.

TEQ levels were estimated both on the basis of applying TEFs to the HRMS analyses and on the basis of the CALUX bioassay method. The CALUX results were higher—by varying amounts—than the HRMS total TEQs in almost all of the site composites. Significant positive correlations were found comparing the data on both a raw basis ($r = 0.82$) and on a log-transformed basis ($r = 0.78$). The likely reason for the high bias in the CALUX data relative to HRMS data is that CALUX responds to all compounds that activate the aryl hydrocarbon receptors, including a number of compounds other than CDDs, CDFs, and PCBs that may be present in soils.

Two observations from this study were unexpected and may warrant further investigation:

- It would be reasonable to expect that PCBs in rural soils should be generally present at greater concentrations than those of CDDs/CDFs. PCBs were produced in large quantities in the United States (571,000 metric tons) from 1929 until their ban in 1978 (ATSDR, 2000). CDDs/CDFs have never been intentionally produced; rather, they are formed in small quantities as by-products of combustion or certain types of chemical manufacturing. Although total PCBs exceeded total CDDs/CDFs at most sites in this study, the opposite was seen at 9 of 27 sites. At two of these sites, the CDD/CDF levels exceeded the PCBs by more than sevenfold.

- The highest total PCBs were found at Big Bend, TX (Site 23). The levels were about eight times higher than the mean across all sites, although total CDD/CDF levels were among the lowest across sites. This is a very remote site and it is unclear why such relatively high PCB levels were found.

Finally, a few thoughts can be offered about the utility of this pilot study to support future surveys. The surface soil sample collection/handling protocol proved to be effective and practical and could be used as a starting point in the design of future studies. Final decisions as to the number of sampling points at each location, sampling depth, and grid size were based on a preliminary single-site survey. This initial survey was used to evaluate the variability in TEQ levels and supported the use of sample compositing as a way to reduce analytical costs. Further TEQ analysis of individual samples and composites at all 27 sites demonstrated that relatively little information was lost by compositing. This experience suggests that future soil surveys with a focus on TEQ levels in rural areas could also reasonably consider analyzing only sample composites. Surveys involving other analytes and other land types should consider preliminary field testing to evaluate the appropriateness of sample compositing.

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