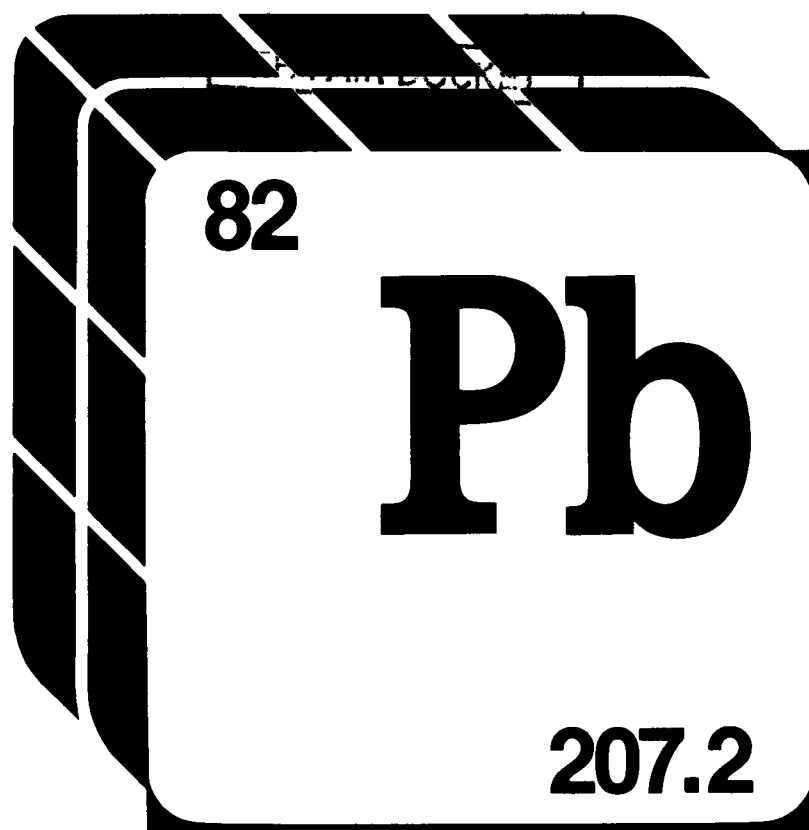


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Air Quality
Criteria for
LEAD

Office of Research and Development
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AIR QUALITY CRITERIA
FOR
LEAD

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
WASHINGTON, D.C. 20460

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PREFACE

This document has been prepared pursuant to Section 108(a)(2) of the Clean Air Act, as amended, and the Administrator's action on March 31, 1976, of listing lead as a criteria pollutant. Under the Act, the issuance of air quality criteria is a vital step in a program of responsible technological, social, and political action to protect the public from the adverse effects of air pollution.

These health and welfare criteria fulfill the regulatory purpose of serving as the basis upon which the Administrator must promulgate national primary and secondary ambient air quality standards for lead under Section 109 of the Clean Air Act. The proposed standards are being published concurrently with the publication of this criteria document.

Although the preparation of a criteria document requires a comprehensive review and evaluation of the current scientific knowledge regarding the air pollutant in question, the document does not constitute a complete, in-depth scientific review. The references cited do not constitute a complete bibliography. The objective is to evaluate the scientific data base and to formulate criteria which may serve as the basis for decisions regarding the promulgation of a national ambient air quality standard for lead.

In the case of lead, as well as other air pollutants, adverse health effects are a consequence of the total body burden resulting from exposure via all routes of intake. It is necessary, therefore, to evaluate the relative contribution made by inhalation and ingestion of atmospheric lead to the total body burden.

The Agency is pleased to acknowledge the efforts and contributions of all persons and groups who have participated as authors or reviewers to this document. In the last analysis, however, the Environmental Protection Agency is responsible for its content.

DOUGLAS M. COSTLE
Administrator
U.S. Environmental Protection Agency

ABSTRACT

This document summarizes current knowledge about the relationships of airborne lead to man and his environment. The effects that have been observed to occur when airborne lead has reached or exceeded specific levels for specific time periods constitute the central criteria on which EPA will base a national ambient air quality standard for lead.

Although this document deals mainly with airborne lead, it also outlines other environmental routes of exposure. Primary exposure to airborne lead occurs directly via inhalation, and its sources are relatively easy to identify. Secondary exposure may occur through ingestion of foods from crops contaminated by airborne lead or, especially in children, through mouthing of nonfood items and materials so contaminated. Exposures to nonairborne lead may also be direct and indirect, and routes include ingestion of foods containing lead attributable to natural uptake and to processing.

In man, lead primarily affects red blood cells, the central and peripheral nervous systems, soft tissues such as liver and kidney, and bone; the latter ultimately sequesters 95 percent of the body's lead burden. Significant biological indices of exposure to lead include microgram quantities of lead and of erythrocyte protoporphyrin (EP) per deciliter of blood ($\mu\text{g}/\text{dl}$). Adverse effects range from elevated EP and mild anemia at 20 to 40 μg Pb/dl—through gastrointestinal, renal, and hepatic pathologies—to severe neurobehavioral impairment at >80 to 120 μg Pb/dl, sometimes culminating at those levels in convulsions and abrupt death. Preschool children and developing fetuses are the populations at greatest risk.

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ABBREVIATIONS AND SYMBOLS

Å	Ångstrom (10 ⁻¹⁰ meter)	FDA	Food and Drug Administration
AAS	Atomic absorption spectroscopy	⁵⁹ Fe	Radioisotope of iron
ALA	Delta-aminolevulinic acid	Fe ₂ O ₃	Ferric oxide
ALAD	Delta-aminolevulinic acid dehydratase	FEP	Free erythrocyte protoporphyrin; also free erythrocyte porphyrin
ALAS	Delta-aminolevulinic acid synthetase	ft	Foot
ALA-U	Delta-aminolevulinic acid in urine	g	Gram
δ-ALA	Delta-aminolevulinic acid	GSH	Glutathione (reduced)
APHA	American Public Health Association	G-6-PDH	Glucose-6-phosphate dehydrogenase
ASTM	American Society for Testing and Materials	ha	Hectare
ASV	Anodic stripping voltammetry	5-HIAA	5-Hydroxyindole acetic acid
b.p.	Boiling point	hr	Hour
B.W.	Body weight	IARC	International Agency for Research on Cancer
°C	Degrees Celsius (centigrade)	ICRP	International Radiological Protection Commission
Ca	Calcium	in	Inch
Cd	Cadmium	i.p.	Intraperitoneal
CDC	Center for Disease Control (Atlanta, Ga.)	K	Potassium
(Ch ₃) ₄ Pb	Tetramethyl lead (also TML or Me ₄ Pb)	kcal	Kilocalorie
(CH ₃) ₆ Pb ₂	Hexamethyl lead	RCR	Respiratory control rate
(C ₂ H ₅) ₄ Pb	Tetraethyl lead (also TEL or Et ₄ Pb)	kg	Kilogram
(C ₆ H ₅) ₄ Pb	Tetraphenyl lead	km	Kilometer
(C ₂ H ₅) ₆ Pb ₂	Hexaethyl lead	l	Liter
cm	Centimeter	LC ₁	Concentration lethal to 1 percent of recipients
CNS	Central nervous system	LC ₅₀	Concentration lethal to 50 percent of recipients
CO ₃ ⁼	Carbonate ion	m	Meter
CP	Coproporphyrin	M	Molar
CPG	Coproporphyrinogen	max	Maximum
CP-U	Coproporphyrin in urine	Me ₃ PbAc	Trimethyl lead acetate
Cu	Copper	(Me ₃ Pb) ₂ S	Trimethyl lead sulfide
DA	Dopamine	MeV	Mega electronvolts (10 ⁶ electronvolts)
dl	Deciliter	MEPPs	Miniature end-plate potentials
DNA	Deoxyribonucleic acid	mg	Milligram
EDTA	Ethylendiaminetetraacetate	Mg	Magnesium
EP	Erythrocyte protoporphyrin; also erythrocyte porphyrin	min	Minute
EPA	U.S. Environmental Protection Agency	MMED	Mass median equivalent diameter
°F	Degrees Fahrenheit	ml	Milliliter
		mo	Month
		m.p.	Melting point

MT	Metric ton	Pb(PO ₃) ₂	Lead metaphosphate
Na	Sodium	Pb ₃ (PO ₄) ₂	Lead orthophosphate
NADH	Reduced (hydrogenated) nicotinamide adenine dinucleotide	Pb ₅ (PO ₄) ₃ OH	Lead hydroxymphm xppqwzn
NAS	National Academy of Sciences	PbS	Lead sulfide
NASN	National Air Surveillance Networks	PbSO ₄	Lead sulfate
NE	Norepinephrine	PBG	Porphobilinogen
ng	Nanogram	pCi	Picocurie (10 ⁻¹² curie)
Ni	Nickel	PIXE	Proton-induced X-ray emissions
nm	Nanometer	pH	Log of the reciprocal of the hydrogen ion concentration
NO ₃ ⁻	Nitrate ion	PO ₄ ⁼	Phosphate ion
NSF	National Science Foundation	PP	Protoporphyrin
NVS	Nonvolatile solids	ppb	Part per billion
P	Phosphorus	ppm	Part per million
Pb	Lead	PVC	Polyvinyl chloride
²⁰⁴ Pb	Isotope of Lead (²¹⁰ Pb, etc.)	RBC	Red blood cell; erythrocyte
Pb ⁺⁺	Divalent lead ion	RNA	Ribonucleic acid
Pb-A	Concentration of lead in air	s.c.	Subcutaneous
Pb-B	Concentration of lead in blood	scm	Standard cubic meter
PbBr ₂	Lead bromide	sec	Second
PbBrCl	Lead (II) bromochloride	SGOT	Serum glutamic oxaloacetic transaminase
PbBrCl·NH ₄ Cl	Lead bromochloride-ammonium chloride	SGPT	Serum glutamic pyruvic transaminase
[Pb(C ₂ H ₃ O ₂) ₂ · 2Pb(OH) ₂]	Basic lead (II) acetate	SH	Sulfhydryl
PbCl ₂	Lead chloride	SO ₂	Sulfur dioxide
PbCO ₃	Lead carbonate	SO ₄ ⁼	Sulfate ion
PbCrO ₄	Lead chromate	⁸⁵ Sr	Radioisotope of strontium
PbF ₂	Lead fluoride	STEL	Short-term exposure limit
Pb(NO ₃) ₂	Lead nitrate	TEL	Tetraethyl lead
PbO	Lead oxide	TML	Tetramethyl lead
PbO _x	Lead oxides	TVL	Threshold value limit
(PbO) ₂	Lead oxide dimer	USPHS	U.S. Public Health Service
Pb ₃ O ₄	Lead (IV) oxide	Zn	Zinc
Pb(OCOCH ₃) ₂	Lead (II) acetate	ZnS	Zinc sulfide
Pb(OH) ₂	Lead hydroxide	ZPP	Erythrocyte zinc protoporphyrin
Pb(OH)Br	Lead (II) hydroxybromide	μg	Microgram
Pb(OH)Cl	Lead hydroxychloride	μl	Microliter
Pb(OH) ₂ CO ₃	Basic lead carbonate	μm	Micrometer
PbO·PbSO ₄	Basic lead sulfate	>	Greater than
Pb ₄ O(PO ₄) ₂	Lead oxyphosphate	<	Less than
		~	Approximately

1. SUMMARY AND CONCLUSIONS

1.1 INTRODUCTION

The first portion of this document is devoted to lead in the environment: its physical and chemical properties; its monitoring and measurement in various environmental media; its environmental sources, emissions, and concentrations; and its transport and transformation within the environment (Chapters 3 through 7).

Chapters 8 through 13 are concerned with the effects of lead on ecosystems and, most important, on human health. Among the questions that have been specifically addressed in this document are:

1. What are the sources of lead in the environment?
2. What are the routes and mechanisms by which lead from these sources enters the body?
3. Once lead enters the body, where is it deposited?
4. Once lead is in the body, what are its health effects?
5. Are there groups within the population that are particularly vulnerable to lead?
6. What is the magnitude of the risk in terms of the number of persons exposed in various subgroups of the population?

This document has been prepared to reflect the current state of knowledge about lead — specifically, those issues that are most relevant to establishing the objective scientific data base that will be used to recommend an air quality standard for lead that will adequately safeguard the public health.

1.1.1 Potential Exposure to Environmental Lead

Lead is unique among the toxic heavy metals in that it is relatively abundant in the earth's crust. Because of its easy isolation and low melting point, lead was among the first metals to be used by man thousands of years ago. The environmental significance of lead is a result both of its utility and of its abundance. World production exceeds 3.5 million

tons/year, a far larger quantity than the production of any other toxic heavy metal.

Lead is present in food, water, air, soil, dustfall, paint, and other materials with which the general population comes in contact. Each of these represents a potential pathway for human lead exposure via inhalation or ingestion. The actual lead content in each source may vary by several orders of magnitude. Potential exposure patterns are further confounded by human activity patterns and by differences between indoor and outdoor environments. The number and extent of variables involved make it very difficult to determine the actual lead intake of individuals in their normal environment.

As a result of centuries of the mining, smelting, and use of lead in human activities, natural background concentrations are difficult to determine. Geochemical data indicate that the concentrations of lead in most surface materials in the United States range from 10 to 30 ppm ($\mu\text{g/g}$). Trace amounts of lead occur naturally in air and water as a result of wind and rain erosion, and in air as a result of volcanic dusts, forest fires, sea salt, and the decay of radon. Natural background concentrations of airborne lead have been estimated to approximate $0.0006 \mu\text{g Pb/m}^3$ of air (or $5 \times 10^{-7} \mu\text{g Pb/g air}$). Natural concentrations in fresh water have been estimated to be about $0.5 \mu\text{g/liter}$ of water (about $5 \times 10^{-4} \mu\text{g Pb/g water}$) and in ocean water about $0.05 \mu\text{g Pb/liter}$ of water (about $4.9 \times 10^{-5} \mu\text{g Pb/g water}$). As a consequence of the extensive and diverse uses of lead, present concentrations of lead in air, soil, and water are substantially higher than these estimated background levels. Nonurban lead concentrations average $0.1 \mu\text{g Pb/m}^3$ of air (about $8 \times 10^{-5} \mu\text{g Pb/g air}$). Concentrations of airborne lead in U.S. cities, at sites not conspicuously influenced by major sources, average $1 \mu\text{g Pb/m}^3$ of air ($8 \times 10^{-4} \mu\text{g Pb/g air}$). Expressed on a weight basis with respect to the total suspended particulate (TSP) in the air, this amount is approximately equivalent to $10^4 \mu\text{g Pb/g TSP}$.

The shape of buildings in urban areas may cause large horizontal and vertical variations in lead con-

centrations. In the absence of such structures, the vertical gradient would usually be relatively small. During periods of maximum traffic density on freeways, airborne concentrations of lead immediately adjacent to the freeways may reach $20 \mu\text{g}/\text{m}^3$ for a few hours. In the immediate vicinity of large stationary sources having no air pollution controls, concentrations of airborne lead may reach $300 \mu\text{g}/\text{m}^3$ under unfavorable meteorological conditions. Consequently, exposure via inhalation of airborne inorganic lead particulates may vary by a factor of at least 100, depending on location and activity patterns. The small number of indoor air lead studies conducted have shown indoor concentrations to be one-third or less the level measured outdoors. Indoor levels vary widely depending on type of structure, air conditioning, wind, etc.

Dust is a generic term and consequently imprecise when used to describe potential human exposure. Dust in the popular sense usually refers to solid particles that have settled on a surface and that can be readily redispersed in the atmosphere. In an aerometric sense, dust is solid particles suspended in the atmosphere; consequently, it is an integral part of total suspended particulates. In an occupational sense, dust may encompass even larger particles discharged into the work environment by mechanical means. Dustfall is a measure of the settled particulate, or that deposited in or on the collection devices; thus dustfall is more closely related to the popular definition of dust. In this document, dustfall is treated as a separate pathway for potential exposure to lead via ingestion of these settled particles, but only in a qualitative manner.

Lead concentrations in dustfall vary widely with the type and distribution of sources. The highest values occur in the immediate vicinity of sources and diminish rapidly with distance. Potential exposure to lead in dustfall depends on the total accumulation of dust in accessible areas. The accumulation depends on the deposition rate and the frequency and efficiency with which accessible surfaces are cleaned. Lead accumulation resulting from deposition from the air may be augmented in the homes of lead workers by transportation of lead-containing dusts from the workplace. The level of accumulated lead potentially available both indoors and outdoors clearly may vary by one to two orders of magnitude.

Concentrations of lead in solution in most urban water supplies are below $10 \mu\text{g Pb}/\text{liter}$ of water ($0.01 \mu\text{g Pb}/\text{g water}$), but some values $>50 \mu\text{g}/\text{liter}$ (the U.S. Public Health Service standard for lead in

drinking water) have been reported. Suspended solids contain the major fraction of lead in river waters. Concentrations of lead in tap water may be considerably higher than those in municipal supplies. Lead values as high as about $2000 \mu\text{g}/\text{liter}$ have been reported for homes with lead pipes and lead-lined storage tanks.

Sea spray, rainwater leaching, and flaking paint from older buildings can contribute significantly to lead levels in adjacent soil. Direct ingestion of the soil or of re-entrained dust, as well as ingestion of the paint chips themselves, constitute an important source of lead in areas where these conditions exist.

The contribution of food to human exposure to lead is highly variable and not well quantified. Estimates of daily intake vary from about 100 to $350 \mu\text{g Pb}/\text{day}$. Recent studies in the United States estimate the adults ingest about $200 \mu\text{g Pb}/\text{day}$ in food. Beverages and foods that are stored in lead-soldered cans or stored or served in lead-glazed pottery have been identified as having high lead content. Processed milk has been reported to contain more lead than fresh cow's milk — about 20 to $40 \mu\text{g}/\text{liter}$ compared to about 5 to $10 \mu\text{g}/\text{liter}$, respectively. If these values are correct, processed milk could be a significant source of lead exposure for infants.

For adults, illicitly distilled whiskey and old automobile batteries used as home heating fuel represent two nonindustrial sources of overt lead poisoning. Of much greater significance as a health problem, however, are various sources of occupational exposure.

Workers involved in uncontrolled (without pollution controls) mining, smelting, and manufacturing processes where lead is used, have the highest level of potential exposure. Although occupational conditions have generally been substantially improved, in some cases lead concentrations in the air in work places have been measured at $1000 \mu\text{g}/\text{m}^3$ or greater. The major occupational exposure problems occur where adequate hygiene programs have not been implemented or where individuals fail to take the recommended precautions. The major route of occupational exposure is the inhalation of dust and fumes; in addition, dust transported on clothing from the work place to the home or automobile may be a significant pathway of exposure for workers and their families.

1.1.2 Sources of Environmental Lead

The mining, smelting, and use of lead in human activities has significantly altered the natural distribution of lead in the environment. Contamination

has occurred primarily in the vicinity of sources and in densely populated areas.

The lead used in gasoline antiknock additives represents a major fraction of the total U.S. lead consumption, and motor vehicle emissions constitute the major source of lead emissions to the atmosphere. In 1975, some 189,000 MT of lead (16 percent of total production) used in antiknock compounds were converted to 142,000 MT of atmospheric emissions (88 percent of total lead emissions). As a result of legislation setting a maximum limit on the lead content of gasoline, the production and use of alkyl lead additives has decreased in recent years and will probably continue to do so.

Based on 1975 estimates, combustion of waste oil and incineration of solid waste are the major contributors of lead emissions from stationary sources (12,060 MT/year). This figure represents only that portion of waste oil that is reprocessed and burned in oil-fired or coal-fired boilers and municipal incinerators. Other stationary sources of lead emissions include iron and steel production in plants with poor pollution controls, primary and secondary smelting, battery manufacturing, and lead alkyl manufacturing. Lead that may be emitted to the environment from these operations includes that in stack emissions and fugitive dusts. Contamination from the major stationary emitters may determine environmental concentrations for a radius of several kilometers around the sources. Fugitive dusts may result in a high level of contamination in the immediate vicinity of small, uncontrolled battery recycling operations.

In terms of mass balance, lead from mobile and industrial sources is transported and distributed mainly via the atmosphere. Certain waste disposal operations that discharge large amounts of lead into soil and water result only in highly localized contamination. Lead is emitted to the atmosphere primarily in the form of inorganic particulates; however, small amounts of organic vapors have been reported in the vicinity of gasoline service stations, garages, and heavy traffic areas. These organic vapors undergo photochemical decomposition in the atmosphere, but they may also be adsorbed on dust particle surfaces.

Based on the limited data available, it is estimated that 75 percent of the particulate lead emitted from automobiles is removed from the atmosphere in the immediate vicinity of traffic sources.

Particles smaller than those from mobile sources, and emissions from tall stacks will remain airborne longer and be transported over greater distances.

Submicron particles may reside in the atmosphere a week or more before they are removed by dry deposition (diffusion and inertial mechanisms) and by precipitation. The tendency toward uniform vertical and horizontal distribution (mixing with concomitant distribution) increases with an increase in residence time.

The chemistry of lead aerosols discharged into the environment has not been studied as extensively as the chemistry of some of the other major air pollutants. Much of the work on lead particulate chemistry before 1973 was limited to elemental analyses and did not include analyses of associated ions. Information from elemental analyses is not sufficient to permit a thorough examination and understanding of (1) transformation and transport processes that occur among the environmental media, (2) mobility of lead in soils, (3) uptake and distribution of lead in plants, and (4) the overall impact of lead pollution on human health and ecosystems. Information is needed on the chemical forms and interactions of lead and its tendency to form compounds of low solubility with the major anions. Only a few studies have been conducted on the chemical forms of lead in soil and plants. They show that the principal lead form found in soils is sulfate, and the principal form found in plants is phosphate.

Lead dissolved from primary lead sulfide ore tends to combine with carbonate or sulfate ions to form relatively insoluble lead carbonate or lead sulfate, or to be absorbed by ferric hydroxide. The amount of lead that can remain in solution in water is a function of the concentration of other ions, especially hydrogen ions.

1.1.3 Monitoring of Environmental Lead

Lead has been monitored in air, water, soil, food, and biological samples such as blood and urine for many years, but the accuracy of the early sampling and analytical techniques was quite low. Consequently, these earlier data can be used only in a qualitative or semiquantitative manner. External contamination has been the major problem in all sampling procedures, particularly in sampling for blood lead analyses. Sampling and analytical techniques for environmental lead have enjoyed considerable improvement and refinement in the past few years. Some of the best methods, however, are tedious and expensive and are available only in relatively specialized laboratories. Those analytical techniques that are less sophisticated produce results of limited value. The capability now exists for achieving high precision in lead monitoring; but in

general practice, precise and accurate results are difficult to obtain, particularly for biological samples. Atomic absorption spectroscopy is the most successful analytical method used in recent years. The primary problem faced in environmental monitoring — that is, sampling and analysis — is to determine the type of monitoring procedures to be used to accomplish specific objectives, and to establish and maintain adequate quality control.

Ambient air monitoring procedures designed specifically for assessing population exposure patterns present particularly difficult problems. Total mass concentration, particle size distribution, and chemical composition of lead aerosols all vary considerably with space and time. In using atmospheric measurements to determine population exposures, human activity patterns are a further complication. Thus the relationship between measurements of atmospheric concentration of lead, duration of exposure, and incremental changes in blood lead levels is not constant. Although measurements of atmospheric lead levels are an essential ingredient in population exposure assessment, other indices of exposure such as blood lead and free erythrocyte porphyrin (FEP) levels are also essential for the characterization of human population exposures.

Blood lead may be measured by several general techniques that presently appear to be satisfactory in the hands of qualified analysts who have a sophisticated technical appreciation of the many problems associated with measuring an element that is both present at trace levels and ubiquitously distributed as a contaminant. Extensive interlaboratory comparisons have demonstrated the need for standardizing methodology, using reference standards, and obtaining blood lead determinations from those laboratories having highly skilled personnel accustomed to handling a large number of samples. The present existence of a number of regional and national analytical proficiency testing programs will help improve the quality of analysis and the reliability of consequent clinical and epidemiological data. Measurements of biological indicators such as erythrocyte porphyrin, δ -ALA, and δ -ALAD are also a problem. A standardized method exists for urinary ALA, and a program is underway in the United States to evaluate standardizations of methodology for determining erythrocyte porphyrin.

1.2 EFFECTS OF LEAD ON MAN AND HIS ENVIRONMENT

In the summary material presented in the preced-

ing section, attention was directed to all the exposure aspects of lead. The biological aspects of the lead pollution problem are discussed in this section. These aspects include not only the effects of lead on man, but also its effects on a myriad of ecosystems that support man and contribute to his general welfare.

1.2.1 Effects of Lead on Man

The effects of lead on man are summarized in sequential statements of present knowledge concerning:

1. Man's metabolism of lead.
2. Biological and adverse health effects in man.
3. Effects of lead on populations.
4. Risks man incurs from exposure to lead.

1.2.1.1 METABOLISM

Metabolism, as discussed here, encompasses the physiological processes in man that relate to absorption, distribution, excretion, and net retention. It can be discussed in terms of routes of lead exposure and the physiological distinctions existing within certain segments of the population that modify these processes. Special attention is focused on the factors that may place the developing fetus and the child in a category of higher risk than the adult.

Nearly all lead exposures result from inhalation and ingestion. The quantities of lead absorbed via these routes are determined by many factors such as the physical and chemical form of the lead, and the nutritional status, metabolic activity, and previous exposure history of those exposed.

Clinical studies on the deposition of airborne lead particulate matter in the human respiratory tract suggest that 30 ± 10 percent of the ambient air lead particulates inhaled will be deposited. Of the lead thus deposited in the respiratory tract, it has been estimated that as much as 50 percent or more is absorbed and enters the blood stream. This deposition may vary considerably, depending on particle size and pattern of respiration. Part of the fraction deposited in the respiratory tract, that portion removed via the mucociliary escalator, is swallowed and enters the gastrointestinal tract. Animal studies suggest that the relative efficiency of lung clearance mechanisms may be impaired at high levels of airborne lead.

In children, approximately 40 percent of the lead taken into the gastrointestinal tract is absorbed, whereas the corresponding value for adults is about 10 percent. In one study assessing net gastrointestinal absorption, an inverse relationship be-

tween calcium intake and lead absorption was shown. This relationship has also been demonstrated in experimental animals.

In discussing the routes by which man may be exposed to environmental lead, it is important to distinguish between primary and secondary exposure to atmospheric lead. Primary exposure is direct, and secondary is indirect. Primary exposure to airborne lead consists of its direct inhalation, whereas secondary exposure to airborne lead consists of ingestion of lead that is of atmospheric origin (that is, lead that is transported by the airborne route to the ingested material).

Lead may contaminate foodstuffs by atmospheric fallout, with subsequent adsorption onto plant surfaces or absorption into plants. This contamination may involve primary food (plants consumed by man) or animal food crops. Soil lead taken into plants may come from atmospheric fallout or from leaching from natural as well as industrial sources. The absorption of soil lead by plants, however, is thought to be relatively poor, although data on lead accumulation in tree rings suggest that absorption from soil may occur in at least some plants. In any case, the contribution of air lead to food lead levels is probably small on the basis of a nationwide food distribution system; but adequate quantification does not yet exist to allow precise statements on this point to be made. It is clear, however, that commercial processing raises the lead content of food significantly.

Another important depot of lead in the environment is soil or dust. The ultimate source of this lead varies from place to place; it can be dustfall from the atmosphere (coming from either stationary or mobile sources), or it can be soil or dust into which leaded paint has eroded. This exposure route is thought to be more important for children than for adults. Studies have consistently shown associations between soil or dust lead levels and blood lead levels in children when such exposures exceed 1000 ppm. It is thought that lead reaches the children through their normal mouthing behavior. Lead is picked up on children's hands through their play and is then transferred to their mouths by their customary habit of putting their hands, objects, and materials in their mouths. There is evidence demonstrating a relationship between dust lead and lead on fingers, but as yet there is no direct evidence linking lead on fingers with lead in the blood. In children with pica, however, the importance of this source could be greatly magnified.

It has been shown repeatedly that levels of lead in

blood increase when oral intake increases, but studies do not show a precise, quantitative expression of this relationship. Rather, a number of studies show that, with sustained daily ingestion of 100 μg of lead, the maximum increase in steady-state levels of blood lead ranges from 6 to 18 $\mu\text{g}/\text{dl}$. These variations probably relate to nutritional factors, biological variability, unreported sources of exposure, differences in analytical techniques, or previous exposure history — or to a combination of these factors. Since children, particularly infants, absorb a larger percentage of lead than adults do, the relative contribution of oral intake is undoubtedly greater for them. Because of higher metabolic activity, children also inhale relatively more airborne lead than do adults. Therefore, the contribution of airborne lead to total lead intake may be greater in children than in adults, but one must keep in mind that children also eat correspondingly more on a body weight basis.

A number of experimental animal studies have assessed the effects of nutrition and other factors on gastrointestinal absorption as reflected by blood lead levels. It is clear from these studies that the status of essential nutrients such as calcium, iron, phosphorus, fat, and protein is very important.

The absorption, distribution, and accumulation of lead in man is conveniently described by a three-compartment model. The first compartment, circulating red blood cells, distributes lead to the other two, soft tissues (primarily liver and kidney) and bone, where it accumulates. This accumulation begins in fetal life as a result of transplacental transfer. In nonoccupationally exposed adults, such storage approaches 95 percent of the total body burden. The skeleton is a repository of lead that reflects the long-term cumulative exposure of the individual; body fluids and soft tissues reflect more recent exposure.

Since the nonaccumulating body burden in soft tissues has a greater toxicological significance than that fraction sequestered in bone, the mobilizable lead burden is a more important concept than total body burden. In this connection, chelatable urinary lead has been shown to provide an index of the mobile portion of the total body burden, as has the lead level in blood, which is the more generally used indicator of internal dose.

There is a time frame in which changes in exposure register as a perturbation in the blood lead level. Clinical studies show that (1) a controlled daily intake results in a constant concentration of blood lead after 110 days, depending on the ex-

posure setting, and (2) a single, acute, controlled exposure yielded a blood lead half-life of about 2 days compared to approximately 17 days in the case of repeated exposures. Following cessation of exposure after long exposure periods (e.g., years), however, the half-life of blood lead can be expected to be substantially longer than 17 days.

Fecal excretion represents the major route by which ingested lead is eliminated from the body. Though excretion by this route is usually much greater than by urinary elimination, the total fecal lead content includes unabsorbed lead as its major component.

1.2.1.2 BIOLOGICAL AND ADVERSE HEALTH EFFECTS OF LEAD IN MAN

There are various physiological levels and exposure ranges at which the effects of lead in man occur. Furthermore, lead affects man at the subcellular, cellular, and organ system levels.

Among subcellular components, both nuclei and mitochondria generally show the most pronounced responses to cellular invasion by lead. The mitochondria, however, are most vulnerable and sustain the greatest functional impairment. Mitochondrial injury, both in terms of cellular energetics and morphological aberration, has been shown in a number of experimental animals. In man, the evidence for mitochondrial impairment has been morphological rather than functional. Those subcellular changes observed are primarily the development of nuclear inclusion bodies in kidney cells as well as mitochondrial changes in renal tubular cells in persons exposed occupationally.

Any discussion of the subcellular effects of lead must consider the question of chromosomal aberrations and carcinogenesis. At the present time, no conclusive statements can be made about the induction of chromosomal damage by lead. The literature on this issue either yields conflicting information or describes studies that are difficult to compare with each other. Some experimental animal studies relate the development of cancer to relatively high doses of lead, but as is true in the case of other suspected carcinogens, there are no data corroborating these findings in man.

Among the systemic and organic effects of lead, important areas are its hematologic, neurobehavioral, and renal effects. Attention must also be given, however, to the effects of lead on reproduction and development as well as its hepatic, endocrine, cardiovascular, immunologic, and gastrointestinal effects.

A number of significant effects of lead on the hematopoietic system in humans have been observed in lead poisoning. These effects are prominent in clinical lead poisoning but are still present to a lesser degree in persons with a lower level of lead exposure.

Anemia is a clinical feature of lead intoxication, resulting from both increased erythrocyte destruction and decreased hemoglobin synthesis. In children, a threshold blood lead level for production of these symptoms of anemia is approximately 40 $\mu\text{g Pb/dl}$, and the corresponding value for adults appears to be 50 $\mu\text{g Pb/dl}$.

Hemoglobin synthesis is impaired by lead via inhibition of synthesis of the globin moiety and inhibition at several steps in the synthesis of heme. The step most sensitive to lead in the heme synthetic pathway is that mediated by the enzyme δ -aminolevulinic acid dehydratase (δ -ALAD), which connects two units of δ -aminolevulinic acid (δ -ALA) to form porphobilinogen. The result is an increase in plasma level and enhanced urinary excretion of δ -ALA. Also inhibited by lead is the incorporation of iron into protoporphyrin to form heme, the prosthetic group of hemoglobin. This results in the accumulation of coproporphyrin, which is excreted in the urine, and of protoporphyrin, which is retained in the erythrocytes. The overall effect of lead is a net decrease in heme synthesis. (This also derepresses δ -ALA synthetase, the enzyme involved in the first step of heme synthesis.)

Inhibition of δ -ALAD occurs at extremely low blood lead levels and has been shown to start at a blood lead level as low as 10 $\mu\text{g/dl}$. Though the health-effect significance of inhibition at a blood level of 10 $\mu\text{g/dl}$ is open to debate, the increased urinary δ -ALA excretion that occurs with increasing inhibition at 40 $\mu\text{g/dl}$ is accepted as a measure of probable physiological impairment *in vivo*. This threshold level for urinary δ -ALA excretion (40 $\mu\text{g/dl}$) appears to be true for both adults and children.

An increase in free erythrocyte protoporphyrin (FEP) occurs at blood lead levels of 16 $\mu\text{g/dl}$ in children. In adult females, this threshold is probably similar. In adult males, the value is 20 to 25 $\mu\text{g/dl}$. The precise threshold for coproporphyrin, while not well established, is probably similar to that for δ -ALA. Elevation of free erythrocyte protoporphyrin has the same implications of physiological impairment *in vivo* as urinary δ -ALA. To the extent that the protoporphyrin elevation is a likely indicator of the impairment of mitochondrial function in

erythroid tissue, it may be even more important. For these reasons, physicians who participated in the development of the 1975 statement by the Center for Disease Control and the American Academy of Pediatrics reached a consensus that elevated FEP should be used as an indicator of increased exposure to lead.

The effects of lead on the nervous system range from acute intoxication and fatal encephalopathy to subtle behavioral and electrophysiologic changes associated with lower level exposures. Changes throughout the range of effects are related to blood lead levels.

It would appear that surprisingly low levels of blood lead may sometimes be associated with the most extreme effects of lead poisoning — severe, irreversible brain damage as indexed by the occurrence of acute or chronic encephalopathy symptoms and/or death. Though for most adults such damage does not occur until blood lead levels substantially exceed 120 $\mu\text{g}/\text{dl}$, some evidence suggests that acute encephalopathy and death may occur in some adults at blood lead levels slightly below 100 $\mu\text{g}/\text{dl}$. For children, the effective blood levels for producing encephalopathy or death are lower than for adults, with such effects being seen somewhat more often, starting at approximately 100 $\mu\text{g}/\text{dl}$. Again, however, evidence exists for the occurrence of encephalopathy in a very few cases at lower levels, down to about 80 $\mu\text{g}/\text{dl}$.

It should be noted that once encephalopathy occurs, death can be a frequent outcome, regardless of the level of medical intervention at the time of the acute crisis. It is also crucial to cite the rapidity with which acute encephalopathy or death can develop in apparently asymptomatic individuals or in those apparently only mildly affected by elevated body burdens of lead. It is not unusual for rapid deterioration to occur, with convulsions or coma suddenly appearing and progressing to death within 48 hr.

This suggests that at high blood lead levels, even when individuals are asymptomatic, rather severe neural damage can exist without overt manifestations. Studies show that apparently asymptomatic children with high blood lead levels of over 80 to 100 $\mu\text{g}/\text{dl}$ are permanently impaired cognitively, as are individuals who survive acute episodes of lead encephalopathy. These studies tend to support the hypothesis that significant if albeit subtle changes in neural function occur at what were once considered tolerable blood lead levels.

Other evidence tends to confirm rather well that some type of neural damage does exist in asympto-

matic children, and not necessarily only at very high levels of blood lead. The body of studies on low- or moderate-level lead effects on neurobehavioral functions present overall an impressive array of data pointing to that conclusion. Several well-controlled studies find effects that are clearly statistically significant, and many others report nonsignificant but borderline effects. Since some of the effects at low levels of lead exposure discussed in this document are of a subtle nature, the findings are not always striking in individual cases. Nevertheless, when the results of all of the studies on neurologic and behavioral effects at subclinical exposures are considered in an overall perspective, a rather consistent pattern of impaired neural and cognitive functions appears to be associated with blood lead levels below those producing the overt symptomatology of lead encephalopathy. The blood lead levels at which neurobehavioral deficits occur in otherwise asymptomatic children appear to start at a range of 50 to 60 $\mu\text{g}/\text{dl}$, although some evidence tentatively suggests that such effects may occur at slightly lower levels for some children.

Data obtained for the effects of lead on the nervous system in laboratory animals are also quite extensive. Encephalopathy is produced by high-level perinatal exposure to lead; in different species, this occurs to varying degrees as characterized by the relative extent of neuronal degeneration and vasculopathy. It seems clear that the animal data support the contention that the developing organism represents the population at greatest risk for central nervous system toxicity.

There is also good evidence that perinatal exposure of laboratory animals to lead at moderate levels will produce delays in both neurological and sexual development. Since these effects have been demonstrated to occur in the absence of either undernutrition or growth retardation, it has been suggested that they may represent more or less direct effects of lead in the respective systems.

In animal studies, locomotor activity has been the most commonly used behavioral index of lead toxicity. Data indicate that increased locomotor activity in young animals occurs only at moderately high exposure levels. It may be, in view of the levels, that the changes in activity currently reported in laboratory animals are more diagnostic of a post-encephalopathic hyperactivity than of subclinical effects. Interestingly, the reactivity changes seen in older animals are associated with much lower blood lead levels.

Finally, reports on the effects of lead exposures on

the acquisition and/or performance of operant responses indicate that perinatal exposure to moderate or low levels of lead may disrupt this type of behavior. Thus at blood lead levels ranging from 30 to 80 $\mu\text{g}/\text{dl}$, cognitive function appears to be disrupted in animals.

Excessive lead exposure can result in acute as well as chronic renal injury in man. The acute renal effects of lead are seen in persons dying of acute lead poisoning where lead-induced anemia and/or encephalopathy may also be seen. These effects are manifested by nonspecific degenerative changes in renal tubular lining cells, cloudy swelling, and some degree of cellular necrosis. In addition, nuclear inclusion bodies form in tubule cells, and there are functional and ultrastructural changes in tubular mitochondria. Aminoaciduria, glycosuria, and hyperphosphaturia are noted, with aminoaciduria being a rather consistent feature of tubular damage in children. These effects are usually reversible. It is not possible at the present time to state what level of lead in blood is associated with aminoaciduria or any of the other specific indices of acute renal injury.

Prolonged lead exposure in humans can result in chronic lead nephropathy. The pathology of these chronic changes is different from that seen in acute renal injury. It is characterized by the gradual onset of pronounced arteriosclerotic changes, fibrosis, glomerular atrophy, hyaline degeneration, and reduction in kidney size. This can be a progressive, irreversible condition resulting in death from renal failure. A threshold of lead exposure for these chronic changes cannot yet be stated, however, as a result of the typical inaccessibility of data needed for the accurate assessment of the preceding long-term exposure history.

Considerable evidence for the adverse effects of lead on reproduction and development in man has been accumulating for many years. Many of the early data on the induction of abortions, stillbirths, and neonatal deaths were for occupationally exposed pregnant women, where such effects were demonstrated at high blood lead levels. Of more pressing present interest are certain recent studies in this area focusing on two aspects of the effects of low to moderate lead exposure on reproduction: gametotoxicity and post-conception events.

In regard to potential lead effects on human ovarian function, one study has shown that short-term exposure at ambient air levels of less than 7 $\mu\text{g}/\text{m}^3$ may cause an increase in the anovular cycle and disturbances in the lutein phase. This study, however, requires confirmation before conclusive

statements can be made. Another recent report involving occupational exposure similarly suggests that moderately increased lead absorption (blood lead mean = 52.8 $\mu\text{g}/\text{dl}$) may result in direct testicular impairment; however, the design of this study is such that this observation also requires verification.

Thus, it is clear that gametotoxic, embryotoxic, and teratogenic effects at a gross level can be induced in laboratory animals with lead, but it should be emphasized that the production of such effects probably requires acute, high exposures. Unfortunately, a paucity of information exists on the teratogenicity and developmental toxicity of chronic low or moderate lead exposures. Available data on the subject do suggest, however, that chronic low-level lead exposure may induce postnatal developmental delays in rats.

Our present knowledge about the effects of lead in man on the hepatic, cardiovascular, immunologic, and endocrine systems is fragmentary, rendering it difficult to make any conclusive statements about quantitative relationships. For example, effects of lead on the endocrine system are not well defined at present. Thyroid function in man, however, has been shown to be decreased in occupational plumbism. Also, effects of lead on pituitary and adrenal function in man have been observed, with decreased secretion of pituitary gonadotrophic hormones being noted but adrenal function effects being a less consistent finding.

The response of the hepatic system to lead has not been well characterized in man; instead, much of the literature deals with hepatic effects in experimental animals. Lead-poisoned animals show significantly impaired drug-metabolizing activities, thus suggesting an effect on the hepatic mixed-function oxidase system. Since detoxification in animals depends on the microsomal heme protein, cytochrome P450, and since heme biosynthesis is impaired in lead exposure, such an effect is a logical consequence of lead poisoning.

Of more direct interest in terms of reproductive efficiency are the effects of lead exposure on pregnant women — not only on fetal health and development, but also on maternal complications. Placental transfer of lead has been demonstrated both by fetal tissue analysis and comparison of newborn umbilical cord blood lead with maternal blood lead. One must not only consider the resulting absorption of lead by the fetus, but also the specific points in embryonic development at which exposure occurs. Fetal tissue uptake of lead occurs by the end of the first tri-

mester, which may be a sensitive period in embryonic development of the nervous system.

Studies comparing umbilical cord blood lead levels in newborns with simultaneously sampled maternal blood show that the newborn and maternal levels are closely correlated. The studies have also shown that the newborns of mothers in an urban setting are born with generally higher blood levels than those of corresponding newborns from rural areas.

That the prenatal exposure of the fetus to lead, even in the absence of teratogenic effects, is of consequence for adverse health effects is shown by studies relating fetal levels to changes in fetal heme synthesis and to the incidence of premature births. Some suggestions in the literature that heme biosynthesis in a newborn may be affected require confirmation.

In evaluating maternal complications related to lead exposure, one must consider that pregnancy is a physiological stress that may place the pregnant woman at higher risk to lead exposure effects. Both iron and calcium deficiency increase the susceptibility of an individual to lead toxicity. Women have an increased risk of both deficiencies during pregnancy and postpartum.

Some available but unconfirmed information indicates that the risk of premature rupture of the amniotic membrane may be higher in cases of elevated exposure than in age-matched controls without such exposure.

The literature leaves little doubt about the deleterious health effects of lead on reproduction, but most reports do not provide specific descriptions of exposure levels at which specific reproductive effects are noted. Maternal blood lead levels of approximately 30 $\mu\text{g}/\text{dl}$ may be associated with a higher incidence of premature delivery and premature membrane rupture, but these observations require confirmation. In adult males, levels of 50 to 80 $\mu\text{g}/\text{dl}$ may be sufficient to induce significant spermatotoxic effects, but this effect has not been conclusively demonstrated.

Lead has not been shown to be teratogenic in man, but animal experiments have demonstrated that high levels of lead that are still compatible with life in sexually mature animals interfere with normal reproduction; these studies include assessment of lead effects in both parents. Reduction in offspring number, weight, and survival and an increase in fetal resorption is a consistent finding in rats, mice, and other species over a range of high-level lead exposures. Effects on offspring have been shown to involve the gametotoxic effect of lead on males as well as females in a number of animal species.

At lead levels presently encountered in occupational exposure, no significant cardiovascular effects are discernible. Clinical data for children suffering from chronic lead poisoning resulting in death indicate that extensive myocardial damage occurs. It is not clear that the associated morphological changes are a specific response to lead intoxication. However, in many instances where encephalopathy is present, the electrocardiographic abnormalities disappear with chelation therapy.

There are insufficient data pertaining to the effects of elevated blood lead levels and the incidence of infectious diseases in man to allow the derivation of a dose-response relationship. Neither can a dose-response relationship be defined for the effects of elevated blood lead levels on the gastrointestinal tract, even though colic is usually a consistent early symptom of lead poisoning in adults exposed occupationally and in infants and young children.

1.2.2 Effects of Lead on the Ecosystem

As a natural constituent, lead does not usually pose a threat to ecosystems. The redistribution of naturally occurring lead in the environment, however, has now caused some concern that lead may represent a potential threat to the ecosystem. For example, studies have shown a fivefold increase in lead in tree rings during the last 50 years; this accumulation may serve as a useful index of patterns of environmental lead accumulation.

There are also documented effects of lead on domestic animals, wildlife, and aquatic life. Lead poisoning in domestic animals produces varying degrees of derangement of the central nervous system, gastrointestinal tract, muscular system, and hematopoietic system. As is true in man, younger animals appear to be more sensitive than older ones.

Wildlife are exposed to a wide range of lead levels. Toxic effects from ingestion of lead shot have long been recognized as a major health problem in waterfowl. Several species of small mammals trapped along roadways were tested for lead concentrations. All but one of the species living in habitats adjacent to high-volume traffic showed high concentrations of lead. This was especially true in urban areas.

Lead toxicity in aquatic organisms has been observed and studied experimentally. Symptoms of chronic lead poisoning in fish include anemia, possible damage to the respiratory system, growth inhibition, and retardation of sexual maturity.

There is evidence that lead has both harmful and beneficial effects on plants. Plants are exposed to lead through the leaves, stems, bark, or roots, and

the extent of the effects depends on the form, amount, and availability of that lead. The morphology of the plant surface plays the major role in determining the type and quantity of material retained by plants. Meteorological factors are also important in determining the fate of lead that comes into contact with plants. Large deposits of inert insoluble metal compounds on the leaves are probably of little consequence to plants, as the most important factor is the solubility of the metal. Thus, because inorganic lead compounds are generally of low solubility, there is little incorporation and accumulation within the leaves of plants.

The majority of studies reporting lead toxicity in plants have been conducted with plants grown in artificial nutrient culture. These studies have promoted the concept that the effects of lead are dependent on a variety of environmental factors, including anions and cations within the plant and in the growth media, and the physical and chemical characteristics of the soil itself. As lead interacts with many environmental factors, specific correlations between lead effects and lead concentrations are extremely difficult to predict.

1.3 EFFECTS OF LEAD ON POPULATIONS

The frequency distribution of blood lead levels in homogeneous human populations has almost invariably been found to be lognormal. Most data sets of homogeneous populations display a geometric standard deviation (GSD) of 1.3 to 1.5. This would roughly correspond, for example, to an arithmetic standard deviation of 5.3 to 8.5 $\mu\text{g}/\text{dl}$ at a mean blood lead of 20 $\mu\text{g}/\text{dl}$.

From the lognormal distribution, given a mean blood lead level and estimated GSD, it is possible to predict the percentage of a population whose blood lead levels exceed or fall below a specified value. It is also possible to estimate the probable increase in mean blood lead levels for a population exposed to a specific increase in environmental lead. These two procedures, used together, provide a method by which air quality standards may be chosen to protect the health of the population.

Blood lead levels vary with geographic location. They are lowest in some remote populations, higher in most rural settings, higher still in suburban areas, and highest in inner-city areas. This gradient follows the presumed lead exposure gradient. Blood lead values also vary by age, sex, and race, although in a somewhat more complex fashion. Generally, young children have the highest levels, with little difference noted between sexes at this age. In older

segments of the population, after elimination of occupational exposure in lead workers, males still have a higher blood lead than females. Only limited published data are available comparing the blood levels of the various racial and ethnic groups of the population. These data suggest that urban blacks have higher lead levels than whites, with levels in Puerto Ricans frequently being intermediate.

Results of the numerous studies of environmental lead exposures of man have indicated strongly that man does indeed have cumulative uptake from each source to which he is exposed. Equally important, these studies have shown that the blood lead level represents a summation of the absorption from each of these sources.

Data for the two most widespread environmental sources of lead other than food permit summary statements concerning their quantitative relationship with blood lead levels: air and soil/dust. Blood lead levels were found to increase with rising air lead concentrations. The relationships were found to be either log-linear or log-log. Evaluation of the equations at various commonly observed air lead levels revealed that the ratio between changes in blood and changes in air lead varied generally between 1 and 2 and that it was not constant over the range of air exposures. This implies that an increase of 1 $\mu\text{g}/\text{m}^3$ of air lead results in an average increase of 1 to 2 $\mu\text{g}/\text{dl}$ in blood lead levels. Suggestive evidence indicates that children may have higher ratios than adults and that males may have higher ratios than females.

One of the most extensive data sets on blood lead in children comes from a study by the U.S. Department of Housing and Urban Development on the blood lead values of approximately 180,000 children in New York City. These data covered the period March 1970 through December 1976. A preliminary analysis of these important research findings was presented to the Subcommittee on Lead of EPA's Science Advisory Board in October 1977. The following patterns appear to be indicated by these data:

1. There is a definite difference in blood lead values for racial and ethnic groups, blacks having higher mean lead levels, and Hispanics and whites having lower levels.
2. Analysis shows that the mean blood lead level is related to race and ethnicity, age, and year of sampling. This age dependence is similar for all years: The 1- to 12-month-old group has the lowest levels, and generally the maximum is found in 2- to 4-year-olds.

- 3. There was a consistent decrease of mean blood lead levels over the course of the study. This decrease was coincident with a reduction in lead levels in gasoline in the New York City area.
- 4. There appears to be a likely corresponding decrease in the air lead. However, it should be pointed out that air lead data for New York City are sparse and that it would be unwise to assume that the air lead level as measured at a single location would be the same for all locations. Because of the height of the sampler, it is also questionable whether the air lead level would represent the level to which the population is exposed.

Consistent relationships between blood lead levels and exposure to lead-containing soil have been shown. Also, children exposed to higher concentrations of soil and house dust lead have been shown to have elevated concentrations of lead on their hands. The intermediate link, from elevated hand levels of lead to elevated blood levels, has not yet been established. Quantitatively, blood lead levels have been shown to increase 3 to 6 percent given a doubling of the soil or dust lead content.

Significant water lead exposures in this country have only occurred in places having a soft water supply and using leaded pipes. Such exposures have been shown to be associated with significant elevations of blood lead. They have also been linked to cases of mental retardation.

Exposure to leaded paint still constitutes a very serious problem for American children in urban settings. Although new regulations of the lead content of paint should alleviate the problem in new housing, the poorly enforced regulation and lack of regulation of the past have left a heavy burden of lead exposures. Most of the studies on lead poisoning in children have assumed an association with leaded paint. It is very difficult in these studies to measure the actual amount of exposure. There is nevertheless incontrovertible evidence that the contribution from this source is very significant for certain segments of the population.

Food lead exposures are thought to be a source of a significant portion of blood lead. Precise quantitative estimates of the relationship between food and blood lead are not available, however. Similarly, precise quantitative estimates are not available for the relative contributions of different sources to the total amount of lead in the diet. It is clear, however, that probably the largest proportion of dietary lead is derived from food processing (e.g., from solder in

the seams of cans), and some is also derived from lead in the air and the soil.

1.4 ASSESSMENT OF RISK FROM HUMAN EXPOSURE TO LEAD

Of the estimated 160,000 metric tons of lead emitted into the atmosphere in 1975, the combustion of gasoline additives and waste oil accounted for 95 percent of the total. Once lead is introduced into the air, it is subject to a variety of processes, including dry deposition, precipitation, and resuspension.

Other uses of lead result in other avenues of exposure: (1) Lead in paint makes lead available by ingestion; (2) lead in plumbing for potable water where the water is soft (low pH) permits leaching and makes lead available by ingestion; (3) lead in the diet, introduced by processing, packaging, and raw food stock, also makes lead available by ingestion. It is therefore important to realize that human exposure to lead is the summation of all these complex and individual sources.

The factors that govern the quantitative aspects of inhalation and ingestion of lead have been pointed out, and attention has been given to the fact that ingestion includes both food and nonfood materials. In the case of children, the nonfood material has especially important implications. Thus the total internal dose is a function of all external sources with which the body comes into contact. The relative significance of any given exposure source depends on the specific exposure circumstances and certain attributes of the population at risk.

1.4.1 Use of Blood Lead Levels in Risk Assessment

The evidence for increased blood lead levels, the usual accepted indicator of lead exposure, has evolved from studies of both single-source and multiple-source exposures. Studies of single sources of air lead have included both epidemiological and clinical investigations. Clinical data uniformly demonstrate and quantify the actual transfer of lead in air to blood. The epidemiological data are not as definitive, but they are more relevant to the real world and clearly support such a relationship.

Studies concerned with dust and soil lead exposures may be considered jointly, since most studies have not attempted to isolate their relative contributions. Strong evidence exists to show that these sources can be significant determinants of blood lead levels. Furthermore, investigations involving children exposed to lead-contaminated dust have demonstrated lead on the children's hands,

providing strong inferential evidence for an oral route of entry.

Lead-based paint is associated with overt clinical intoxication and widespread excess absorption in children. Screening programs in all major urban areas have sought to abate this severe public health problem, but only with limited success. These children represent a particularly high risk group with respect to the incremental lead exposure attributable to direct inhalation of atmospheric lead as well as with respect to the ingestion of dust contaminated by lead from the atmosphere.

Studies centered around primary lead smelters and secondary industrial sources in urban settings have consistently and independently demonstrated a relationship between blood lead levels and these mixed sources. Most characteristics that mediate the relationship between blood lead level and lead exposure have been examined in several studies. Age is certainly a significant factor in determining blood lead levels, particularly in children under 6 years of age. With regard to sex differences, there appear to be none among children, whereas in adults, males generally exhibit higher levels than females. Though one study has reported that black children have higher lead levels than white children, the overall data are too sparse to establish a conclusive relationship. Socioeconomic variables such as income and education, as well as general health status, have not been examined in these studies.

A number of summary statements may be made about the quantitative relationships pertaining to blood lead. The weight of evidence indicates that blood lead levels follow a log-normal distribution with a geometric standard deviation of about 1.3 to 1.5. The log-normal distribution possesses properties that make it of value in arriving at acceptable maximal exposures, since it makes it possible to estimate a proportion of a population whose blood lead levels exceed any specified level.

The increase in blood lead level resulting from an increase in air lead concentration is not constant in magnitude over the range of air lead levels commonly found in the environment. The relationship is dependent on many factors, including rate of current exposure and the history of past exposure. The observed ratios vary from air lead level to air lead level; they are generally between 1 and 2. Evidence suggests that the ratios for children may be higher than those of adults; also it suggests that ratios for males may be higher than those for females.

There is general agreement that blood lead levels begin to increase when soil levels are 500 to 1000

ppm. Mean percent increases in blood lead levels, given a twofold increase in soil lead levels, ranged from 3 to 6; this is remarkably consistent given the divergence of the populations studied.

One of the most important aspects of risk assessment is the evaluation of effects of long-term, low-level, or intermittent exposures. In such circumstances, blood lead levels do not always correlate well with the exposure history. In one clinical study of lead exposure by inhalation, an average air level of $3.2 \mu\text{g}/\text{m}^3$ over a period of about 7 weeks was related to a significant rise in blood lead after about 7 weeks. When exposed to clean air, the blood lead levels of these same subjects returned to pre-exposure levels.

1.4.2 Use of Biological and Adverse Health Effects of Lead in Risk Assessment

Lead is not conclusively known to have any biological effect on man that can be considered beneficial. Therefore, any of the biological and adverse health effects on man at this time must be considered from a medical point of view that acknowledges the absence of any health benefit/health cost ratio.

Earlier discussion considered the biological and adverse health effects of lead across the entire range of lead exposures. In risk assessment, the primary focus is on those biological and adverse physiological effects that relate to the general population.

Though the literature dealing with the health effects of lead embraces virtually all of the major organ systems in man, hematological and neurological effects are of prime concern. These effects are summarized in Table 1-1. It should be pointed out that Table 1-1 is a lowest-observed-effects level tabulation; i.e., it lists the lowest blood lead levels at which particular effects have been credibly reported for given subpopulations. Four hematological effects are considered: anemia, inhibition of the enzyme δ -ALAD, urinary δ -ALA excretion, and elevation of free erythrocyte porphyrin (FEP).

Anemia is found in children with and without concomitant iron deficiency. Increased lead intake prompts a more severe anemia. This is of special importance in children 1 to 6 years old of lower socioeconomic status, since this group also has a high incidence of iron deficiency.

The literature relating blood lead levels to a statistically significant reduction in hemoglobin points to a threshold level of $40 \mu\text{g}/\text{dl}$ for children and a corresponding value of $50 \mu\text{g}/\text{dl}$ for adults. The question of a low-threshold or no-threshold

TABLE 1-1. BLOOD LEAD LEVELS VERSUS LOWEST-OBSERVED-EFFECTS LEVELS

Lowest level for observed effects, $\mu\text{g Pb/dl}$ whole blood	Observed effect	Population group
10	ALAD inhibition	Children and adults
15 to 20	Free erythrocyte porphyrin elevation	Adult females and children
20 to 25	Free erythrocyte porphyrin elevation	Adult males
40	Increased urinary ALA excretion	Children and adults
40	Anemia	Children
40	Coproporphyrin elevation	Adults and children
50	Anemia	Adults
50 to 60	Cognitive (CNS) deficits	Children
50 to 60	Peripheral neuropathies	Adults and children
80 to 100	Encephalopathy symptoms	Children
100 to 120	Encephalopathy symptoms	Adults

level for the inhibitory effect of lead on the enzyme δ -ALAD is overshadowed by the larger issue of the health significance of this observation. In any event, a value of 10 $\mu\text{g/dl}$ blood lead appears to represent a threshold level. Elevation of urinary δ -ALA levels, however, appears to be considered an index of physiological impairment, and the threshold level of this effect is approximately that for anemia in children (i.e., 40 $\mu\text{g/dl}$). This value seems to apply for both children and adults.

Elevation of erythrocyte porphyrin is better accepted as an indicator of physiological impairment. On the basis of a number of studies, threshold values of blood lead at which erythrocyte protoporphyrin is elevated appear to be 15 to 20 $\mu\text{g/dl}$ for children and adult females and 20 to 25 $\mu\text{g/dl}$ for adult males.

The hematological effects described above are the earliest physiological impairments encountered as a function of increasing lead exposures as indexed by blood lead elevations; as such, those effects may be considered to represent critical effects of lead exposure. Although it may be argued that certain of the initial hematological effects (such as ALAD inhibition) constitute relatively mild, nondebilitating symptoms at low blood lead levels, they nevertheless signal the onset of steadily intensifying adverse effects as blood lead elevations increase. Eventually, the hematological effects reach such magnitude that they are of clear-cut medical significance as indicators of undue lead exposure.

Of even greater concern than early symptoms of lead exposures (i.e., hematological impairments) are the neurologic effects of lead that begin to be encountered as the hematological deficits reach clinical magnitudes. Children are most clearly the population at risk for neurologic effects. The neurologic effects, including both peripheral neuropathies and signs of CNS damage, are first encountered for some children as blood lead levels reach 50 to 60 $\mu\text{g/dl}$; and they very rapidly intensify in severity as a function of increasing blood lead elevations. Of great medical concern is the very steep upward rise in the risk for permanent, severe neurological damage or death as blood lead elevations approach and exceed 80 to 100 $\mu\text{g/dl}$ in children. Inner city children are of particular concern with respect to the manifestation of lead-induced neurologic deficits, as documented by the evidence discussed in Section 11.5.

Some evidence has recently been advanced that suggests that long-term neurobehavioral deficits may also be induced by *in utero* exposures of human fetuses to lead, as indicated by the apparent higher incidence of postnatal mental retardation among children born of mothers experiencing elevated lead exposure before or during pregnancy. Thus women of childbearing age may be another group at special risk by virtue of the potential *in utero* exposures of fetuses. However, the paucity of information on exact exposures experienced by these mothers and the lack of other confirmatory studies do not allow firm statements to be made about probable threshold lead exposure levels for pregnant women that may induce later neurobehavioral deficits in their children.

It is even more difficult to speak of risk-to-health assessment in terms of threshold levels for effects of lead on reproduction, since the relevant data are sparse. However, in no other aspect of health effects is the potential for deleterious health effects of lead as inherently great as in the area of reproduction and development. In particular, lead crosses the placental barrier, placing the human fetus at direct risk. And such exposure begins at a stage of gestation when neural embryonic development is beginning. Placental transfer, coupled with the fact that an effective blood-brain barrier is not present in human fetus, means that there is effectively a direct path from maternal lead exposure to the fetal nervous system.

Available information suggests that there are several possible consequences to the newborn arising from lead exposure. Premature birth is suggested as

being associated with elevated blood lead levels in women, and some impairment in the heme biosynthetic pathway may exist in the newborn children of mothers having elevated blood lead levels.

Much of the discussion above has dealt with relationships between blood lead levels and various biological effects of lead. This discussion was primarily concerned with threshold levels at which health effects of lead are first observed in different population groups. Of additional interest is the proportion of a population exhibiting a health effect at a given blood lead level (i.e., the dose-response curve). Three different assessments of dose-response relationships for hematological effects have been carried out and published. These effects are the inhibition of ALAD, elevation of ALA-U, and elevation of EP levels in the blood. As noted elsewhere in this summary, some question exists concerning the relevance of ALAD inhibition to human health. The other two hematological effects are relevant. Table 1-2 shows ALA-U data from two studies, one published and one done by EPA (see Chapter 13).

TABLE 1-2. ESTIMATED PERCENTAGE OF SUBJECTS WITH ALA-U EXCEEDING 5 mg/liter FOR VARIOUS BLOOD LEAD LEVELS

Blood lead level, $\mu\text{g}/\text{dl}$	Zielhuis estimate, %	Azar et al. estimate, %
10	0	2
20	0	6
30	6	16
40	24	31
50	48	50
60	76	69
70	96	84

Published studies (see Chapter 13) of dose-response relationships also exist for erythrocyte protoporphyrin and are presented in Table 1-3.

TABLE 1-3. ESTIMATED PERCENTAGE OF CHILDREN WITH EP EXCEEDING SPECIFIED CUTOFF POINTS FOR VARIOUS BLOOD LEAD LEVELS

Blood lead level, $\mu\text{g}/\text{dl}$	Zielhuis estimate, ^a %	Roels et al. estimate, ^b %	Piomelli estimate, ^c %
10	0	3	9
20	6	27	11
30	22	73	48
40	37	100	80
50	49	--	--
60	--	--	--
70	--	--	--
80	--	--	--

^aEP > EP of children with blood lead levels < 20 $\mu\text{g}/\text{dl}$.

^bEP > 82 $\mu\text{g}/\text{dl}$ cells.

^cEP > 33 $\mu\text{g}/\text{dl}$.

1.4.3 Populations at Risk

The concept of "special risk" is defined as a population segment exhibiting characteristics associated significantly higher probability of developing a condition, illness, or other abnormal status as a result of exposure to a given toxic agent. With respect to lead, two such segments of human populations are currently definable: preschool children and unborn fetuses, with pregnant women as the recipient population of concern.

1.4.3.1 PRESCHOOL CHILDREN

There is an impressive body of data that indicates that children are inherently more susceptible to lead by virtue of physiology and that they have a different relationship to exposure sources. These physiological factors include: (1) greater lead intake on a per-unit-body-weight basis; (2) greater net respiratory intake as well as greater net absorption and retention of lead entering the gastrointestinal tract; (3) rapid growth, which reduces the margin of safety against a variety of stresses, including nutritional deficiency; (4) certain incompletely developed defense mechanisms in very young children, such as the blood-brain barrier in newborns; and (5) different partitioning of lead in the bones of children compared to that of adults, with only 60 to 65 percent of the lead body burden occurring in bone, and that fraction probably being more labile than in adults.

An important aspect of the dietary habits of very young children in connection with lead exposure is their normal mouthing activity, such as thumb-sucking or tasting of nonfood objects. Such behavior poses a risk of increased contact with dust and soil contaminated with lead. Clinical evidence also exists to indicate children are at special risk for lead effects. Thresholds for anemia and erythrocyte protoporphyrin elevation are lower for children, and a number of neurological effects appear at lower levels of lead in children than in adults.

1.4.3.2 PREGNANT WOMEN

Considerable evidence indicates that pregnant women are a population segment at risk with respect to lead mainly because of increased risk to the fetus and maternal complications. Lead crosses the placental barrier and does so at an early stage in embryonic development. Although quantitative expressions of this risk cannot be stated, certainly the potential for damage exists.

Pregnancy places a physiological stress on a woman in terms of nutritional states that lead to iron and calcium deficiency, in consequence of which

bone lead may be mobilized and the hematopoietic system may be placed at higher risk to lead exposure. In addition, data suggest that elevated blood lead levels in pregnant women may result in increased incidence of premature membrane rupture, placing the mother as well as her newborn in a special risk category.

1.4.3.3 UNITED STATES POPULATION IN RELATION TO PROBABLE LEAD EXPOSURES

With the exception of those living in areas with primary lead smelters, most populations exposed to lead live in urban areas. Residents of the central city are at the highest risk in these urban areas. Therefore, for other than point stationary sources of lead, it is the urban population that is at risk, and in particular, central city residents. Blacks and Hispanics are probably subject to greater exposure to airborne lead because higher proportions of these segments of

the population live in urban areas. In the United States in 1970, 149 million persons were reported to live in urban areas, and 64 million in the central cities. These figures include about 12 million children under 5 years of age, with approximately 5 million of these children living in central-city areas. There are an estimated 600,000 children in the United States with blood lead values greater than 40 $\mu\text{g}/\text{dl}$. These values do not result from exposure to airborne lead alone; they also include exposure to leaded paint and lead in food. In view of the narrow margin of safety from currently observed urban blood lead levels, children exposed to an additional increment of lead from the air would be at great risk for adverse health effects.

Of the roughly 3 million U.S. pregnancies per year, inner-city women are estimated to account for 500,000. In view of available data, these women and their unborn children are also at high risk.

2. INTRODUCTION

According to Section 108 of the Clean Air Act of 1970, as amended in June 1974, a criteria document for a specific pollutant or class of pollutants shall

. . . accurately reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of such pollutant in the ambient air, in varying quantities.

Air quality criteria are of necessity based on presently available scientific data, which in turn reflect the sophistication of the technology used in obtaining those data as well as the magnitude of the experimental efforts expended. Thus air quality criteria for atmospheric pollutants are a scientific expression of current knowledge and uncertainties. Specifically, air quality criteria are expressions of the scientific knowledge of the relationships between various concentrations — averaged over a suitable time period — of pollutants in the same atmosphere and their adverse effects upon public health and the environment. Criteria are issued to help make decisions about the need for control of a pollutant and about the development of air quality standards governing the pollutant. Air quality *criteria* are *descriptive*; that is, they describe the effects that have been observed to occur as a result of external exposure at specific levels of a pollutant. In contrast, air quality *standards* are *prescriptive*; that is, they prescribe what a political jurisdiction has determined to be the maximum permissible exposure for a given time in a specified geographic area.

In the case of criteria for pollutants that appear in the atmosphere only in the gas phase (and thus remain airborne), the sources, levels, and effects of exposure must be considered only as they affect the human population through inhalation of or external contact with that pollutant.

Lead, however, is found in the atmosphere primarily as inorganic particulate, with only a small fraction normally occurring as vapor-phase organic lead. Consequently, inhalation and contact are but two of the routes by which human populations may be exposed to lead. Some particulate lead may remain suspended in the air and enter the human body only by inhalation, but other lead-containing particles will be deposited on vegetation, surface waters,

dust, soil, pavements, interior and exterior surfaces of housing — in fact, on any surface in contact with the air. Thus criteria for lead must be developed that will take into account all principal routes of exposure of the human population.

This criteria document sets forth what is known about the effects of lead contamination in the environment on human health and welfare. This requires that the relationship between levels of exposure to lead, via all routes and averaged over a suitable time period, and the biological responses to those levels be carefully assessed. Assessment of exposure must take into consideration the temporal and spatial distribution of lead and its various forms in the environment.

This document focuses primarily on lead as found in its various forms in the ambient atmosphere; in order to assess its effects on human health, however, the distribution and biological availability of lead in other environmental media have been considered. The rationale for structuring the document was based primarily on the two major questions of exposure and response. The first portion of the document is devoted to lead in the environment — physical and chemical properties; the monitoring of lead in various media; sources, emissions, and concentrations of lead; and the transport and transformation of lead within environmental media. The latter section is devoted to biological responses and effects on human health and ecosystems. An effort has been made to limit the document to a highly objective analysis of the scientific data base. The scientific literature has been reviewed through March 1977. The references cited do not constitute a complete bibliography but they are hoped to be sufficient to reflect the current state of knowledge on those issues most relevant to the establishment of an air quality standard for lead.

The status of control technology for lead has not been treated. For information on the subject, the reader is referred to appropriate control technology documentation published by the Office of Air Quality Planning and Standards (OAQPS), EPA. The subject of adequate margin of safety stipulated in Section 108 of the Clean Air Act also is not treated here; this topic will be considered in depth by EPA's Office of Air Quality Planning and Standards in documentation prepared as a part of the process of establishing an air quality standard.

3. CHEMICAL AND PHYSICAL PROPERTIES

3.1 ELEMENTAL LEAD

Lead is a gray-white metal of bright luster that, because of its easy isolation and low melting point (327.4°C), was among the first of the metals to be placed in the service of man. Lead was used as early as 2000 B.C. by the Phoenicians, who traveled as far as Spain and England to mine it. Its most abundant ore is galena, in which lead is present as the sulfide (PbS), and from which metallic lead is readily obtained by roasting. The metal is soft, malleable, and ductile; it is a poor electrical conductor, and it is highly impervious to corrosion. This unique combination of physical properties has led to its use in piping and roofing, and in containers for corrosive liquids. By the time of the Roman Empire, it was already in wide use in aqueducts and public water systems, as well as in cooking and storage utensils.

Lead is unique among the toxic heavy metals in that it is relatively abundant in the earth's crust; its abundance is estimated¹ to be more than 100 times that of cadmium and mercury, two other systemic metallic poisons. The great environmental significance of lead is the result both of its utility and of its abundance; lead is produced in far larger quantities than any other toxic heavy metal, with world production exceeding 3.5 million tons per year.² The properties of elemental lead (Pb) are summarized in Table 3-1.

TABLE 3-1. PROPERTIES OF ELEMENTAL LEAD

Property	Description
Atomic weight	207.19
Atomic number	82
Oxidation states	+2, +4
Density	11.35 g/cm ³ at 20°C
Melting point	327.4°C
Boiling point	1744°C
Covalent radius (tetrahedral)	1.44 Å
Ionic radii	1.21 Å (+2), 0.78 Å (+4)
Resistivity	21.9 x 10 ⁻⁶ ohm/cm

There are eight isotopes of lead: Four are stable and four are radioactive. The average abundances of the stable isotopes and the decay characteristics of the radioactive isotopes are listed in Table 3-2. The

stable isotopic compositions of naturally occurring lead ores are not identical, but rather show variations reflecting geological evolution.³ There is no radioactive progenitor for ²⁰⁴Pb. However, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb are produced by the radioactive decay of ²³⁸U, ²³⁵U, and ²³²Th, respectively. Thus the observed isotopic ratios depend on the U/Pb and Th/Pb ratios of the source from which the ore is derived and the age of the ore deposit. The ²⁰⁶Pb/²⁰⁴Pb isotopic ratio, for example, varies from approximately 16.5 to 21, depending on the source.⁴

TABLE 3-2. ISOTOPES OF LEAD

Isotope	Average abundance, %	Decay mode	Energy, MeV	Half-life
²⁰⁴ Pb	1.4	Stable	—	Stable
²⁰⁶ Pb	26.3	Stable	—	Stable
²⁰⁷ Pb	20.8	Stable	—	Stable
²⁰⁸ Pb	51.5	Stable	—	Stable
²¹⁰ Pb	—	β	0.017	22 yr
²¹⁰ Pb	—	α	0.047	22 yr
²¹¹ Pb	—	β	1.4	36.1 min
²¹¹ Pb	—	α	0.82	36.1 min
²¹² Pb	—	β	0.36	10.6 hr
²¹² Pb	—	α	0.24	10.6 hr
²¹⁴ Pb	—	β	0.72	26.8 min
²¹⁴ Pb	—	α	0.35	26.8 min

3.2 GENERAL CHEMISTRY OF LEAD

Lead is the heaviest element in Group IVB of the periodic table; this is the group that also contains carbon, silicon, germanium, and tin. Unlike the chemistry of carbon, however, the inorganic chemistry of lead is dominated by the divalent (+2) oxidation state rather than the tetravalent (+4) oxidation state. This important chemical feature is a direct result of the fact that the strengths of single bonds between the Group IV atoms and other atoms generally decrease as the atomic number of the Group IV atom increases.⁵ Thus, the average energy of a C-H bond is 100 kcal/mole, and it is this factor that stabilizes CH₄ relative to CH₂. For lead, the Pb-H energy is only approximately 65 kcal/mole, and this is too small to compensate for the Pb(II) → Pb(IV) promotional energy. It is this same feature, of course, that explains the marked difference in the

tendencies to catenation shown by these elements. Though C-C bonds are present in literally millions of compounds, lead is not known to form any catenated inorganic compounds.

A listing of the solubilities and physical properties of the more common compounds of lead is given in Appendix B. As can be discerned from those data, most inorganic lead salts are sparingly soluble (e.g., PbF_2 , PbCl_2) or virtually insoluble (PbSO_4 , PbCrO_4) in water; the notable exceptions are lead nitrate, $\text{Pb}(\text{NO}_3)_2$, and lead acetate, $\text{Pb}(\text{OCOCH}_3)_2$. Inorganic lead (II) salts are generally relatively high-melting-point solids with correspondingly low vapor pressures at room temperatures. The vapor pressures of the most commonly encountered lead salts are also tabulated in Appendix B. The decay of

lead salts in the atmosphere is discussed in Section 6.2.2.

3.3 ORGANOMETALLIC CHEMISTRY OF LEAD

The properties of organolead compounds (i.e., compounds containing bonds between lead and carbon) are entirely different from those of the inorganic compounds of lead. The Pb-C bond energy is approximately 130 kcal/mole,⁶ or twice the Pb-H value cited above. Consequently, the organic chemistry of lead is dominated by the tetravalent (+4) oxidation state. An important property of most organolead compounds is that they undergo photolysis when exposed to light. The physical properties of some of the more important organolead compounds are summarized in Table 3-3.

TABLE 3-3. PROPERTIES OF MAJOR ORGANOLEAD COMPOUNDS

Compound	Formula	Appearance	m.p., C	b.p., C
Tetramethyl lead	$(\text{CH}_3)_4\text{Pb}$	Colorless liquid	-27.5	110
Tetraethyl lead	$(\text{C}_2\text{H}_5)_4\text{Pb}$	Colorless liquid	-130	82 ^a
Tetraphenyl lead	$(\text{C}_6\text{H}_5)_4\text{Pb}$	White solid	223	Decomposes
Hexamethyl lead	$(\text{CH}_3)_6\text{Pb}_2$	Pale oil	38	Decomposes
Hexaethyl lead	$(\text{C}_2\text{H}_5)_6\text{Pb}_2$	Yellow oil	36	100 ^b

^aAt 13 mm pressure.

^bAt 2 mm pressure.

Because of their use as antiknock agents in gasoline and other fuels, the most important organolead compounds are the tetraalkyl compounds tetraethyl lead (TEL) and tetramethyl lead (TML). As would be expected for such nonpolar compounds, TEL and TML are insoluble in water but soluble in hydrocarbon solvents (e.g., gasoline). These two compounds are manufactured in extremely large quantities (Chapter 5) by the reaction of the alkyl chloride with lead-sodium alloy:⁷

$$4\text{NaPb} + 4\text{C}_2\text{H}_5\text{Cl} \rightarrow (\text{C}_2\text{H}_5)_4\text{Pb} + 3\text{Pb} + 4\text{NaCl}$$

The methyl compound, TML, is also manufactured by a Grignard process involving the electrolysis of lead pellets in methylmagnesium chloride:⁷

$$2\text{CH}_3\text{MgCl} + 2\text{CH}_3\text{Cl} + \text{Pb} \rightarrow (\text{CH}_3)_4\text{Pb} + 2\text{MgCl}_2$$

These lead compounds are removed from auto or other internal combustion engines by a process called lead scavenging, in which they react in the combustion chamber with halogenated hydrocarbon additives (notably ethylene dibromide and ethylene dichloride) to form lead halides, usually bromochlorolead. Such inorganic compounds apparently originate as vapors in the combustion chamber of an automobile engine. During their passage through the exhaust system, however, they condense to form small spherical particles with

diameters on the order of a few tenths of a micrometer; they also condense or absorb onto the surfaces of co-entrained particles derived from the intake air or from corrosion of the exhaust system. Consequently, lead halides emitted from automobile exhaust are present as vapors, as pure solid particles, and as a coating on the surface of particulate substrates. Mobile source emissions are discussed in detail in Chapter 6 (Section 6.2.2.1).

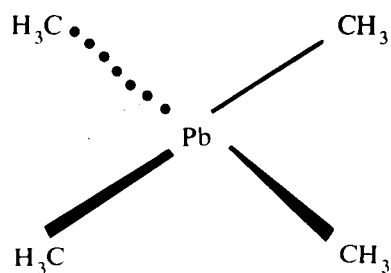
Several hundred other organolead compounds have been synthesized, and the properties of many of them are reported by Shapiro and Frey.⁷ Some of these are used in the commercial preparation of organomercury compounds used as fungicides, and their use as catalysts and stabilizers in industrial processes has been investigated extensively.

3.4 COMPLEX FORMATION AND CHELATION

The bonding in organometallic derivatives of lead is principally covalent rather than ionic because of the small difference in the electronegativities of lead (1.8) and carbon (2.6). As is the case in virtually all metal complexes, however, the bonding is of the donor-acceptor type, in which both electrons in the bonding orbital originate from the carbon atom.

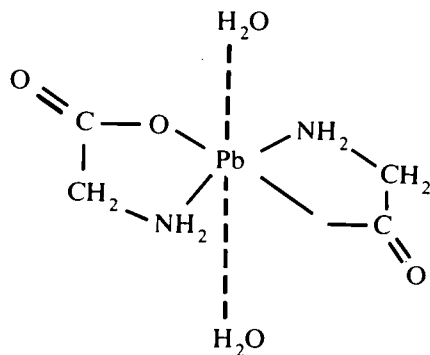
The donor atoms in a metal complex could, of

course, be almost any basic atom or molecule; the only requirement is that a donor, usually called a ligand, must have a pair of electrons available for bond formation. In general, the metal atom occupies a central position in the complex, as exemplified by the lead atom in tetramethyl lead (a), which is



(a)

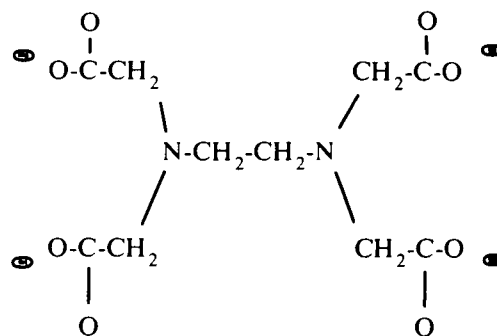
tetrahedrally surrounded by four methyl groups. In these simple organolead compounds, the lead is usually present as Pb(IV), and the complexes are relatively inert. These simple ligands, which bind to metal at only a single site, are called monodentate ligands. Some ligands, however, can bind to the metal atom by more than one donor atom, so as to form a heterocyclic ring structure. Rings of this general type are called chelate rings, and the donor molecules which form them are called polydentate (as opposed to monodentate) ligands or chelating agents. In the chemistry of lead, chelation normally involves Pb(II), leading to kinetically quite labile (although highly stable) complexes that are usually six-coordinate. A wide variety of biologically significant chelates with ligands, such as amino acids, peptides, nucleotides, and similar macromolecules, are known. The simplest structure of this type is with the amino acid, glycine, as represented in (b) for a 1:2 (metal: ligand) complex.



(b)

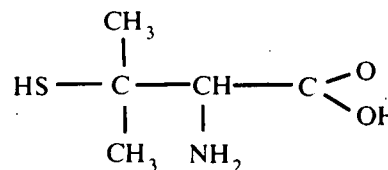
The importance of chelating agents in the present context is their widespread use in the treatment of lead and other metal poisoning.

Since Pb(II) is a relatively soft (or class b) metal ion,⁸ it forms strong bonds to soft donor atoms like the sulfur atoms in the cysteine residues of proteins and enzymes; it also coordinates strongly with the imidazole groups of histidine residues and with the carboxyl groups of glutamic and aspartic acid residues. In living systems, therefore, lead atoms bind to these peptide residues in proteins, thereby preventing the proteins from carrying out their functions by changing the tertiary structure of the protein or by blocking the approach by a substrate to the active site of the protein. The role of the chelating agents is to compete with the peptides for the metal by forming stable chelate complexes that can then be transported from the protein and eventually excreted by the body. For simple thermodynamic reasons (see Appendix B), chelate complexes are much more stable than monodentate metal complexes, and it is this enhanced stability that is the basis for their ability to compete favorably with proteins and other ligands for the metal ions. The chelating agents most commonly used for the treatment of



EDTA

(c)



PENICILLAMINE

(d)

lead poisoning are ethylenediaminetetraacetate ions (EDTA) (c), D-penicillamine (d), and their derivatives. EDTA is known to act as a hexadentate ligand toward metals.⁹ Recent X-ray diffraction studies have demonstrated that D-penicillamine is a tridentate ligand (binding through S, N, and O) toward cobalt,¹⁰ chromium,¹¹ and lead,¹² but monodentate toward mercury.¹³⁻¹⁵

It should be noted that both the stoichiometry and structures of metal chelate depend on pH, and that different structures may occur in crystals from those manifest in solution. It will suffice to state, however, that several ligands can be found that are capable of sufficiently strong chelation with lead present in the body under physiological conditions to enable their use in the effective treatment of lead poisoning.

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4. SAMPLING AND ANALYTICAL METHODS FOR LEAD

4.1 INTRODUCTION

Monitoring for lead in the environment, which includes sampling and measurement, is a demanding task that requires careful attention. Lead is receiving careful scrutiny as a pollutant, and the accurate assessment of its impact on the environment is contingent on the acquisition of valid monitoring data. Furthermore, the movement and accumulation of lead in ecosystems occur via complex pathways and compartments. In addition, many difficulties are inherent in the identification and tracing of lead in its various forms in the environment. Airborne lead originates from manmade sources, primarily the automobile, and is extracted from the atmosphere by animals, vegetation, soil, and water. Knowledge of the concentrations of lead in these various media and the movement of lead between and among them is critical for controlling lead pollution and for mitigating the adverse effects of lead in the environment on people.

Sampling and analytical methods for monitoring lead have been devised for almost every purpose. Some methods are too tedious or expensive for general use; others are relatively easily applied but produce results of limited utility or questionable validity; and others are appropriate for use in monitoring lead in certain systems but not in others. The monitoring of environmental lead can be carried out with almost any precision deemed necessary, but actually obtaining precise and accurate results is not a trivial task in many instances. (See Chapter 9 for a discussion of the difficulties in reproducing blood lead analyses.) The primary problem is that of determining what types of monitoring procedures are necessary to realize societal objectives for protecting human health on a practical basis. The objective of this chapter is to review the status of the monitoring procedures available. Another serious problem is the present lack of instrumentation for the continuous analysis of aerosol.

Monitoring for lead involves an operational sequence, based on the scientific method, as shown

schematically in Figure 4-1. The type of data to be collected must be defined clearly on the basis of the question(s) to be answered. The required accuracy of the data must be determined and assured by means of a quality assurance strategy for all aspects of the monitoring operation. Similarly, the sampling strategy must be based on the type of data needed and yet take into account requirements imposed by the analytical methods to be used. The selection and application of the analytical methods are in turn influenced by the kind of data needed, the types of samples collected, the analytical capabilities available, and other factors. Ultimately, analysis of the data obtained determines whether the sequence has reached a satisfactory conclusion or if modifications of any particular segments of the sequence are required. Although there are numerous technical sources of information concerning sampling strategy, sampling methods, sample preparation, and analyses, only a few of the most noteworthy are cited here. These include the National Academy of Sciences report on lead,¹ Stern's three-volume compendium on air pollution,² the Geological Survey review of lead in the environment,³ and the National Science Foundation publication, "Monitoring for Lead in the Environment."⁴

In succeeding sections, the specific operations involved in monitoring are discussed. Site selection is treated succinctly because of the dearth of criteria in the literature and the necessity for establishing specific site criteria for each sampling requirement. Much remains to be done toward establishing criteria for location of samplers. The various samplers used to collect lead data are described. Methods for collecting dustfall, water, soil, and vegetation samples are reviewed along with current sampling methods specific for mobile and stationary sources. The processing of samples for analysis is critical and influences the selection of filter materials and characteristics. This is an area of monitoring that is receiving much attention because of the interferences that have been encountered.

The analytical section is lengthy because of the

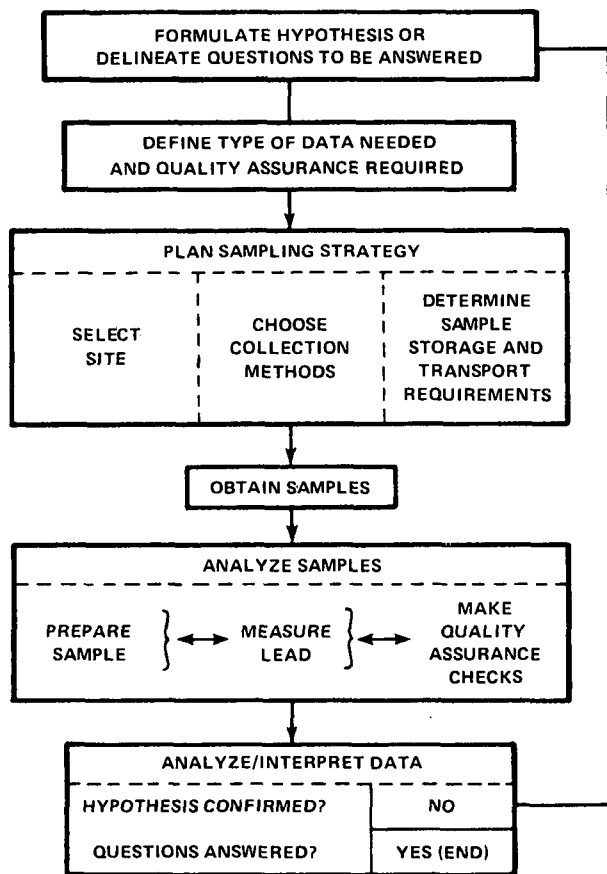


Figure 4-1. Sequence of operations involved in monitoring for lead in the environment.

large variety of methods applied to lead analysis. Analysis is the most advanced area of monitoring operations, and if used properly, analytical methods are already available that are capable of providing all the required data.

4.2 SAMPLING

The purpose of sampling is to obtain lead-containing particles, adsorbed gases, liquids, and solid samples that will provide a measure of the nature and concentration of lead at various points in the environment. Sampling encompasses not only the method of sample collection, but also the selection of sampling sites and procedures applicable to the processing of samples.

4.2.1 Sampler Site Selection

The location of sample collection devices has important and pervasive effects on the data obtained. In monitoring ambient air for lead, the proximity to the sampler of mobile and stationary sources is of prime importance. Also of importance are the height of the sampler intake above the ground and the local topography, climate, and lead level in the soil. Ott⁵

has enumerated the problems and difficulties encountered in comparing data obtained from air monitoring stations in different cities.

General guidelines for locating ambient air samplers include the following:

1. Samplers should be a uniform height above the ground, although to assess the risk to children, some samplers should also be located at a child's height (2 to 3 ft).
2. Sampler inlets should be at least 3 m from any obstruction.
3. Samplers should be located in areas free of local source influence and convection or eddy currents.

Most existing sampler sites do not meet these criteria, and information on sampler location is not usually provided with data.⁵ The number of monitoring sites in an air monitoring network should be related to geography, population, and sources.⁶ Since there is no suitable, continuous method for measuring lead in air, the sampling period and frequency are also important in the overall sampling strategy. It should be noted, however, that it is not possible to discuss sampling plans outside the context of a particular objective (e.g., characterization of rural or urban background levels, assessment of health hazards to people, determination of source effects, or delineation of transport mechanisms).⁴ The treatment of sampling in detail is outside the scope of this discussion, but reference should be made to the available sources.^{6,7}

4.2.2 Sampling Errors

The fidelity with which a sample reflects the quantity and nature of lead in any medium being sampled is basic to the obtaining of valid data and therefore to an understanding of the phenomena being investigated. In Section 4.2.1, the importance of site selection for collecting samples of airborne lead was noted. In Section 4.2.6.2, the problems of dilution of samples from mobile sources are noted. A general sampling error associated with sampling of airborne particulates is discussed here.

Most ambient sample collections are obtained nonisokinetically; that is, as the air is drawn into the sampler inlet, the speed and direction of the air are changed. The inertial characteristic of suspended particulates bring about losses of larger particles both by drift from the sampled air stream and by impaction on the surface of the sampler inlet. It has been shown that appreciable errors may result from nonisokinetic sampling, primarily because of the loss of large particles (those with diameters exceeding 10

μm).⁸ Generally, it is not possible to estimate the error under any specified conditions. But such errors may be minimized by avoiding eddy formation, turbulence, divergence or convergence, and changes in direction of the sampled air stream.

4.2.3 Sampling for Airborne Particulate Lead

Airborne lead is primarily carried by particulates or aerosols, but in smaller concentrations, it may occur in the form of organic gases. Samplers range from the widely used high-volume filter sampler to a variety of other collectors that employ filters, impactors, and impingers.

4.2.3.1 HIGH-VOLUME SAMPLER

The most widely used method for sampling airborne particulates in the 0.1- to 10- μm range is the high-volume air sampler,^{9,10} which is routinely used in the National Air Surveillance Networks. The method requires a vacuum cleaner type of air blower that draws air through a filter at rates as high as 2 m^3/min . Since the normal sampling period is 24 hr, particulates from a sample volume of about 2000 m^3 are collected. Because the air flow varies with filter type and the degree of filter loading, it is necessary at least to measure initial and final air flows. Gross particulate loading is determined by carefully weighing the filter before and after sample collection. The lead content is then determined by one of the analytical methods described in the following.

Commercial high-volume samplers in which the filter is held in a horizontal plane and protected from dustfall by a housing are available.⁹ An 8- by 10-in. glass fiber filter is usually recommended. Problems with filter selection are discussed in a subsequent section.

High-volume samplers are inexpensive, easy to operate, and in widespread use. A measure of their precision and ease of operation can be deduced from the observation that an interlaboratory relative standard deviation for total particulate collection has been reported of 3.7 percent over the range 80 to 125 $\mu\text{g}/\text{m}^3$. The disadvantages of the high-volume sampler include the lack of separation of particulates by size, the interferences by impurities in the filters with some analytical procedures, and the particle fracturing that occurs on impact, which precludes subsequent determination of size distribution.⁹ In addition, high-volume samplers are usually operated *nonisokinetically*; this results in an underestimation of the airborne concentration of large particles.¹¹ If there is appreciable mass in particles with aerodynamic diameters greater than

about 10 μm , this effect may be important. Isokinetic impactor measurements run in Los Angeles have indicated that the mass median equivalent diameters are apparently larger than those measured under nonisokinetic conditions.¹² This topic is also discussed in Section 6.3.2.1.

An interlaboratory comparison program being conducted in Europe has compared total particulate results from high- and low-volume samplers.¹³ Based on the low-volume sampler data, the precision of total particulate collection of the high-volume sampler is estimated at $\pm 0.5 \mu\text{g}/\text{m}^3$. Of course, such comparisons apply only to the particular conditions and methodology of sampling and analysis used in that study.

4.2.3.2 DICHOTOMOUS SAMPLER

The size distribution of airborne particulates can be determined by using multistage impactors and impingers or by analyzing unfractionated samples. Such information is desirable for monitoring sources of a pollutant as well as for assessing potential effects of the pollutant on human health. The above techniques are expensive to use on a large scale and generally require extended sampling periods. Measurements¹⁴ have indicated that airborne particulates usually have a bimodal size distribution and also that there is a distinct difference in the effects of small and large particles on humans.¹⁵

A dichotomous sampler for particulates has been designed to collect and fractionate samples into two size ranges.¹⁶ The dichotomous sampler uses virtual impaction to avoid the particle bounce errors frequently encountered with cascade impactors.¹⁷ Virtual impaction involves the separation of particles into separate air streams by inertial means.¹⁶ In the apparatus, the largest portion of the air stream is pulled through an annular path so that it changes direction, while a small air flow is maintained in a straight path. The inertia of the larger particulates tends to keep them in the straight path while the smaller particles are diverted with the main stream. Two stages of virtual impaction have been used to obtain better fractionation. Membrane filters in the two air paths collect the respective samples. The particle diameter demarcation of the two fractions is normally between 2.0 and 3.5 μm in various designs. Commercial dichotomous samplers are available, but they are considerably more expensive than high-volume samplers.

Tests of a prototype dichotomous sampler in St. Louis indicated¹⁶ that 80 percent of the particulate lead was contained in particles less than 2 μm in

diameter, whereas only 20 percent was found to be in larger particles. Other tests to evaluate the performance of dichotomous samplers are under way.¹⁸

4.2.3.3 TAPE SAMPLER

Though dustfall and high-volume collectors usually require 24 hr sampling periods to obtain a sufficient analytical sample, there may be a need in source and transport studies to monitor airborne particulates for shorter time intervals. The tape sampler draws air through a spot on a filter tape that advances automatically at preset intervals (e.g., every 2 hr).⁹ At a sampling rate of about 0.56 m³/hr (20 ft³/hr) for a 2-hr interval and with a 2.54-cm (1-in.) spot diameter, it is possible to analyze the collected sample for lead using anodic stripping voltammetry analysis.¹⁹ Atmospheric concentrations of lead ranging from 0.1 to 2.0 μg/m³ were measured at monitoring stations in Chicago and Washington using tape samplers.¹⁹ Diurnal cycles in airborne lead concentrations were obtained that correlate with manmade sources of lead.

4.2.3.4 IMPACTORS AND IMPINGERS

Impactors are multistage particulate collection devices designed to provide a number of size fractions. The modified Andersen cascade impactor used in the National Air Surveillance Networks (NASN) is described here.²⁰ Others are described in standard texts.^{2,21}

The cascade impactor fractionates particles in a series of five or six collection stages.²⁰ Particles pass through a series of jets, 400 per stage, that are progressively smaller. Under each series of jets is a collection plate. The size fraction of particles collected at each stage depends on the air velocity, geometry, and previous stages. The last stage consists of a filter. Air is pumped through the impactor at 0.14 to 0.17 m³/min by means of an air pump on the downstream side. Aluminum foil is used as the collector, and the size fraction is determined by weighing before and after a 24-hr sample is collected. Five fractions are usually obtained: < 1.1, 1.1 to 2.0, 2.0 to 3.3, 3.3 to 7, and > 7 μm.

Results obtained by the NASN²² indicate that lead particulates typically have mass median diameters in the range of 0.25 to 1.43 μm. Analysis by optical emission spectrography indicated that for particles less than 0.5 μm in diameter, the lead content was 2 to 4 percent. A cascade impactor has also been applied to multielement size characterization of urban aerosols.²³

A size-selective particle sampler using cyclones

has also been described,²⁴ and a ten-fraction-size sample can be obtained with the Lundgren impactor.²⁵

Impingers collect atmospheric aerosols by impingement onto a surface submerged in a liquid.^{2,9} Impactors are sometimes called dry impingers. As in impactors, impingement relies on the inertial characteristics of the particle for collection on a surface. High collection efficiencies for particles as small as 0.1 μm may be obtained in wet impingers.²

4.2.4 Sampling for Vapor-Phase Organic Lead Compounds

In determining the total quantity of lead in the atmosphere, air is drawn through a membrane or glass filter for collecting particulate lead and then through a suitable reagent or absorber for collection of gaseous compounds that pass through the filter.²⁶ Since the normal filter used has a nominal 0.45-μm pore size, analysis by this method will include any material that passes through these pores, although it is considered to be primarily organic lead. Organic lead may be collected on iodine crystals, adsorbed on activated charcoal, or absorbed in an iodine monochloride solution.⁴ Reviews of the procedures are available.^{27,28}

The procedures using iodine monochloride have been described and are claimed to be effective.²⁶ In one experiment, two bubblers containing the solution were placed in series in the sampling train. Head levels corresponding to about 2.0 μg/m³ of organic lead were obtained in the first bubbler, whereas the second gave a blank response, indicating that the collection efficiency of the first bubbler was essentially 100 percent and that the method is quantitative. Analyses were accomplished with atomic absorption spectrometry after chelation of the lead and extraction into an organic solvent. It should be noted, however, that the detection sensitivity was low and that the use of bubblers limits the sample volume.

4.2.5 Sampling for Lead in Other Media

In some respects, sampling for lead in water, soil, dustfall, or vegetation can be easier than sampling for airborne lead. However, the sampling conditions may be equally as complex and have a first-order impact on the measurements.

4.2.5.1 WATER

Heavy metals may be distributed in water as ions, as chemical complexes, or as species adsorbed on suspended matter.⁴ Methods for sampling and

analysis of lead in water have been extensively described.^{29,30} Sample containers may be either glass or plastic. The dynamics of the water body should be considered, and defined procedures and precautions should be followed.⁴ A variety of procedures, each associated with particular objectives, exists (e.g., separation of dissolved and suspended lead and preservation of water samples to retain their original state).

Analysis of lead in water is typically accomplished with atomic absorption and emission spectroscopy, although analytical methods for other media are also applicable. The natural lead content of lakes and rivers lies in the range of 1 to 10 $\mu\text{g}/\text{liter}$, with an average value of 6.6 $\mu\text{g}/\text{liter}$ for North American rivers.¹ Thus, it is commonly found necessary to concentrate the sample by chelating and extracting the lead or by evaporating the water.³ Techniques for water analysis have been reviewed recently by Fisherman and Erdman.³¹

4.2.5.2 SOIL

Lead in soil samples collected from nearly 1000 locations around the United States ranges from less than 10 to about 700 ppm, with a mean concentration of 16 ppm.³ Deposition of lead on soil from the atmosphere results in extreme vertical concentration gradients, since lead is relatively immobile in soil.⁴ It has been estimated that an average of 1 $\mu\text{g Pb}/\text{cm}^2 \cdot \text{year}$ from rainout or washout or both, and 0.2 $\mu\text{g Pb}/\text{cm}^2 \cdot \text{year}$ from dust accumulates at or near the soil surface.³² Horizontal gradients of lead concentrations in soil occur as the result of natural and manmade sources. The lead content of soil decreases rapidly with distance from emission sources; for example, reductions of 75 percent are observed in moving from 8 to 32 m from a highway.³³ This point is discussed in detail in Chapter 6.

Soil sampling is not complex.⁴ Vegetation and large objects should be avoided, and a representative site should be selected. The vertical integrity of the sample should be preserved and noted. The sample should be air-dried and stored in sealed containers. The sampling should be planned to obtain results representative of the conditions being investigated. Most of the analytical procedures used for airborne particulates are applicable to soils, but the results may not be comparable. Many techniques, including optical emission spectrography, X-ray spectrography, atomic absorption, and the electron microprobe have been used for soil lead analysis.³ X-ray diffraction has been used to analyze soil samples for lead emitted by automobiles.³⁴

4.2.5.3 DUSTFALL

All particles suspended in air are affected by gravitational settling. The settling velocities of larger particles (≈ 5 to 10 μm) are such that they will be transported shorter distances than the smaller particles (≈ 1 μm), which have nearly negligible settling velocities. Thus dustfall collections can be used to monitor the dispersion of particulate lead from a specific source. The collections are made by placing open containers at appropriate sites free of overhead obstructions.^{9,10} Using buckets to measure dustfall can lead to inaccurate data; wind eddies created by the walls of the bucket may greatly affect deposition. The dustfall surface should be smooth and flat, presenting as little disturbance to the wind as possible. These points are discussed by Patterson.³⁵

Dustfall is generally reported in units of grams per square meter per month ($\text{g}/\text{m}^2\text{-mo}$) and may be analyzed by the methods described for particulates collected on filters.⁹ The "ASTM Standard Method for Collection and Analysis of Dustfall" provides detailed procedures.³⁶ One comparison of lead quantities collected by dustfall and by filtration indicated consistently that the lead content of particulates collected by filtration in the high-volume sampler was higher than in dustfall.³⁷ This is a result primarily of the low settling velocities of the smaller particles, which make up a significant fraction of the total particulate.

4.2.5.4 VEGETATION

Lead analysis of plant tissues has been less extensive than studies in other media. Lead deposited on leaf surfaces by fallout can be removed and analyzed.³⁸ Lead in plants is usually observed to be less than 1 $\mu\text{g}/\text{g}$ dry weight, although levels as high as 31 $\mu\text{g}/\text{g}$ have been cited.¹ Plants can absorb soluble lead from soils, but most soil lead is in forms not available to plants.¹ Leafy portions of plants often exhibit higher concentrations of lead, but in general, at least 50 percent of this lead can be removed by washing.¹ Since the presence of lead inside the plants may manifest different effects than that on the plant surface, attempts should be made to differentiate between these two conditions.

Little mention appears in the literature of methods for the field sampling of plant life for environmental studies. The standard methods and procedures usually are focused on statistical sampling for determination of nutrient elements in food crops.

Plant tissue collection and treatment have been reviewed by Skogerboe et al.⁴ Sampling of plant

materials is generally carried out by random selection of the indigenous species representative of a given area of interest. Where the entire plant is not collected, emphasis is usually placed on the portion of the plant consumed by herbivores or harvested for market. In developing sampling plans, there should be close coordination between plant and animal sampling groups, especially where foodchains are involved.

Before analysis, a decision must be made as to whether or not the plant material should be washed to remove surface contamination from fallout and soil particles. If the plants are sampled in a study of total lead contamination, or if they serve as animal food sources, washing should be avoided. If the effect of lead on plant processes is being studied, or if the plant is a source of human food, the plant samples should be washed. In either case, the decision must be made at the time of sampling, as washing cannot be effectively used after the plant materials have dried. Neither can fresh plant samples be stored for any length of time in a tightly closed container before washing, because molds and enzymatic action may affect the distribution of lead on and in the plant tissues. Freshly picked leaves stored in sealed polyethylene bags at room temperature generally mold in a few days. Storage time may be increased to approximately 2 weeks by refrigeration.

Methods reported in the literature for removing surface contamination vary considerably, ranging from mechanical wiping with a camel-hair brush to leaching in mineral acids or EDTA. Removal of surface contamination with minimum leaching of constituents from leaf tissue can generally be accomplished by using dilute solutions of selected synthetic detergents followed by rinsing in deionized water.

After collection, plant samples should be dried as rapidly as possible to minimize chemical and biological changes. Samples that are to be stored for extended periods of time or to be ground should be oven-dried for at least 4 hr at 70°C to arrest enzymatic reactions and render the plant tissue amenable to the grinding process. Storage in sealed containers is always advisable.

4.2.5.5 FOODSTUFFS

In 1972, lead was included in the Food and Drug Administration Market Basket Survey, which involves nationwide sampling of foods representing the average diet of an 18-year-old male (i.e., the individual who on a statistical basis eats the greatest quantity of food).³⁹ Various food items from the

different food classes are purchased in local markets and made up into meals in the proportion that each food item is ingested; they are then cooked or otherwise prepared as they would be consumed. Foods are grouped into 12 food classes, then composited and analyzed chemically. The quantities represented in the Total Diet Survey and the percentages of these foods grouped in the diet are presented in Table 4-1.

TABLE 4-1. DAILY FOOD INTAKE³⁹

Food group	Food consumption	
	Avg. g/day consumed	% of total diet
I Dairy products	756	26.1
II Meat, fish, and poultry	290	9.9
III Grain and cereal products	369	12.6
IV Potatoes	204	7.0
V Leafy vegetables	59	2.0
VI Legume vegetables	74	2.5
VII Root vegetables	34	1.2
VIII Garden fruits	88	3.0
IX Fruits	217	7.4
X Oils, fats, and shortening	52	1.8
XI Sugar and adjuncts	82	2.8
XII Beverages (including water)	697	24.9
Total	2922	—

4.2.6 Source Sampling

Sources of lead have been well identified and include automobiles, smelters (lead and other non-ferrous metals), coal-burning facilities, battery manufacturing plants, chemical processing plants, and facilities for scrap processing and welding and soldering operations. An important secondary source is fugitive dust from mining operations and from soils contaminated with automotive emissions.³⁴ A complete discussion of sources of lead emissions is given in Chapter 5. The following sections discuss the sampling of stationary and mobile sources, which require different sampling methods.

4.2.6.1 STATIONARY SOURCES

Sampling of stationary sources for lead requires the use of a sampling train at the source to sample the effluent stream. Both particulates and vapors must be collected by the sampling train, and often a probe is inserted directly into the stack or exhaust stream. In the tentative ASTM method for sampling for atmospheric lead, air is pulled through a 0.45- μ m membrane filter and an activated carbon adsorption tube.⁴⁰ In a study of manual methods for

measuring emission concentrations of lead and other toxic materials,⁴¹ use of a filter, a system of impingers, a metering system, and a pump was recommended. The recommended solution in the impingers was nitric acid. More recently, impinger solutions containing iodine monochloride have been shown to be effective.²⁶

Since lead in stack emissions may be present in a variety of physical and chemical forms, source sampling trains must be designed to trap and retain both gaseous and particulate lead.

4.2.6.2 MOBILE SOURCES

A variety of procedures has been used to obtain samples of auto exhaust aerosols for subsequent analysis for lead compounds.

In one such procedure, a large horizontal air dilution tube was designed to segregate fine combustion-derived aerosols from larger lead particles ablated from combustion chamber and exhaust deposit.⁴² In this procedure, hot exhaust was ducted into a 56-cm-diameter, 12-m-long, air dilution tunnel and mixed with filtered ambient air in a 20-m-diameter mixing baffle in a concurrent flow arrangement. Total exhaust and dilution air flow rate was 28 to 36 m³/min, which produced a residence time of about 5 sec in the tunnel. At the downstream end of the tunnel, samples of the aerosol were obtained by means of isokinetic probes facing upstream, using filters or cascade impactors. Properly designed air dilution tubes of this type have very few aerosol losses for particles smaller than about 2 μ m, the size that can be respired into human lungs.⁴³

Air-diluted aerosols from cyclic auto emissions tests have been accumulated in a large plastic bag. Filtration or impaction of aerosols from the bag samples produces samples suitable for lead analysis.⁴⁴ Because of the rather lengthy residence time, the bag technique may result in the measurement of anomalously large aerosol sizes because of condensation of low-vapor-pressure organic substances onto the lead particles. This effect may be offset, however, by fallout processes that apply primarily to larger particles (see above).

A low-residence-time sampling system has been used that is based on proportional sampling of raw exhaust, followed by air dilution and filtration or impaction.^{45,46} A relatively large sample of aerosol constituents can be obtained because of the high sampling rates of the raw exhaust. Since a constant proportion of the sample flow to the total exhaust flow must be maintained, this technique may be limited by the response time of the equipment to

operating cycle phases that cause relatively small transients in the exhaust flow rate.

Most research on aerosol emissions in recent years has used various configurations of the horizontal air dilution tunnel.⁴² Several polyvinyl chloride dilution tunnels have been used with good success.^{43,47,48} These 46-cm-diameter tunnels of varying lengths have been limited by exhaust temperatures to total flows above approximately 11 m³/min. Buildup of electrostatic charge on the walls of these plastic systems can cause abnormally high wall losses, but these can be avoided by wrapping the tunnel with a grounded conductive cable at about 30-cm intervals.⁴⁷ Similar tunnels have been used in which a centrifugal fan located upstream is used rather than a positive displacement pump located downstream.⁴³ This geometry produces a slight positive pressure in the tunnel and expedites transfer of the aerosol to holding chambers for studies of aerosol growth. Since the total exhaust plus dilution air flow is not held constant in this system, there may be slight sample disproportionation. However, these errors can be minimized by maintaining a very high dilution air/exhaust flow ratio.⁴³

There have also been a number of studies performed using total filtration of the exhaust stream to arrive at material balances for lead using rather low back-pressure metal filters.^{45,49-51} The cylindrical filtration unit used in these studies is better than 99 percent effective in retaining lead particles.⁵¹ Supporting data for lead balances generally confirm this conclusion.⁵²

Thus a wide variety of sampling and total exhaust filtration procedures have been used to measure the mass emissions of lead compounds from automobiles. Each has its appropriate area of application, depending on the objectives of the various research program carried out. The air dilution tunnel technique is most convenient, is compatible with the usual gas emission measurements, and has therefore been most commonly used.

4.2.7 Filter Selection and Sample Preparation

In sampling for lead particulates, air is drawn through filter materials such as fiber glass, asbestos, cellulosic paper, or porous plastics.^{2,4} These materials include trace elements that can interfere in the subsequent analysis.⁵³⁻⁵⁵ If the sample is large, then the effects of these trace elements are negligible, but this is not always the case.⁵⁶ When samples are prepared for analysis, reduction of the mass of filter material is often accomplished by ashing, either chemically or in an oven.⁴ The nature of the

filter determines the ashing technique. In other methods of analysis — X-ray fluorescence, for example — analysis can be performed directly on the filter if the filter material is suitable.¹⁶ Because the nature and performance of filter materials are still under investigation, general criteria for their selection cannot be given.⁴ A general review of filter materials is available.⁵⁷

The main advantages of glass-fiber filters are their low pressure drop and high particle collection efficiency at high flow rates. The main disadvantage is the variable lead content. In one investigation of Nuclepore filters, examples were given in which the analysis of samples and blanks showed results that did not differ sufficiently to allow use of the data.⁴ Others have shown that the variability of residual impurities in some glass filters makes their use inadvisable in most cases,^{54,55} and they place a high priority on the standardization of a suitable filter for high-volume samples.⁵⁶ Other investigations have indicated, however, that glass-fiber filters are available now that do not present a lead interference problem.⁵⁸ The collection efficiencies of filters, and also of impactors, have been shown to be dominant factors in the quality of the derived data.⁵⁹ The relative effectiveness of dry ashing (either at low temperatures in an oxygen plasma or at high temperatures) and of wet ashing by acid dissolution is a subject of current concern. Either technique will give good results if employed properly.^{4,55}

4.3 ANALYSIS

A variety of useful analytical procedures is available for determination of lead in the environmental samples. The choice of the best method in a given situation depends on the nature of the data required, the type of sample being analyzed, the skill of the analysts, and the equipment available. For general determination of elemental lead, atomic absorption spectroscopy is coming into wider use. However, if multielement analysis is required, and if the equipment is available, X-ray fluorescence has been shown to be capable of rapid, inexpensive analyses.¹⁶ Other analytical methods have specific advantages that call for their continued use in special studies. Only those analytical techniques receiving current use in lead analysis are described in the following. More complete reviews are available in the literature.^{3,4,29}

4.3.1 Colorimetric Analysis

Colorimetric or spectrophotometric analysis for lead using dithizone (diphenylthiocarbazone) as the

reagent has been used for many years.⁶⁰⁻⁶² This method is the primary one recommended in a National Academy of Sciences report on lead,¹ and it is the basis of the tentative method of testing for lead in the atmosphere by the American Society for Testing and Materials.⁴⁰ Because of its history, it has served as a reference by which other methods have been tested.

Dithizone is an organic compound that reacts with lead salts to form an intensely colored chelated complex. This complex has an absorption maximum, with a known extinction coefficient, at a wavelength of 510 nm, which is the basis of the measurement. Standards can be prepared for calibration purposes by adding known quantities of lead to reagents.

The procedures for the colorimetric dithizone analysis require a skilled analyst if reliable results are to be obtained. The method has been analyzed,⁴ and the procedures are given in the literature.^{4,40} The American Society for Testing and Materials conducted a collaborative test of the dithizone method⁶³ and concluded that the ASTM dithizone procedure gave satisfactory precision in the determination of particulate lead in the atmosphere.

The colorimetric dithizone method has the advantage of acceptability by professional organizations. In addition, the required apparatus is simple and relatively inexpensive, the absorption is linearly related to the lead concentration, the method requires only a few micrograms of lead in the sample, large samples can be used, and interferences can be removed.⁴ Realization of these advantages depends on meticulous attention to the procedures and reagents. This requires a relatively lengthy procedure and thus a high cost per sample.

4.3.2 Atomic Absorption Analysis

Atomic absorption (AA) spectroscopy is the more generally accepted method for the measurement of lead in environmental sampling.⁴ A variety of lead studies using AA analysis have been reported.^{26,55,58,64,65}

In AA, the lead determination is made by measuring the resonance absorption of lead atoms. The attenuation of the light beam passing through the sample is logarithmically related to the concentration of the atoms being measured. The lead atoms in the sample must be vaporized either in a precisely controlled flame or in a nonflame medium. The sample solution enters the flame through a nebulizer. The lead absorption wavelengths are precisely at 217.0 nm and 283.3 nm. These wavelengths are produced in a hollow cathode lamp containing lead. The light

beam, after passing through the flame, is separated in a monochromator and detected with a photomultiplier. AA requires frequent use of calibration standards to obtain precision and accuracy. Typical precision is 1 to 5 percent. Several hundred samples can be analyzed in an 8-hr day if sample preparation procedures are simple.

In an analysis using AA and high-volume samplers, atmospheric concentrations of lead were found to be 0.63 ± 0.30 ng/scm at the South Pole.⁶⁴ Lead analyses of 995 particulate samples from the NASN were accomplished by AA to an indicated precision of 11 percent, with a $0.15 \mu\text{g}/\text{m}^3$ detection limit.⁵⁸

Atomic absorption requires as much care as other techniques to obtain highly precise data. Background absorption, chemical interferences, background light losses, and other factors can cause errors. A major problem with AA is that it has become so popular that untrained operators are using it in many laboratories. But for general purposes, AA is the most readily applicable of any of the analytical methods.

Techniques for AA are still evolving, and improved performance involving nonflame atomization systems, electrode-less discharge lamps, and other equipment refinements and technique developments are to be expected.⁴

4.3.3 Anodic Stripping Voltammetry

Electroanalytical methods of microanalysis based on electrochemical phenomena are found in a variety of forms.^{66,67} They are characterized by a high degree of sensitivity, selectivity, and accuracy derived from the relationships between current, charge, potential, and time for electrodes in solutions. The electrochemistry of lead is based primarily on the plumbous ion, which behaves reversibly in ionic solutions and has a reduction potential near -0.4 volt versus a standard calomel electrode.⁴ Voltammetry, the electrometric method with greatest sensitivity for lead, is discussed here. Other methods are described in the references cited above.

Anodic stripping voltammetry (ASV) describes the process by which the component of interest, lead, is selectively deposited on an electrode by reduction in order to concentrate the component.⁶⁶ The working electrode may be a mercury film on a wax-impregnated graphite electrode. After all of the lead in solution is reduced onto the electrode, the analysis involves a stripping process. In this, the lead is oxidized by means of a linearly variable voltage that is applied to the electrode. The voltammogram,

a plot of current versus voltage, shows a peak corresponding to the oxidation of the lead. The area of the peak corresponds to the quantity of lead ions available at the stripping voltage.

ASV was applied to the analysis of lead in 2-hr samples obtained with a spot tape sampler.¹⁹ Between 80 ng and $2.4 \mu\text{g}$ of lead was present in the samples. The average standard deviation obtained in the lead measurements was 5.9 percent. A detailed procedure for sample preparation and analysis has been published.¹⁹

Voltammetry was also used in analysis of particulate lead collected by an impactor from the ambient atmosphere.⁶⁸ Lead concentrations found were in the 600- to $3000\text{-ng}/\text{m}^3$ range.

Current practice with commercially available ASV equipment allows lead determination at the 1 ppb level with routine 5- to 10-percent relative precision.⁴ Extension to 0.1-ppb levels is attainable with modified techniques.

Differential ASV⁶⁹ and differential-pulsed ASV⁷⁰ are reported to give improved sensitivity and to facilitate more rapid analysis, thus lowering the cost.

4.3.4 Emission Spectroscopy

Optical emission spectroscopy has been used to determine the lead content of soils, rocks, and minerals at the 5- to 10-ppm level with a relative standard deviation of 5 to 10 percent;⁶² this method has also been applied to the analysis of a large number of air samples.^{58,71} The primary advantage of this method is that it allows simultaneous analysis for a large number of elements in a small sample of the material.

Emission spectroscopy essentially consists of observing the optical emission spectra of material excited in a spark, arc, or flame. The wavelength and intensity of the characteristic emission wavelengths of the elements provide both qualitative and quantitative data on composition. Before 1960, the emission spectrometer was the most common instrument in trace-detection laboratories.⁷²

When used for a single element such as lead, emission spectroscopy is at a disadvantage because of the expense of the equipment, the required special operator training, and the use of photographic film in the detection process.⁴ In a study of environmental contamination by automotive lead, sampling times were much reduced by using a sampling technique in which lead-free porous graphite was used both as the filter medium and the electrode in the spectrometer.^{70,73} Lead concentrations of 1 to 10

$\mu\text{g}/\text{m}^3$ could be detected after a half hour flow at 800 to 1200 ml/min through the filter.

Scott et al. analyzed composited particulate samples obtained with high-volume samplers for about 24 elements, including lead, using a direct-reading emission spectrometer.⁷⁴ Over 1000 samples collected by the NASN in 1970 were analyzed. Careful consideration of accuracy and precision led to the conclusion that optical emission spectrometry is a rapid and practical technique for analysis of particulates.

4.3.5 Electron Microprobe

When an intense electron beam is incident on a material, it produces, among other forms of radiation, X rays whose wavelengths depend on the elements present in the material and whose intensity depends on the relative quantities of these elements. This X-radiation is the basis of the electron microprobe method of analysis. An electron beam that gives a spot size as small as $0.2 \mu\text{m}$ is possible. The microprobe is often incorporated in a scanning electron microscope that allows precise location of the beam. Under ideal conditions, the analysis is quantitative, with an accuracy of 1 to 3 percent. The mass of the analyzed element may be in the 10^{-14} to 10^{-16} g range.⁷⁵

Ter Haar and Bayard⁷⁶ applied the electron microprobe method to the analysis of the composition of airborne lead-containing particles. Particles collected on membrane filters were mounted on special substrates and analyzed for lead compounds.⁷⁶ The analysis was based on the ratios of elemental X-ray intensities. From an environmental monitoring viewpoint, the ability to determine the composition of complex lead particulates with high precision was demonstrated. The percentage composition of lead compounds in the sample ranged from a low of 0.1 percent to a high of over 37 percent.

Electron microprobe analysis is not a widely applicable monitoring method. It requires expensive equipment, complex sample preparation, and a highly trained operator. The method is unique, however, in providing composition information on individual lead particles, thus permitting the study of dynamic chemical changes and perhaps allowing improved source identification.

4.3.6 X-Ray Fluorescence

X-ray fluorescent emissions that characterize the elemental content of a sample occur when atoms are irradiated at sufficient energy to remove an inner-

shell electron.⁴ This fluorescence allows simultaneous identification of a range of elements, including lead. For example, 22 elements were identified and quantitatively analyzed in particulate samples from dichotomous samplers without intermediate sample preparation.¹⁶ This analytical method is identical to that described for the electron microprobe in the preceding section but utilizes different excitation sources.

X-ray fluorescence requires a high-energy irradiation source. X-ray tubes,^{16,23} electron beams,⁷⁵ and radioactive isotope sources⁷⁷ have been used extensively.^{78,79} To reduce background, secondary fluorescers have been employed.¹⁶ The fluorescent X-ray emission from the sample may be analyzed with a crystal monochromator and detected with scintillation, with proportional counters,⁴ or with low-temperature semiconductor detectors that discriminate the energy of the fluorescence. The latter technique requires a very low level of excitation.¹⁶

X-ray emission induced by charged-particle excitation (proton-induced X-ray emission, or PIXE) offers an attractive alternative to the more common techniques.⁸⁰⁻⁸² Recognition of the potential of heavy-particle bombardment for excitation occurred in 1970, and an interference-free sensitivity down to the picogram range was demonstrated.⁸⁰ The excellent capability of accelerator beams for X-ray emission analysis is partially due to the relatively low background radiation associated with the excitation. The main contribution is Bremsstrahlung from secondary electron emission. The high particle fluxes obtainable from accelerators also contribute to the sensitivity of the PIXE method. Literature reviews⁸³⁻⁸⁶ on approaches to X-ray elemental analysis agree that protons of a few MeV energy provide a preferred combination for high sensitivity analyses under conditions less subject to matrix interference effects. As a result of this premise, a system designed for routine analysis has been described,⁸¹ and papers involving the use of PIXE for aerosol analysis have recently appeared.^{81,82}

Advantages of X-ray fluorescence methods include the ability to detect a variety of elements, the ability to analyze with little or no sample preparation, and the availability of automated analytical equipment. Disadvantages include the need for low blank filters, expensive equipment, liquid nitrogen (e.g., for energy-dispersive models, and highly trained analysts. The detectability level for lead is about $20 \text{ ng}/\text{cm}^2$ of filter area, which is well below

the quantity obtained in normal sampling periods with the dichotomous sampler.¹⁶

4.3.7 Methods for Compound Analysis

Colorimetry, atomic absorption, and anodic stripping voltammetry are restricted to measurement of total lead and thus cannot identify the various compounds of lead. The electron microprobe and other X-ray fluorescence methods provide approximate data on compounds on the basis of the ratios of elements present.⁷⁶ Gas chromatography using the electron capture detector has been demonstrated to be useful for organic lead compounds.²⁸ Powder X-ray diffraction techniques have been applied to the identification of lead compounds in soil.³⁴

4.4 CONCLUSIONS

To monitor lead aerosol in air, sampling with the high-volume sampler and analysis by atomic absorption spectrometry have emerged as the most widely used method. Sampling in this way does not provide for fractionation of the particles according to size, nor does it allow determination of the gaseous (organic) concentrations; these capabilities may prove important for special studies. The size distribution of lead aerosol is important in considering questions regarding exposure by inhalation; sampling with cascade impactors or dichotomous samplers is necessary to such evaluations. To determine gaseous lead, it is necessary to back the filter with chemical scrubbers or a crystalline iodine trap.

X-ray fluorescence and optical emission spectroscopy are applicable to multielement analysis and are convenient to apply to the measurement of lead in such studies. Because of the many environmental variables implicit in site monitoring, the development of useful biological monitoring techniques may be of more direct utility.

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5. SOURCES AND EMISSIONS

5.1 NATURAL SOURCES

Lead enters the biosphere from lead-bearing minerals in the lithosphere through both natural and human-mediated processes. Measurements of surface materials taken at 8-in. depths in the continental United States¹ show a median lead concentration of 15 ppm. Ninety-five percent of these measurements show 30 ppm of lead or less, with a maximum sample concentration of 700 ppm. In natural processes, lead is first incorporated in soil in the active soil zone, from which it may be absorbed by plants, leached into surface waters, or eroded into windborne dusts.²⁻⁵ In addition, minute amounts of radioactive ²¹⁰Pb reach the atmosphere through the decay of radon gas released from the earth.⁶

Because lead has been used for centuries, it is difficult to determine the range of natural background levels. Calculations of natural contributions using geochemical information, however, indicate that natural sources contribute a relatively small amount of lead to the environment. For example, if the typical 25 to 40 $\mu\text{g}/\text{m}^3$ or rural airborne particulate matter were derived from surface materials containing 15, and rarely more than 30, ppm lead as cited above, then the natural contribution to airborne lead would range from 0.0004 to 0.0012 $\mu\text{g}/\text{m}^3$. In fact, levels as low as 0.0012 to 0.029 $\mu\text{g}/\text{m}^3$ have been measured at a site in California's White Mountains.⁷ In contrast, however, annual average lead concentrations in urban suspended particulate matter⁸ range as high as 6 $\mu\text{g}/\text{m}^3$. Clearly, therefore, most of this urban particulate lead stems from man-made sources.

5.2 MAN-MADE SOURCES

5.2.1 Production

Lead occupies an important position in the U.S. economy, ranking fourth among the nonferrous metals in tonnage used. The patterns of its flow through industry are identified in Figure 5-1.⁹ Approximately 85 percent of the primary lead produced in this country is from native mines,¹⁰ where it is often associated with minor amounts of zinc, cad-

mium, copper, bismuth, gold, silver, and other minerals.¹⁰ Missouri ore deposits account for about 80 percent of the domestic production.

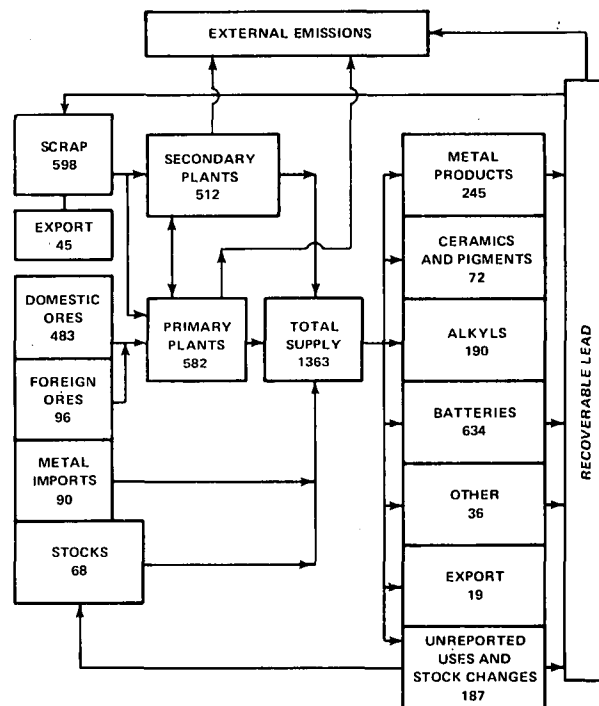


Figure 5-1. Approximate flow of lead through U.S. industry in 1975, metric tons.⁹

5.2.2 Utilization

The reported uses of lead, listed by major product categories in Table 5-1,¹¹ stood at nearly 1.2 million MT in 1975, with an estimated consumption for 1976 of 1.35 million MT.¹²

Certain products, especially batteries, cables, plumbing, weights, and ballast, contain lead that is economically recoverable as secondary lead. This reserve of lead in use is estimated at 3.8 million MT, of which about 0.6 million MT is recovered annually. Lead in pigments, gasoline additives, ammunition, foil, solder, and steel products is widely dispersed and therefore is largely unrecoverable.

TABLE 5-1. U.S. CONSUMPTION OF LEAD BY PRODUCT CATEGORY¹¹
(MT/yr)

Product category	1971	1972	1973	1974	1975
Storage batteries	616,581 (679,803) ^a	661,740 (729,592)	697,888 (769,447)	772,656 (851,881)	634,368 (699,414)
Gasoline antiknock additives	239,666 (264,240)	252,454 (278,340)	248,890 (274,410)	227,847 (251,210)	189,369 (208,786)
Pigments and ceramics	73,701 (81,567)	80,917 (89,214)	98,651 (108,766)	105,405 (116,213)	71,718 (79,072)
Ammunition	79,423 (87,567)	76,822 (84,699)	73,091 (81,479)	78,991 (87,090)	68,098 (75,081)
Solder	63,502 (70,013)	64,659 (71,289)	65,095 (71,770)	60,116 (66,280)	52,011 (57,344)
Cable coverings	47,998 (52,920)	41,659 (45,930)	39,006 (43,005)	39,387 (43,426)	20,044 (22,099)
Caulking lead	27,204 (29,993)	20,392 (22,483)	18,192 (20,057)	17,903 (19,739)	12,966 (14,296)
Pipe and sheet lead	41,523 (45,781)	37,592 (41,447)	40,529 (44,685)	34,238 (37,749)	35,456 (39,092)
Type metal	18,876 (20,812)	18,089 (19,944)	19,883 (21,922)	18,608 (20,516)	14,703 (16,211)
Brass and bronze	18,180 (20,044)	17,963 (19,805)	20,621 (22,735)	20,172 (22,240)	12,157 (13,404)
Bearing metals	14,771 (16,285)	14,435 (15,915)	14,201 (15,657)	13,250 (14,609)	11,051 (12,184)
Weight ballast	15,830 (17,453)	19,321 (21,302)	18,909 (20,848)	19,426 (21,418)	18,156 (20,018)
Other	41,128 (45,345)	43,803 (48,294)	42,110 (46,428)	42,680 (47,056)	36,368 (40,097)
Total	1,298,383 (1,431,514)	1,349,846 (1,488,254)	1,397,876 (1,541,209)	1,450,679 (1,599,427)	1,176,465 (1,297,098)

^a Short tons/yr given in parentheses.

5.2.3 Emissions

Lead or its compounds may enter the environment at any step during its mining, smelting, processing, use, or disposal. Recent estimates of the dispersal of lead emissions into the environment by principal sources indicate that the atmosphere is the major initial recipient. Estimated lead emissions to the atmosphere in 1975 are shown in Table 5-2.

Mobile and stationary sources of lead emissions, although found throughout the nation, tend to be concentrated in areas of high population density, with the exception of smelters. Figure 5-2 shows the approximate locations of major lead mines, primary smelters, alkyl lead plants, and manufacturers of lead storage batteries.¹³

5.2.3.1 MOBILE SOURCES

The largest source, by far, of lead emissions to the

atmosphere is the exhaust of motor vehicles powered by gasoline that contains lead additives.¹⁴ These mobile-source emissions collectively constitute an estimated 88 percent of total lead emissions (Table 5-2).⁹ Other mobile sources, including aviation usage of leaded gasoline and diesel and jet fuel combustion, contribute insignificant lead emissions to the atmosphere.

Lead particulates emitted in automotive exhaust may be divided into two size classes. Particles initially formed by condensation of lead compounds in the combustion gases are quite small in size (well under 0.1 μm in diameter). Particles in this size category that become airborne can remain suspended in the atmosphere for long periods and thus can travel substantial distances from the original sources. Larger particles are also formed as a result of agglomeration of smaller condensation particles.

TABLE 5-2. ESTIMATED ATMOSPHERIC LEAD EMISSIONS FOR THE UNITED STATES, 1975.^a

Source category	Annual emissions, MT/yr	Emissions as percentage of	
		Subtotal	Total
Mobile subtotal	142,000	100	—
Gasoline combustion	142,000	100	88.1
Stationary subtotal	19,225	100	—
Waste oil combustion	10,430	54.3	6.5
Solid waste incineration	1,630	8.5	1.0
Coal combustion	400	2.1	0.2
Oil combustion	100	0.5	0.1
Gray iron production	1,079	5.6	0.7
Iron and steel production	844	4.4	0.5
Secondary lead smelting	755	3.9	0.4
Primary copper smelting	619	3.2	0.4
Ore crushing and grinding	493	2.5	0.3
Primary lead smelting	400	2.1	0.2
Other metallurgical	272	1.4	0.2
Lead alkyl manufacture	1,014	5.3	0.6
Type metal	436	2.3	0.3
Portland cement production	313	1.6	0.2
Pigments	112	0.6	0.1
Miscellaneous	328	1.7	0.2
Total	161,225	—	100

^a Inventory does not include emissions from exhausting workroom air, burning of lead-painted surfaces, welding of lead-painted steel structures, or weathering of painted surfaces.

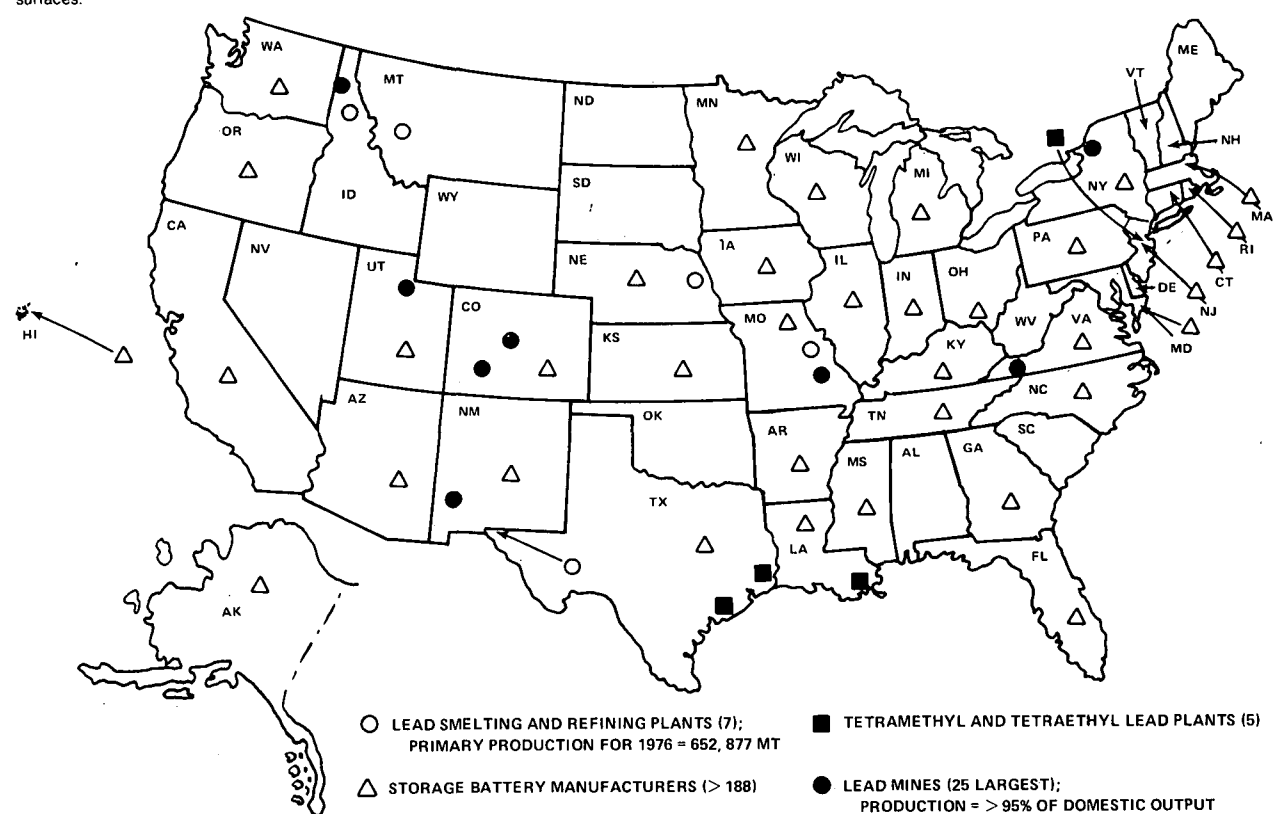


Figure 5-2. Location of major lead operations in the United States, 1976.¹³

These larger particles, which may be tens of micrometers or larger in diameter, behave in the atmosphere like the larger lead particulates emitted from most stationary sources and fall to the ground in the vicinity of the traffic producing them. The distribution of lead exhaust particles between the smaller and larger size ranges appears to depend on a number of factors, including the particular driving pattern in which the vehicle is used and its past driving history (Chapter 6). But as an overall average, it has been estimated¹⁵ that during the lifetime of the vehicle, approximately 35 percent of the lead contained in the gasoline burned by the vehicle will be emitted as fine particulate, and approximately 40 percent will be emitted as coarse particulate. The remainder of the lead consumed in gasoline combustion is deposited in the engine and exhaust system. Engine deposits are, in part, gradually transferred to the lubricating oil and removed from the vehicle when the oil is changed. Moreover, some oils and lubricants contain lead naphthenate as a detergent. The fate of spent oil and its lead content is of considerable importance. A measure of its significance is reflected in the waste oil combustion values in Table 5-2. In addition, some of the lead deposited in the exhaust system gradually flakes off, is emitted in the exhaust as extremely large particles, and rapidly falls into the streets and roads where it is incorporated into the dust and washed into sewers or onto adjacent soil.

The use of lead additives in gasoline, which was increasing in total volume for many years, is now decreasing as cars designed to use lead-free gasoline constitute a growing portion of the total automotive population (see Section 7.1.1). Regulations promulgated by EPA¹⁶ that limit the average concentration of lead additives in gasoline will contribute to a further reduction in future automotive lead emissions.

5.2.3.2 STATIONARY SOURCES

As shown in Table 5-2 (based on 1975 emission estimates⁹), solid waste incineration and combustion of waste oil are the principal contributors of lead emissions from stationary sources, accounting for two-thirds of stationary source emissions. The manufacture of consumer products such as lead glass, storage batteries, and lead additives for gasoline also contributes significantly to stationary source lead emissions. Since 1970, the quantity of lead emitted from the metallurgical industry has decreased somewhat because of the application of control equipment and the closing of several plants,

particularly in the zinc and pyrometallurgical industries.

A new locus for lead emissions emerged in the mid-sixties, however, with the opening of the "Viburnum Trend" or "New Lead Belt" in southeastern Missouri. The presence of seven mines and two accompanying lead smelters in this area makes it the largest lead-producing district in the world and has moved the United States into first place among the world's lead-producing nations. An extensive study to assess the impact of the expanding lead industry in Missouri and to stimulate new emission control technology has been initiated.¹⁷

Although some contamination of soil and water occurs as a result of such mechanisms as leaching from mine and smelter wastes, quantitative estimates of the extent of this contamination are not available. Spillage of ore concentrates from open trucks and railroad cars, however, is known to contribute significantly to contamination along transportation routes. For example, along two routes used by ore trucks in southeastern Missouri, lead levels in leaf litter ranged from 2000 to 5000 $\mu\text{g/g}$ at the roadway, declining to a fairly constant 100 to 200 $\mu\text{g/g}$ beyond about 400 ft from the roadway.¹⁷

Another possible source of land or water contamination is the disposal of particulate lead collected by air pollution control systems. The potential for impact on soil and water systems of the disposal of dusts collected by these control systems has not been quantified.

The lead-containing particles emitted from stationary sources occur in various sizes. Those emitted from uncontrolled stationary sources generally include particles larger than 1- to 2- μm mass mean diameter, and therefore tend to settle out near the source. These large-particle emissions add considerable lead to the dust, soil, water, and vegetation in the neighborhood of the source (see Section 7.2). Uncontrolled sources also contribute substantial quantities of smaller-diameter particles to the atmosphere, where long-range transport may occur. When controls are applied to stationary sources, the total mass of the emissions is reduced significantly. But the number of particles being emitted may not be affected greatly if most of the particles emitted are small, because current particulate control methods are usually more effective in removing the larger-diameter particles. The smaller-diameter particles (below 2 μm) may be far greater in number than the larger, more massive particles; and with diminishing size, an increasing proportion is likely to escape collection. Generally, control methods are

applied to emissions from stacks, vents, and other process outlets. But lead-containing particles may also be emitted as fugitive dusts in the larger size range ($>2\text{-}\mu\text{m}$ diameter) from less controllable sources such as windows and doors, conveyors, and waste piles. Available emission inventories do not include emissions from the exhaust of workroom air, burning of lead-painted surfaces, weathering of lead-painted surfaces, etc. The magnitude of emissions from these sources is unknown.

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6. TRANSFORMATION AND TRANSPORT

6.1 INTRODUCTION

The circulation of lead in the environment (shown conceptually in Figure 6-1) illustrates that lead released into the atmosphere can be delivered to man (animals) via several routes. At present, it is possible to obtain only qualitative or semiquantitative estimates of the movement of lead within and among the various environmental media. This is largely because the physical and chemical transformations occurring within the lead cycle are not well understood. The purpose of this chapter is to summarize the available data that reflect what is known about the transformation and transport mechanisms controlling the distribution and fate of lead in the environment in its various chemical forms. Primary emphasis is placed on the atmosphere, since it serves as the principal medium for transport of lead from manmade sources.

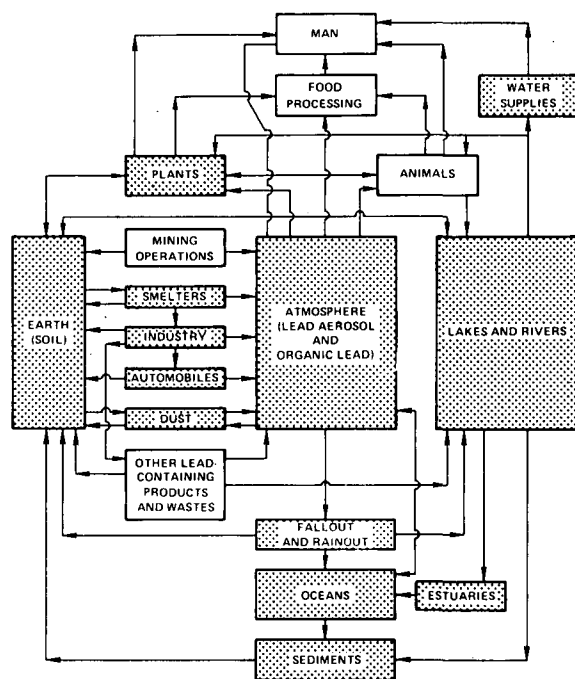


Figure 6-1. Simplified ecologic flow chart for lead showing principal cycling pathways and compartments.

6.2 PHYSICAL AND CHEMICAL TRANSFORMATIONS IN THE ATMOSPHERE

Although lead is introduced into the atmosphere primarily in the particulate form, relatively small amounts are also emitted in the vapor phase. Once lead is introduced into the atmosphere, important physical and chemical changes occur before its transfer to other environmental media. The discussion of these changes will be divided into mobile and stationary source categories. This division is somewhat arbitrary in that the pollutants from both source categories are well mixed in the atmosphere. In those cases in which one type of source predominates (e.g., freeways or smelters), the approach should be reasonably realistic.

6.2.1 Physical Transformations

6.2.1.1 SIZE DISTRIBUTION OF PARTICLES FROM MOBILE SOURCES

Automotive exhaust is the primary source of particulate lead introduced ubiquitously into the atmosphere in urban areas. The size of the particles emitted may range from a few hundredths of a micrometer in diameter to several millimeters, depending on the operating mode, age of exhaust system, fuel lead content, speed and load, acceleration, deceleration, engine condition, and other factors.

Numerous environmental processes, including transformation, transport, deposition, and mechanisms of impact, are prominently influenced by the particle sizes. It is significant, for example, that the sizes of the particles directly affect the probability of lead's being transported via the respiratory system. Because of the importance of lead particle sizes in relation to numerous environmental questions, the size distributions of those particles emitted from automobiles have been studied by many investigators.¹⁻¹⁰

Figure 6-2 shows the results of a series of variable speed tests made by Hirschler and Gilbert⁴ on an auto after about 25,000 miles of deposit accumula-

tion in the exhaust system. The data demonstrate that smaller lead particles make up the largest fraction of those exhausted, and that there is significant exhaust system accumulation of lead particles in both size categories under city-driving conditions. During acceleration, release of these accumulations is quite rapidly induced, but the increased emission drops off during the period of constant highway speed. The effect of speed on the particle size distribution shown in Figure 6-3, as found by Ganley and Springer,³ also demonstrates that the mean particle sizes emitted decrease with increasing speed. The results of these two studies imply that although larger lead particles are most likely to be deposited in the exhaust system, the deposits are released by ablative processes that cause decreases in particle size. Figure 6-4 compares size distributions at receptor sites in California with those typical of undiluted auto exhaust. The smaller sizes at the receptor sites reflect the decrease in the mean size caused by gravitational settling and other scavenging processes that occur during atmospheric transport. Figure 6-5 compares differential mass distributions at the California receptor sites with those at a freeway site. These distributions are generally bimodal, indicating that particulate lead in the atmosphere may consist of lead emitted by autos and lead that has been deposited on surfaces (soil) and re-entrained via atmospheric turbulence (fugitive dust); or the bimodal distribution may reflect emission patterns. The results of these studies generally indicate that more than half of the lead particles are typically less than $1 \mu\text{m}$ in diameter, but these estimates may be biased by the failure to use isokinetic sampling techniques (see Section 4.2.3.1).

Lee et al.⁹ measured the concentrations and size distributions of particulate emissions from automobile exhaust and found that 95 percent of the total particulate lead was in particles with mass median equivalent diameters (MMED) less than $0.5 \mu\text{m}$. All samples were taken at steady-cruise conditions and thus do not represent the typical discharge of particles under wide-open-throttle accelerations, decelerations, and short-term cruise and idle conditions typical of urban traffic. The varying modes result in the discharge of much larger particles. Robinson and Ludwig¹¹ reported MMED of $0.25 \mu\text{m}$ for urban and rural areas; 25 percent of the particles were smaller than $0.16 \mu\text{m}$, and 25 percent were larger than $0.43 \mu\text{m}$ (Table 6-1). Cholak et al.,¹² Lee et al.,¹³ and Flesch¹⁴ observed similar distributions; however, their data also indicate that these distributions change very little over distances.

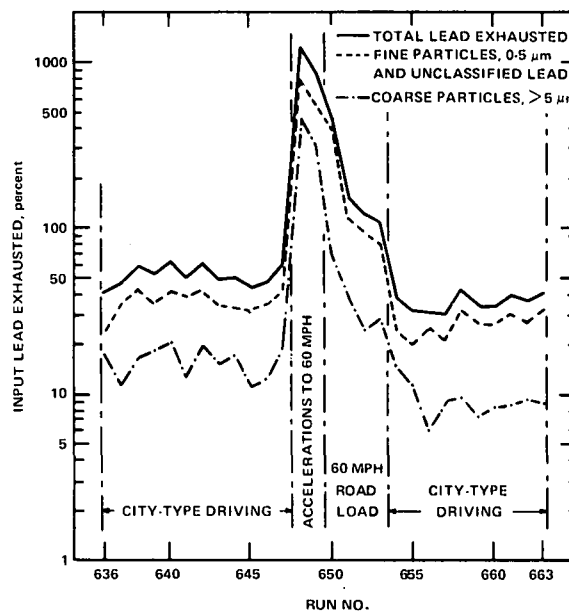


Figure 6-2. Effect of various driving conditions on the amount of lead exhausted.⁴

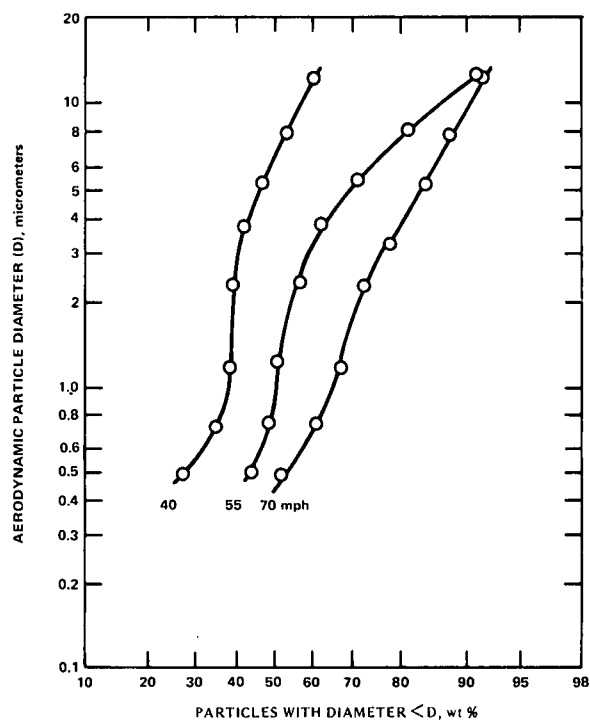


Figure 6-3. Effect of speed on size distribution of exhaust particles at different road load cruise conditions and using indolene HO 0 fuel.³

Gillette and Winchester¹⁵ examined the effect of age on the size distribution of lead aerosols. They found that lead aerosol size distributions do not vary greatly from one source area (essentially an area of heavy automobile traffic) to another, and that the

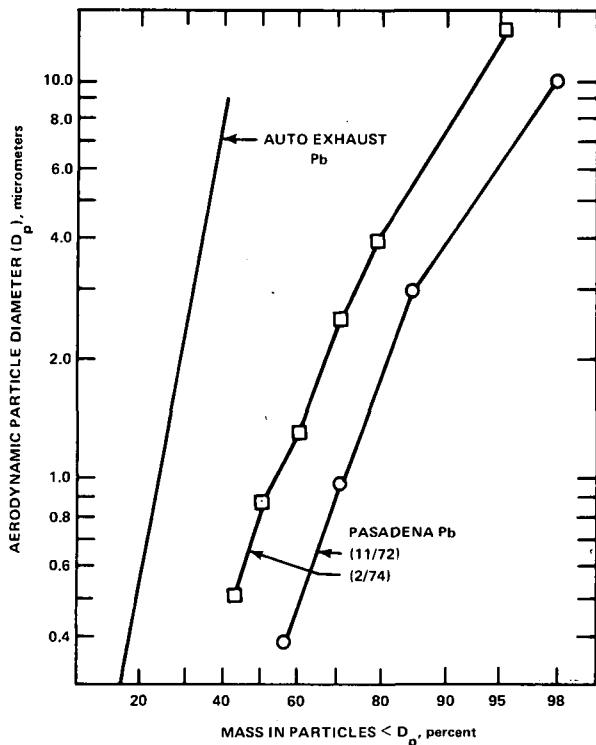


Figure 6-4. Cumulative mass distributions for lead aerosol in auto exhaust and at Pasadena, a receptor sampling site. The abscissa is a log-normal scale, and D_p is the aerodynamic, unit density particle diameter.¹⁰

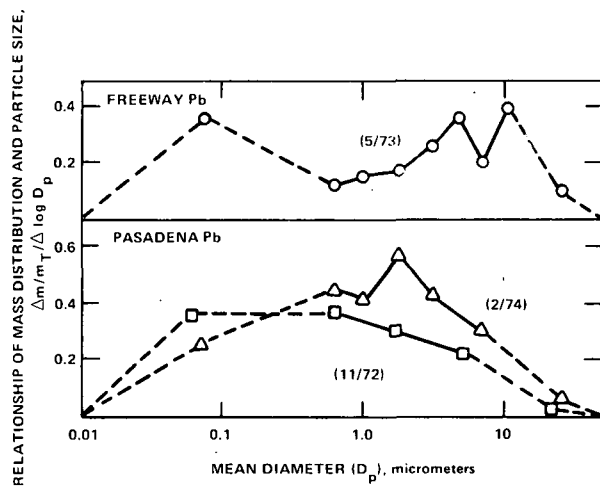


Figure 6-5. Differential mass distributions for lead 1 m from a freeway, May 1973, and at Pasadena sampling sites, November 1972 and February 1974. (The abscissa is the mean diameter, and the dashed lines assume that the smallest particle size is $0.01 \mu\text{m}$ and the largest $50 \mu\text{m}$. $\Delta \log D_p$ = interval of log of aerodynamic particle diameter; m_T = total mass loading of lead in airborne particulates; Δm = mass of lead occurring in a fraction, defined in terms of size, of the total particulates; $\Delta m/m_T$ = fraction of mass occurring in a given particle size range.)¹⁰

lead aerosol size distributions do not respond noticeably to changes in weather within a source area during 24-hr sampling periods. The results of their study suggest little modification of the characteristics of the lead aerosol size distribution as a result of nonprecipitative atmospheric mechanisms for equivalent particle radii larger than $0.2 \mu\text{m}$.

Electron microscope studies have shown that many of the fine particles in exhaust emissions are nearly spherical in shape and are electron-dense. The coarser particles are much more irregular, and some are filamentous in outline. Particles collected at a constant cruise speed of 30 mph were found to be composed of a carbon core or matrix, on or in which were distributed spherical or crystalline electron-dense lead particles $< 0.1 \mu\text{m}$ in diameter.^{3,16} Electron micrographs of the exhaust particles have shown that although the particle aggregates of about $0.5 \mu\text{m}$ were stable, samples of the gas that had been inhaled showed more homogeneous aggregates 1 to 2 micrometers in diameter than larger aggregates in the exhaled gas. A similar effect was obtained by drawing the gas through a humidifier.¹⁷

6.2.1.2 SIZE DISTRIBUTION OF PARTICLES FROM STATIONARY SOURCES

High-temperature combustion and smelting processes generate submicrometer-sized lead particulate, whereas lead emissions from material handling and mechanical attrition operations associated with smelters consist of larger ($> 1 \mu\text{m}$) dust particles. Actual data on the size distribution of lead particles emitted from stationary sources are limited. Fugas et al.,¹⁸ using a five-stage impactor, obtained samples in the Meza Valley (influenced by a lead smelter) and in the urban area of Zagreb. The results are shown in Figure 6-6. A considerable difference was found in the size distribution of lead particles in the industrial (Meza Valley) versus the urban (Zagreb) area. In the industrial area, only 10 percent of the lead particles had diameters smaller and $1 \mu\text{m}$, whereas in the urban area, 75 percent were smaller than $1 \mu\text{m}$. This implies that the fugitive dust from the mechanical rather than the direct-smelting operation is the primary emission.

Lead emissions from stationary sources are probably affected by topographic influences in a manner similar to other pollutants. Because of the mountainous location of half of the six primary lead smelters in the United States, however, and because these three smelters are probably the largest single-point emitters of lead, the topographic influence on transport and dispersion is important.

TABLE 6-1. COMPARISON OF SIZE DISTRIBUTIONS OF LEAD-CONTAINING PARTICLES IN MAJOR SAMPLING AREAS¹¹

Sample area	No. of samples	Distribution by particle size, μm					
		25%		MMED ^a		75%	
		Avg.	Range	Avg.	Range	Avg.	Range
Chicago	12	0.19(7) ^b	0.10-0.29	0.30	0.16-.64	0.40(10)	0.28-0.63
Cincinnati	7	0.15(3)	0.09-0.24	0.23	0.16-0.28	0.44	0.30-0.68
Philadelphia	7	0.14(3)	0.09-0.25	0.24	0.19-0.31	0.41	0.28-0.56
Los Angeles (DTN)	8	0.16(7)	0.10-0.22	0.26	0.19-0.29	0.49(7)	0.39-0.60
Pasadena	7	0.18	0.05-0.25	0.24	0.08-0.32	0.48(6)	0.13-0.67
Vernon (rural)	5	0.17(4)	0.12-0.22	0.24	0.18-0.32	0.40	0.28-0.47
San Francisco	3	0.11	0.06-0.13	0.25	0.15-0.31	0.45(2)	0.44-0.46
Cherokee (rural)	1	0.25	—	0.31	—	0.71	—
Mojave (rural)	1	—	—	0.27	—	0.34	—

^aMMED = mass median equivalent diameter.

^bNumbers in parentheses indicate number of samples available for a specific value when different from total number of samples.

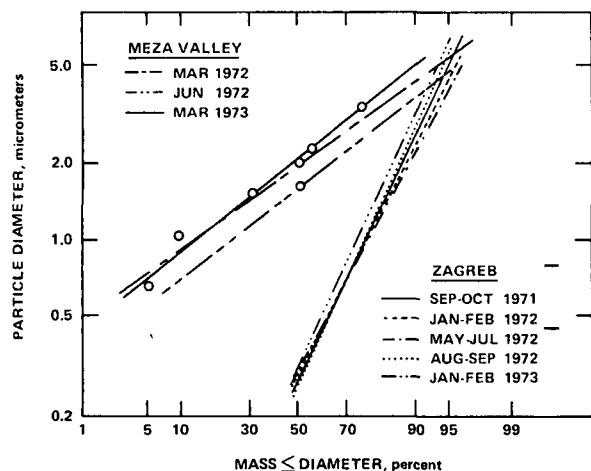


Figure 6-6. Cumulative mass distribution of lead particles by size.¹⁸

At least four general conclusions about lead from mobile and stationary sources can be based on the results of the above studies:

1. Lead is emitted into the atmosphere principally in the particulate form.
2. The mass median equivalent diameters of the lead-bearing particles are typically less than $1 \mu\text{m}$, and the size distributions are fairly uniform from area to area.
3. The particle sizes in urban and rural areas are such that the lead can be transported over relatively large distances via typical atmospheric convection and turbulence processes.
4. The size distributions are such that significant fractions of the total atmospheric lead concentrations are within the respirable size range.

6.2.2 Chemical Transformations

6.2.2.1 MOBILE SOURCE EMISSIONS

Tetraethyl lead (TEL) and tetramethyl lead (TML), as well as the mixed-lead alkyls, are used widely as additives in gasoline. Although these organic compounds are less volatile than gasoline, small amounts may escape to the atmosphere by evaporation from fuel systems or storage facilities. TEL and TML are light-sensitive and undergo photochemical decomposition when they reach the atmosphere.^{10,19} The lifetime of TML appears to be longer than that of TEL. Exposure of dust to TEL, both in the presence and absence of water vapor, results in sorption of organic lead on dust particle surfaces.²⁰ Laveskog²¹ found that transient peak lead alkyl concentrations up to $5000 \mu\text{g}/\text{m}^3$ in exhaust gas may be reached in a cold-started, fully choked, and poorly tuned vehicle. If a vehicle with such emissions were to pass a sampling station on a street where the lead alkyl level might typically be 0.02 to $0.04 \mu\text{g}/\text{m}^3$ of air, a peak of about $0.5 \mu\text{g}/\text{m}^3$ could be measured as the car passed by. The data reported by Laveskog were obtained with a procedure that collected very small (100 ml), short-time (10 min) air samples. The sensitivity reported was much better than that reported by other investigators, who have not been able to duplicate his results.²² Harrison et al.²² found levels as high as $0.59 \mu\text{g}/\text{m}^3$ (9.7 percent of total lead) at a busy gasoline service station.

Purdue et al.²³ measured particulate and organic lead in atmospheric samples. Some results are shown in Tables 6-2 through 6-4. These data demonstrate that in all of the cities studied, particulate lead levels are much higher (an average of approximately 20

times higher) than organic lead levels. The results are entirely consistent with the studies of Huntzicker et al.,¹⁰ who report an organic component of 6 percent of the total airborne lead in Pasadena for a 3-day period in June 1974, and of Skogerboe,²⁴ who measured fractions in the range of 4 to 12 percent at a site in Fort Collins, Colorado. It is noteworthy, however, that in the underground garage (Table

6-4), total lead concentrations are approximately five times those in the urban areas, and the percentage of organic lead increases to approximately 17 percent. Consequently, the concentration of organic lead in an underground garage site is ten times that in the open urban environment (see Tables 6-2 and 6-4), and the potential exposure level is similarly magnified.

TABLE 6-2. RESULTS OF ATMOSPHERIC SAMPLING FOR ORGANIC AND PARTICULATE LEAD²³($\mu\text{g}/\text{m}^3$)

Sample no. ^a	Cincinnati		Denver		Washington, D.C.		St. Louis		Philadelphia		Chicago	
	Organic ^b	Particulate ^c	Organic	Particulate	Organic	Particulate	Organic	Particulate	Organic	Particulate	Organic	Particulate
1	0.2	1.5	0.2	2.3	0.0	1.4	0.5	2.0	0.5	1.3	0.2	5.9
2	0.0	0.9	0.5 ^d	1.8	0.2	1.4	0.2	2.0	1.1 ^d	1.7	0.4	5.6
3	0.0	0.9	1.4 ^d	1.6	0.1	1.5	0.4	1.8	0.2	2.9	0.2	5.3
4	0.2	1.9	0.3	1.7	0.3	1.0	0.2	2.5	0.4	2.4	1.6 ^d	3.5
5	0.4	3.7	0.2	1.0	0.1	1.1	0.3	1.9	0.8	1.1	0.2	4.6
6	0.2	1.6	0.1	1.8	0.1	0.8	0.2	1.8	0.4	1.1	0.2	5.5
7	0.2	1.8	0.0	2.2	0.1	1.7	0.3	2.2	0.0	1.7	0.3	5.8
8	0.4	1.3	0.2	1.8	0.2	1.2	0.4	2.2	0.3	2.1	0.1	4.8
9	0.2	1.5	0.2	2.0	0.4	0.8	0.4	2.0	0.1	1.8	0.2	5.0
10	0.2	2.4	0.5 ^d	—	0.2	1.6	1.3 ^d	1.2	0.1	2.3	0.2	5.1
Avg.	0.2	1.7	0.2	1.8	0.2	1.2	0.3	2.0	0.3	1.8	0.2	5.1

^aSample no. represents order in which samples were taken. Cities were not sampled concurrently.
^bAll values are average of two determinations.
^cDetermined by NASN method (6).
^dOrganic lead averages do not include these values because the replicate values for these samples were more than twice the standard deviation from the average.

TABLE 6-3. PERCENTAGE OF PARTICULATE VERSUS VAPOR-PHASE LEAD IN URBAN AIR SAMPLES²³

City	Total lead ^a		
	Organic, $\mu\text{g}/\text{m}^3$	Particulate, $\mu\text{g}/\text{m}^3$	Particulate, % of total
Cincinnati	0.2	1.7	89
Denver	0.2	1.8	90
Washington, D.C.	0.2	1.2	86
St. Louis	0.3	2.0	87
Philadelphia	0.3	1.8	86
Chicago	0.2	5.1	96

^aAll values are averages of ten determinations.
^bPercent particulate Pb = $\frac{\text{particulate Pb} \times 100}{\text{organic Pb} + \text{particulate Pb}}$

TABLE 6-4. ANALYSES OF FIVE REPLICATE SAMPLES TAKEN IN AN UNDERGROUND PARKING GARAGE²³

Sample no.	Organic lead, $\mu\text{g}/\text{m}^3$	Organic lead, %	Particulate lead, $\mu\text{g}/\text{m}^3$	Total lead, $\mu\text{g}/\text{m}^3$
1	1.9	15.7	10.3	12.2
2	1.9	17.1	9.2	11.1
3	1.9	17.6	8.9	10.8
4	1.8	14.9	10.3	12.1
5	2.2	18.0	10.0	12.2
Average (\bar{X})	1.9	16.7	9.7	11.6
Relative standard deviation (Srel) ^a	7.9%	7.9%	6.7%	5.2%

^aSrel = $\frac{\text{Standard deviation}}{\text{Average}} \times 100$

As the lead alkyl compounds of gasoline are subjected to the elevated temperatures and pressure of combustion, they are converted to lead oxides, which function to inhibit engine knock. The lead oxides react with other additives in the fuel and leave the combustion chambers in a variety of complex compounds. The results of composition studies by Hirschler and Gilbert,⁴ Ter Haar et al.,² and Ter Haar and Bayard²⁵ are shown in Tables 6-5 and 6-6, respectively.

Habibi et al.⁵ determined the composition of particulate matter emitted from a test car operating on a typical driving cycle. The main conclusions drawn from the study were:

1. Composition of emitted exhaust particles is related to particle size.
2. Very large particles greater than 200 μm have a composition similar to lead-containing material deposited in the exhaust system, confirming that they have been re-entrained or have flaked off from the exhaust system. These particles contain approximately 60 to 65 percent lead salts, 30 to 35 percent ferric oxide (Fe_2O_3), and 2 to 3 percent soot and carbonaceous material. The major lead salt is lead bromochloride (PbBrCl), with large amounts (15 to 17 percent) of lead oxide

TABLE 6-5. AVERAGE COMPOSITION OF PARTICULATE LEAD COMPOUNDS EMITTED IN AUTO EXHAUST^{a,2,4}

Exhaust source	Compound, ^b wt. %				
	PbCl-Br	α -NH ₄ Cl- 2PbCl-Br	β -NH ₄ Cl- 2PbCl-Br	2NH ₄ Cl- PbCl-Br	3Pb ₃ (PO ₄) ₂ - PbCl-Br
Car B:					
City type cycle, fuel plus TEL motor mix only.....	68	24	6	2	—
City type cycle, added sulfur ^c	70	30	—	—	—
City type cycle, added phosphorus ^d	35	18	17	10	20
Constant speed, 60 mph, road load.....	60	20	20	—	—
Full-throttle accelerations.....	85	10	5	—	—
Car M:					
City type cycle, fuel plus TEL motor mix only.....	33	40	5	22	—
Constant speed, 60 mph, road load.....	30	30	35	5	—
Full-throttle accelerations.....	90	10	—	—	—

^aX-ray diffraction analyses made *in situ* on material deposited on glass slides mounted within the precipitator of the sampler.

^bIn addition to the tabulated compounds, PbSO₄ and PbO·PbCl-Br·H₂O occurred occasionally in concentrations of 5 percent or less.

^cSulfur content increased from 0.025 to 0.105 weight percent by addition of disulfide oil.

^d0.4 theory phosphorus added.

TABLE 6-6. EFFECTS OF AGING ON LEAD COMPOUNDS IN SAMPLES OF AUTO EXHAUST AS DETERMINED BY ELECTRON MICROPROBE²⁵

Lead compound	Percentage of total particles sampled				
	Black bag ^a		Eight-Mile Road ^b		Rural site ^c
	Zero time	18 hour	Near road	400 yd	
PbCl ₂	10.4	8.3	11.2	10.5	5.4
PbBr ₂	5.5	0.5	4.0	0.7	0.1
PbBrCl	32.0	12.0	4.4	0.6	1.6
Pb(OH)Cl	7.7	7.2	4.0	8.8	4.0
Pb(OH)Br	2.2	0.1	2.0	1.1	—
(PbO) ₂ ·PbCl ₂	5.2	5.6	2.8	5.6	1.5
(PbO) ₂ ·PbBr ₂	1.1	0.1	0.7	0.3	—
(PbO) ₂ ·PbBrCl	31.4	1.6	2.0	0.6	1.0
PbCO ₃	1.2	13.8	15.6	14.6	30.2
Pb ₃ (PO ₄) ₂	—	—	0.2	0.3	—
PbO _x	2.2	21.2	12.0	25.0	20.5
(PbO) ₂ ·PbCO ₃	1.0	29.6	37.9	21.3	27.5
PbO·PbSO ₄	—	0.1	1.0	4.6	5.0
PbSO ₄	0.1	—	2.2	6.0	3.2

^aSample collected directly from tailpipe in black bag to prevent irradiation of exhaust. Analyzed immediately and again 18 hr later to determine effect of aging.

^bState highway in Detroit carrying about 100,000 cars a day.

^cSamples were taken 400 yd from a lightly traveled roadway.

(PbO) occurring as the 2 PbO·PbBrCl double salt. Lead sulfate and lead phosphate account for 5 to 6 percent of these deposits. (These compositions resulted from the combustion of low-sulfur and low-phosphorus fuel.)

3. PbBrCl is the major lead salt in particles of 2 to 10 micrometers equivalent diameter, with 2 PbBrCl·NH₄Cl present as a minor constituent.
4. Submicrometer-sized lead salts are primarily 2PbBrCl·NH₄Cl.
5. Lead-halogen molar ratios in particles of less than 10 microns MMED indicate that much more halogen is associated with these solids than the amount expected from the presence of 2PbBrCl·NH₄Cl, as identified

by X-ray diffraction. This is particularly true for particles in the 2- to 0.5-micrometer size range.

6. There is considerably more soot and carbonaceous material associated with small particles than with coarse particles re-entrained after having been deposited after emission from the exhaust system. This carbonaceous material accounts for 15 to 20 percent of the finer particles.
7. Particulate matter emitted under typical driving conditions is rich in carbonaceous-type material. There is substantially less such material emitted under continuous hot operation.
8. Only small quantities of 2PbBrCl·NH₄Cl were found in samples collected at the tail-

pipe from the hot exhaust gas. Its formation therefore takes place primarily during cooling and mixing of exhaust with ambient air.

Hirschler and Gilbert⁴ found similar results and speculated that higher gas temperature during full-throttle operations reduced the tendency for the ammonium-lead halide complexes to be present since they are unstable at high temperatures.

Based on the above studies, it seems quite clear that the size distribution of lead particles emitted from automobiles and the relative concentrations of the complex compounds in those particles vary significantly with driving conditions, engine condition, type of fuel, and age of exhaust system. Particles $> 2 \mu\text{m}$ in the exhausted particulate are primarily lead bromochloride. The very large particles, a consequence of deposits in the exhaust system, are also primarily lead bromochloride.

The fates of these lead compounds, once they are introduced into the atmosphere from automobiles, are not completely understood. There is disagreement in the early literature concerning the loss of halogens by these lead compounds. Pierrard²⁶ suggested that PbBrCl undergoes photochemical decomposition with the formation of a lead oxide and the release of free bromine and chlorine, but later suggested a hydrolytic conversion mechanism. Ter Haar and Bayard²⁵ and Robbins and Snitz²⁷ confirm the loss of halogen from freshly emitted Pb salts, but they do not support the photochemical mechanism. Ter Haar and Bayard²⁵ suggest that lead halides are eventually converted to lead carbonates and lead oxides. Pierrard²⁶ obtained data on aged lead aerosol that indicated that the lead particle surfaces had already been converted to a relatively insoluble form such as oxide, carbonate, or basic halide; this would be consistent with a conversion mechanism expected to release the less reactive hydrogen halide rather than the more reactive molecular halogen. Dzuby and Stevens²⁸ observed a diurnal variation in the bromine-to-lead concentration ratio in atmospheric particulate indicative of the loss of halogens during atmospheric transport. Ter Haar and Bayard²⁵ studied the effects of aging on automobile exhaust collected in a black bag, using an electron probe. The results, shown in Table 6-6, indicate that 75 percent of the bromine and 30 to 40 percent of the chlorine associated with the compounds contained in the particulates were lost in 18 hr; data presented suggest that the proportions of lead carbonates and lead oxides increased. Since these chemical reactions occurred in a black bag, photolytic processes would not likely be

responsible for the decrease in halides. At the very least, therefore, this experiment demonstrates the existence of nonphotolytic decomposition pathways for lead halides in the atmosphere. Consequently, the chemical composition of lead in the atmosphere from automobile emissions almost certainly depends to some extent on the age of the particles as well as the presence of other pollutants with which the lead compounds can react.

The results of Lee et al.⁹ show that the percentage of water-soluble particulate lead increased when diluted exhaust was irradiated by light in the wavelength region of 3000 to 6000 Å. This region is in the near-ultraviolet and visible regions of the spectrum and is available from direct sunlight. The percentage of water-soluble lead in the diluted exhaust also was increased by irradiation in the presence of 0.5 ppm SO_2 . Irradiation significantly increased the sulfate concentration of the particulates and was accompanied by a shift to smaller particle sizes. A shift of nitrate-bearing particles to smaller sizes, with and without addition of SO_2 , was also observed with irradiation. The amount of nitrate present was decreased in the presence of SO_2 . The lead nitrate, which is much more soluble in water than the other lead salts present, cannot be totally responsible for the increased water solubility observed if the NO_3 concentrations decrease.

The information available regarding the chemical composition of lead particles emitted from automobiles may be summarized as follows:

1. Lead halogen compounds are the principal forms emitted; lead chlorobromide is the most prominent of these.
2. The particulates undergo compositional changes during transport away from the source. These changes appear to consistently involve:
 - a. Losses of halogens, the rate of which might be photochemically enhanced, but which also occur in the absence of light.
 - b. General increases in the water solubilities of the particles with concomitant shifts toward smaller mean particle sizes. These latter changes are enhanced by the presence of SO_2 , in which case the amounts of nitrate present decrease.
3. Although several reports have suggested that the lead halogen compounds are converted to oxides and/or carbonates, the only specific examination of the composition after aging was that of Ter Haar and Bayard.²⁵ Unfortunately, their experimental approach did

not rely on a particularly definitive method of identification. Indeed, the electron microprobe approach used can only be regarded as a crude qualitative tool for the identification of compounds; the simultaneous occurrences of other elements in lead-bearing particles and the general morphological characteristics of the particles can provide only circumstantial indications of the compounds that are present. This is particularly true for lead-bearing particles because compounds of several other elements are also typically present. Habibi et al.,⁵ for example, have shown that the particles often include iron as well as lead compounds. The percentage composition data given in Table 6-6 should also be evaluated, taking into account that they are number rather than mass percentages. Thus, although lead carbonate, for example, may comprise a relatively high number percentage of the total, its mass percentage may be quite different, depending on the size distributions involved and whether the particle compositions are size dependent.

These general conclusions and qualifications are consistent with and supportive of the results of the study reported by Olson and Skogerboe.²⁹ They determined that the principal form of lead found in lead-contaminated soils from highway medians as well as in street dusts was lead sulfate. Although this study included evaluation of 18 soil and/or dust samples collected from different U.S. locations, significant amounts of the lead halogen compounds were found in any case. The conversion of lead halides to other compounds appears to have been quite complete for these aged lead aerosol deposits.

6.2.2.2 STATIONARY SOURCE EMISSIONS

Measurements are not available to confirm the chemical form of lead emissions from stationary sources. Barltrop and Meek³⁰ indicate the presence, without reference to specific measurements, of lead sulfide or lead chloride in the mining industry, lead oxide in smelters, and lead carbonate and lead chromate in pigments used in older paints. Lead oxide is the principal form of the metal used in battery manufacturing.

The association of lead sulfide with mining is clearly rational, since this is the primary mineral form (galena). While lead oxide may certainly be derived from the smelting process, the amounts produced may be relatively small in comparison to the amounts of lead sulfide released as fugitive dust to

the atmosphere around a smelter. Moreover, the release of SO₂ usually associated with lead smelting operations, coupled with the possible interactions between lead particles and SO₂, imply that the compounds released may well undergo conversion to other forms. Thus, although the compounds generally associated with stationary sources are not particularly soluble, the possibility of conversion to more soluble compounds or accumulation of the particles in the lungs of exposed populations should not be ignored.

6.3 TRANSPORT IN AIR

The mechanisms of atmospheric transport, removal, and resuspension of lead particulates interact in a complex manner. The transport mechanisms are functions of the particle size distribution, particle morphology, meteorology, and local topography.

6.3.1 Distribution Mechanisms

The transport and diffusion of gaseous and particulate materials in the atmosphere are consequences of molecular diffusion and the three-dimensional motion field, the latter being the dominant factor. A detailed treatment of these phenomena will be found in many standard textbooks on meteorology. The three-dimensional motion field can be assumed to be composed of a mean wind (transport) vector and a turbulent component. The turbulent component is analogous to molecular diffusion, but the coefficient of turbulent eddy diffusion is usually of much greater magnitude. The turbulent component tends to spread the material vertically and laterally about the mean horizontal transport vector. Therefore, assuming a pollution plume from a local line or point source, the atmospheric motion serves to dilute and transport the pollutants.

Since lead emitted to the atmosphere is primarily in the inorganic particulate form, its transport and dispersion will depend primarily on particle size as well as chemical stability, the height of injection, and the intensity and stability of the atmospheric motion field. Large particles injected at low elevations will settle to the surface in the immediate vicinity of the source, whereas the smaller particles will be transported over greater distances.

A study by Daines et al.³¹ related atmospheric lead to traffic volume and distance from a highway. They found the effect of traffic on lead content of the air to be striking, but limited to a rather narrow zone bordering primarily the lee side of the highway, as shown in Figure 6-7. About 65 percent of the lead in

the air between 30 and 1750 ft from the highway consisted of particles under 2 μm , and 85 percent were under 4 μm in diameter. Figure 6-8 shows a typical relationship of particle size to distance from the highway. Cholak et al.¹² and Schuck and Locke³² did similar studies with similar results. As shown in Figures 6-4 and 6-5, Huntzicker et al.¹⁰ demonstrated that the large particle mode ($D_p > 7 \mu\text{m}$) in the freeway distribution is severely attenuated at the Pasadena site.

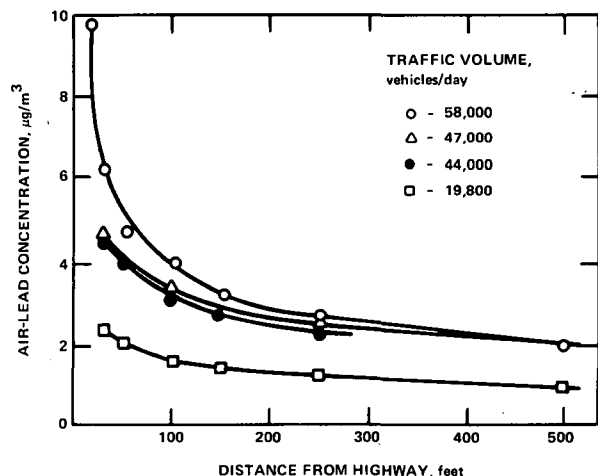


Figure 6-7. Air-lead values as a function of traffic volume and distance from the highway.³¹

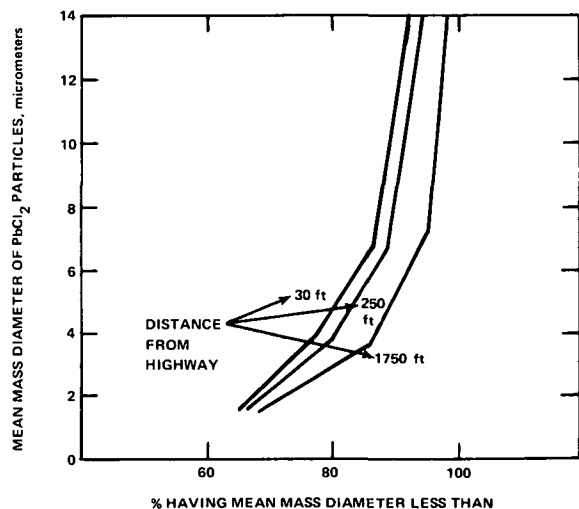


Figure 6-8. Relationship of the diameter of the particles (mass) to distance from the highway.³¹

Knowledge of lead concentrations in the oceans and glaciers provides some insight into the degrees of atmospheric mixing and long-range transport. Tatsumato, Patterson, and Chow³³⁻³⁵ measured dissolved lead concentrations in sea water off the coast of California, in the Central North Atlantic (near

Bermuda), and in the Mediterranean. The profiles obtained are shown in Figure 6-9. Surface concentrations in the Pacific were found to be higher than those of the Mediterranean or the Atlantic, and decreased abruptly to relatively constant levels with depth. The vertical gradient was found to be much less in the Atlantic. Based on the Pacific data, Tatsumato and Patterson³³ estimated an average surface lead concentration of 0.2 $\mu\text{g}/\text{kg}$ in the northern hemispheric oceans. Chow and Patterson³⁵ revised this estimate downward to 0.07 $\mu\text{g}/\text{kg}$. There appears to be no difference between lead concentrations in deep water in the Atlantic and Pacific. These investigators calculated that industrial lead is currently being added to the oceans at about 10 times the rate of introduction by natural weathering, with significant amounts being removed from the atmosphere by precipitation and deposited directly into the ocean. Their data suggest considerable contamination of surface waters near shore, diminishing toward the open ocean.³⁵ These investigators conclude that lead emissions from automobiles are the primary source of pollution of ocean surface water.

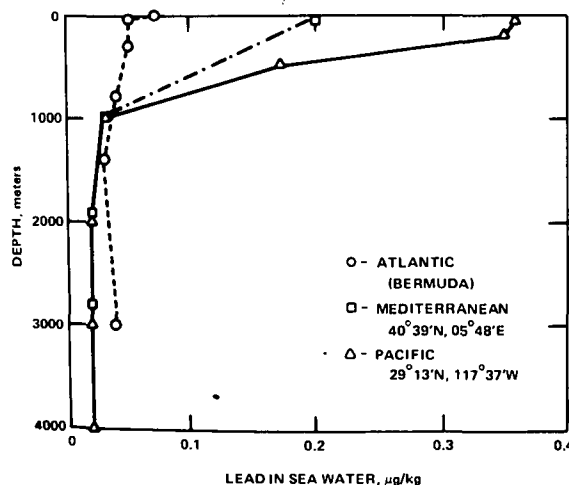


Figure 6-9. Lead concentration profiles in the oceans.³³⁻³⁵

Duce, Taylor, Zoller, and their co-workers³⁶⁻³⁸ have investigated trace-metal concentrations (including lead) in the atmosphere in remote northern and southern hemispheric sites. The natural sources for such atmospheric trace metals include the oceans and the weathering of the earth's crust, whereas the manmade source is particulate pollution. Enrichment factors for concentrations relative to standard values for the oceans and the crust were calculated (Table 6-7); the mean crustal enrichment factors for the North Atlantic and the South Pole are shown in Figures 6-10 and 6-11. The significance of the com-

parison in Figure 6-11 is that 90 percent of the particulate pollutants in the global troposphere are injected in the northern hemisphere.³⁹ Since the residence times for particles in the troposphere⁴⁰ are much less than the interhemispheric mixing time, it is unlikely that significant amounts of particulate pollutants can migrate from the North Atlantic to Antarctica via the troposphere; however this does not rule out stratospheric transfer. In the case of lead (and all other metals studied except vanadium), the enrichment factors were very similar at the two locations. This suggests (but does not prove) that the atmospheric concentrations of these metals may originate primarily from natural (rather than man-made) sources.

TABLE 6-7. CONCENTRATION RANGE AND MEAN EF_{crust} VALUES FOR ATMOSPHERIC TRACE METALS COLLECTED OVER THE ATLANTIC NORTH OF 30° N³⁶

Element	Concentration range, ng/scm	EF_{crust} , geom. mean ^a
Al	8-370	1.0
Se	0.0008-0.011	0.8
Fe	3.4-220	1.4
Co	0.006-0.09	2.4
Mn	0.05-5.4	2.6
Cr	0.07-1.1	11
V	0.06-14	17
Zn	0.3-27	110
Cu	0.12-10	120
Cd	0.003-0.62	730
Pb	0.10-64	2,200
Sb	0.05-0.64	2,300
Se	0.09-0.40	10,000

^aCalculated on the basis of the mean crustal abundances of Taylor³⁷

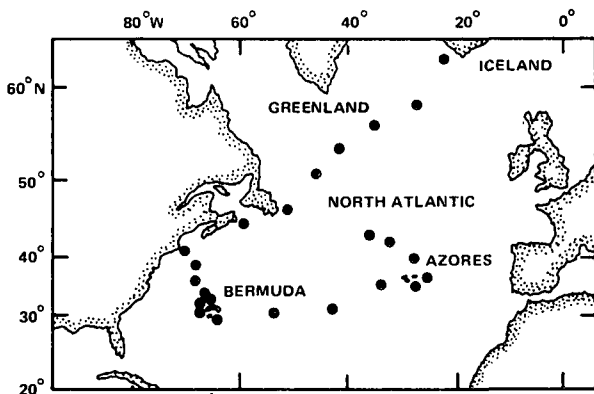


Figure 6-10. Midpoint collection location for atmospheric samples collected from R. V. Trident north of 30°N, 1970 through 1972.^{36,38}

Murozumi et al.⁴¹ have presented supportive evidence. Their data show that long-range transport of lead aerosols emitted from automobiles has significantly polluted the polar glaciers. They collected

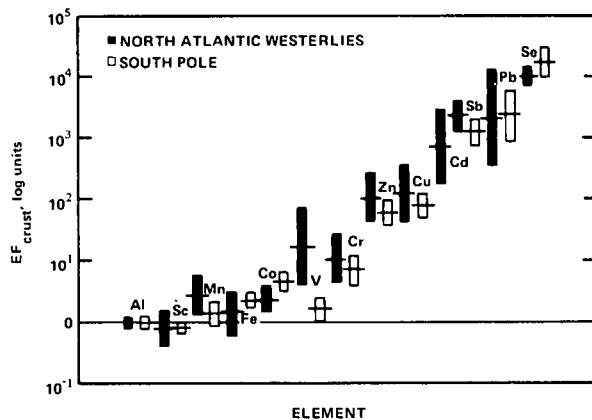


Figure 6-11. The EF_{crust} values for atmospheric trace metals collected in the North Atlantic westerlies and at the South Pole. The horizontal bars represent the geometric mean enrichment factors, and the vertical bars represent the geometric standard deviation of the mean enrichment factors. The EF_{crust} for lead at the South Pole is based on the lowest lead concentration (0.2 mg/scm).^{36,38}

samples of snow and ice from Greenland and the Antarctic. As shown in Figure 6-12, they found that the concentration of lead varied inversely with the geological age of the sample. The authors attribute the gradient increase after 1750 to the Industrial Revolution and the enhanced increase after 1940 to the increased use of lead alkyls in gasoline. The most recent levels found in the antarctic snows were, however, less than those found in Greenland by a factor of 10 or more. Before 1940, the concentrations in the Antarctic were below the detectable level (< 0.001 $\mu\text{g}/\text{kg}$) and have risen to 0.2 $\mu\text{g}/\text{kg}$ in recent snow. A graph of the world lead smelter and lead alkyl production presented by Murozumi et al.⁴¹ is shown in Figure 6-13; supporting data are shown in Table 6-8.

The results and conclusions of Murozumi et al. were criticized by Mills,⁴² who suggested the increase in the snow lead after 1940 could be due to aircraft operating from Thule Air Force Base. Bryce-Smith⁴³ countered Mills' argument by stating that the greatest amount of lead found to be deposited in the snow was during winter months when air traffic was lightest; there was no horizontal gradient between the air base and the collecting site; the collecting site was predominantly upwind from the air base; and, finally, the major increase in lead levels began about 20 years before the nearest operating base was established.

Jaworowski⁴⁴ found that lead concentrations in two glaciers have increased by a factor of 10 during the last century. The concentrations in the most re-

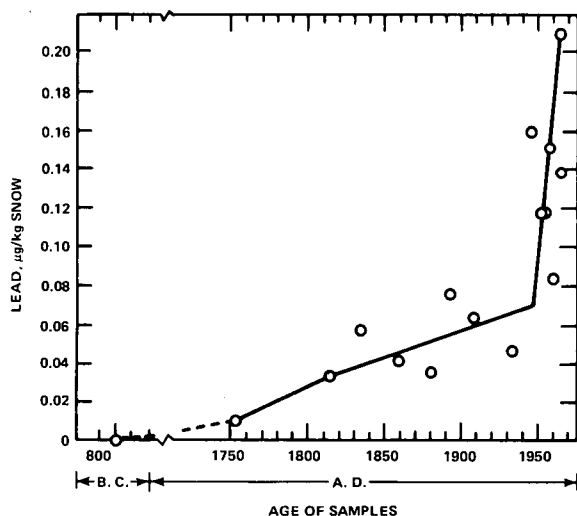


Figure 6-12. Lead concentration profile in snow strata of Northern Greenland.⁴¹

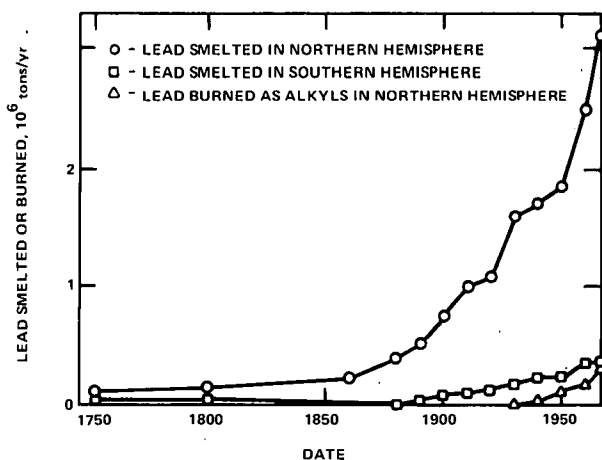


Figure 6-13. World lead smelter and alkyl lead production since 1750 A.D.⁴¹

TABLE 6-8. LEAD AEROSOL PRODUCTION IN THE NORTHERN HEMISPHERE COMPARED WITH LEAD CONCENTRATIONS IN CAMP CENTURY, GREENLAND, SNOW AT DIFFERENT TIMES⁴¹

Date	Lead smelted. 10 ³ tons/yr	Fraction converted to aerosols. %	Lead aerosols produced from smelteries. 10 ³ tons/yr	Lead burned as alkyls. 10 ³ tons/yr	Fraction converted to aerosols. %	Lead aerosols produced from alkyls. 10 ³ tons/yr	Total lead aerosols produced. 10 ³ tons/yr	Lead concentration at Camp Century. µg/kg snow
1753	1	2	2	—	—	—	2	0.01
1815	2	2	4	—	—	—	4	0.03
1933	16	16	8	0.1	40	4	12 ^a	0.07
1966	31	0.06	2	3	40	100	102 ^a	0.2

^aValues corrected.

cent ice layers were extremely high (148 µg/kg). Jaworowski et al.⁴⁵ also studied stable and radioactive pollutants from ice samples from Storbreen glaciers in Norway. The mean stable lead concentration in Storbreen glacier ice in the 12th century was 2.13 µg/kg. The mean for more recent samples was 9.88 µg/kg. Around 1870, the average lead concentration in Norwegian glacier ice was 5.86 µg/kg, whereas that for glaciers in Poland was 5.0 µg/kg. A century later, the mean concentration in the Norwegian glacier was 9.88 µg/kg, whereas the mean concentration in the Polish glacier reached 148 µg/kg. Jaworowski et al.⁴⁵ attributed the large increase of lead concentrations in the Polish glacier to local sources.

Jaworowski et al.⁴⁵ also measured ²¹⁰Pb in the glacier ice. The values found in the Storbreen glacier ice are shown graphically in Figure 6-14. The highest value was found in 1961. A similar value was found in Polish glaciers and in the Alps the same year.⁴⁴ The values and irregularities observed in ²¹⁰Pb concentrations in the investigations suggest that part of the atmospheric ²¹⁰Pb may have origi-

nated from artificial sources — nuclear explosions in the Arctic, or energy production in fossil-fuel power stations. Based on their findings, Jaworowski et al.⁴⁵ concluded that long-range transport of lead

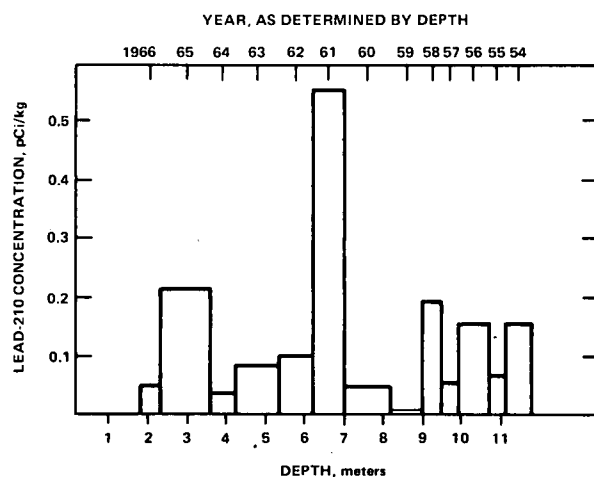


Figure 6-14. ²¹⁰Pb in Storbreen, Norway, glacier ice, 1954-1966.⁴⁵

pollutants in the atmosphere is a reality, but the authors suggest that the rate of contamination of glacier ice correlates better with the total annual input of coal burning to the energy system of the world than with lead emissions from automobiles.

6.3.2 Removal Mechanisms

The principal mechanisms for removal of inorganic lead particulate from the atmosphere are dry deposition and precipitation. Detailed discussions of these processes will be found in standard textbooks by Sutton,⁴⁶ Pasquill,⁴⁷ Fletcher,⁴⁸ Junge,⁴⁹ Green and Lane,⁵⁰ and Slade.⁵¹ The removal efficiency of these processes varies significantly, depending on physical characteristics of the suspended material, atmospheric conditions, and the nature of the receiving surface.

6.3.2.1 DRY DEPOSITION

Dry deposition removal processes include sedimentation, diffusion, and inertial mechanisms such as impaction. Sedimentation, or settling of particles, occurs when the mass of the particle is large enough to overcome the buoyancy force and the lifting forces of convective currents. Freely falling particles of the size range found in suspended aerosols rapidly attain their terminal, or constant, velocity when the aerodynamic drag on the particle is equal to the weight of the particle. The terminal velocity depends on the particle size, its density, and gravitational acceleration. When a particle is of a size comparable to the mean free path of the gas molecules, bombardment by the molecules results in a random or Brownian motion that is superimposed on its downward motion. If a particle is very small and its motion is observed for only a short period of time, its fall may be completely masked by the Brownian motion. Residence times or, conversely, the rate of fallout of aerosols or dust particles containing lead in the atmosphere are then primarily a function of particle size. The shape of the suspended particles also has a significant effect on the settling velocity. Usually the settling velocity of particles of various geometrical forms is calculated in terms of the settling velocity of spherical particles of the same volume. The aerodynamic particle size, conventionally used when discussing airborne particulate, is defined as the size of a sphere of unit density that has identical aerodynamic behavior to the particle in question. Particles having the same aerodynamic size may have differing shapes and dimensions.

Airborne particles are generally divided into three size ranges: Aitken nuclei (particle radius

< 0.1 μm), large nuclei (particle radius 0.1 to 1 μm), and giant nuclei (particle radius > 1 μm). Extremely small particles (radius < 0.001 μm) tend to coagulate rapidly to form larger (~ 0.05 to 0.5 μm), less mobile particles.⁵⁰ Fletcher⁴⁸ derived an approximate equation to predict the rate at which the concentration number, n, of particles of radius, r, will decrease in a relatively uniform aerosol. For r = 0.005 μm and n = 10⁵/cm³ (typical in urban air), the time required for particle concentration to decrease by one-half was calculated to be 30 min. For r = 0.1 μm and n = 10³/cm³, 50 percent reduction was calculated to require 500 hr. The size distributions of large and giant nuclei are not significantly affected by coagulation.

Settling or terminal velocities of spherical particles, as reported by Green and Lane⁵⁰ and Israel and Israel,⁵² are shown in Table 6-9.

TABLE 6-9. TERMINAL VELOCITIES OF SPHERICAL PARTICLES OF UNIT DENSITY AT GROUND LEVEL

Particle radius. μm	Terminal velocity, cm/sec	
	Israel and Israel ⁵²	Green and Lane ⁵⁰
0.01	1.43 x 10 ⁻⁵	—
0.05	—	8.71 x 10 ⁻⁵
0.1	2.32 x 10 ⁻⁴	2.27 x 10 ⁻⁴
0.2	—	6.85 x 10 ⁻⁴
0.5	—	3.49 x 10 ⁻³
1.0	1.32 x 10 ⁻²	1.29 x 10 ⁻²
2.0	—	5.00 x 10 ⁻²
5.0	—	3.03 x 10 ⁻¹
10.0	1.23 x 10 ⁰	1.20 x 10 ⁰
20.0	—	4.71
50.0	—	24.7

Airborne particles are also removed from the atmosphere by inertial mechanisms. In turbulent inertial deposition, turbulent wind fluctuations perpendicular to a horizontal surface impart sufficient inertia to propel the particles through the boundary layer and onto the surface. This mechanism is important for both smooth and rough surfaces. When the roughness elements on a surface protrude sufficiently far into the windstream, inertial impaction may become important. The mean horizontal flow of the wind, rather than turbulent fluctuations, controls impaction. This mechanism occurs when particles cannot follow the air streamlines as they pass around a roughness element. In this case, the mean windflow supplies the inertia that drives the particles onto the surface.

Inertial mechanisms are dependent on atmospheric conditions and the characteristics of the surface. The small-scale surface structure may be especially significant. For example, small particles

are preferentially retained on leaf surfaces, where they may be tightly retained by small hairs on the leaf, by surface pores, and by tacky substances excreted by the leaves. Impaction of submicrometer-sized particles on leaf surfaces is possible at normal wind speeds.⁵³ Pine needles and similarly shaped surfaces appear to be aerodynamically attractive for impaction of particulate matter. Therefore, pine trees near a surface source of lead particulate pollution may increase the rate at which lead aerosols are removed from the atmosphere. Heichel and Hankin⁵⁴ reported soil lead concentrations in front of and within a roadside windbreak of pine trees as being 50 percent and 100 percent higher, respectively, than soil lead concentrations at corresponding distances in a nearby open field that bordered the same side of the road.

Particle removal rates from the atmosphere are usually described in terms of deposition velocity. Historically, deposition velocities have been defined as the ratio of deposition flux to the airborne concentration with units of length/time usually reported as cm/sec.⁴⁹ Sehmel and Hodgson⁵⁵ have published a model for the prediction of dry deposition velocities based on this concept.

$$K_1 = \frac{N}{C} \quad (6-1)$$

where K is the deposition velocity, N is the deposition flux, and C is the airborne concentration for monodispersed particles measured 1 cm above the deposition surface. The deposition velocity, K , assumes that particle deposition is described by a one-dimensional, steady-state continuity equation. The basic assumptions in the model are that the flux is constant with height, that a relationship for particle eddy diffusivity can be determined, that the effect of gravity can be described by the terminal settling velocity, that agglomeration does not occur, and that particles are completely retained on the surface. The model was designed to predict deposition velocities for simple surfaces. Actual removal rates are non-steady-state processes dependent on the delivery capability of the upper atmosphere and the surface resistance. Based on the above assumptions, Sehmel and Hodgson⁵⁵ write the equation for deposition flux as:

$$N = -(\epsilon + D) \frac{dC}{dz} - v_t C \quad (6-2)$$

where v_t is the absolute value of the terminal settling velocity, ϵ is the particle eddy diffusivity, D is the Brownian diffusivity, C is the airborne concentration, and z is the reference height. For small parti-

cles, the sedimentation term ($-v_t C$) is negligible so that deposition velocity is a function of the Brownian and eddy diffusivity term only. For large particles, the diffusivity term is negligible, and the deposition velocity is equal to the terminal velocity. Incorporating the concepts of friction velocity:

$$u_* = \frac{u}{K} \frac{1}{\ln(z/z_0)} \quad (6-3)$$

where k is von Karman's constant, u is the windspeed, z is height, and z_0 is the roughness height. Roughness height is defined as a measure of the roughness of a surface over which fluid is flowing:

$$z_0 = H/30 \quad (6-4)$$

where H is the average height of surface irregularities. Sehmel and Hodgson⁵⁵ developed prediction deposition velocity curves for a range of roughness heights and friction velocities. Representative curves are shown in Figures 6-15 through 6-17. Deposition velocities are shown to be a function of particle diameter and have their smallest values in the 0.1 to 1 μm particle diameter range. The mean diameter of lead-containing particles in the atmosphere, remote from major sources, falls approximately in this range. In the case of larger particles, both increased effective eddy diffusion in surface boundary layer (as a result of greater particle inertia) and increased gravitational settling rates tend to increase the predicted deposition velocities above the minimum. The lower limit of the predicted deposition velocities is the sedimentation velocity. For smaller particles, deposition velocities increase with decreasing particle diameters because of increased mass transfer by Brownian motion. Deposition velocities for 0.01- μm particles are relatively insensitive to changes in particle diameter at elevated heights above 10 cm. Deposition velocities at 1 cm above the ground are extremely large; consequently, in the 0.01- μm particle-diameter range, the deposition velocities are controlled by atmospheric diffusion in the layers immediately above the canopy. As indicated by Sehmel and Hodgson,⁵⁵ the model should predict reasonably well the deposition velocities for simple surfaces, assuming the wind direction is persistent over sufficient distance. It should not, however, be expected to predict deposition velocities for a city because of the complexity in the geometry of the surface and because of local wind conditions.

Values of lead deposition velocities found in the literature generally range from about 0.1 to 0.5 cm/sec.⁵⁶ These values are based on total lead flux and total airborne concentrations, without regard to

particle size. Since large particles may control lead deposition in certain cases, it is necessary to examine the entire size distribution of particles in order to calculate deposition rates. Further, accurate isokinetic measurements of large airborne particles are required to relate airborne concentrations to deposition. Davidson⁵⁶ found a deposition velocity of 0.29 cm/sec in Pasadena, based on total flux and total airborne concentrations. Based on the fraction of lead particles greater than 10 microns, however, the deposition velocity was 1.3 cm/sec. Huntzicker et al.¹⁰ found a deposition velocity of 1.80 cm/sec on a Teflon plate placed on the shoulder of a Los Angeles freeway.

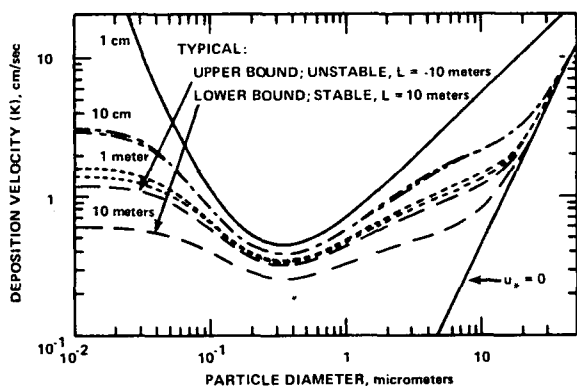


Figure 6-15. Predicted deposition velocity of particles at indicated height for $u_* = 20$ cm/sec and $z_0 = 3.0$ cm.⁵⁵

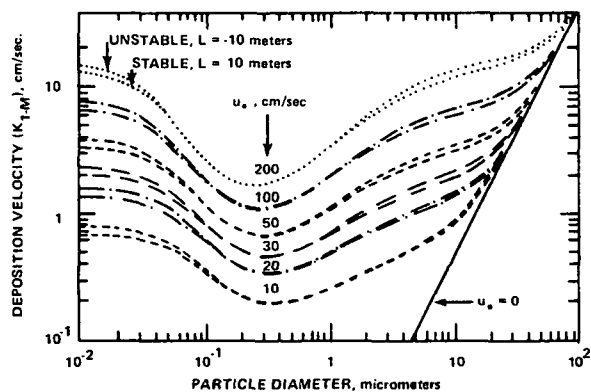


Figure 6-16. Predicted deposition velocities of particles at 1-m height for $z_0 = 3.0$ cm.⁵⁵

Johnson⁵⁷ sampled particles with an instrumented aircraft flying at 300 m altitude in the vicinity of St. Louis, Missouri. Particles were collected by exposing a small (1.0- by 7.5-cm) glass slide covered with a thin layer of high-viscosity silicone oil to the free air stream outside the skin of the aircraft. Particles were counted and sized manually from photographs. Samples were obtained upwind and downwind of St.

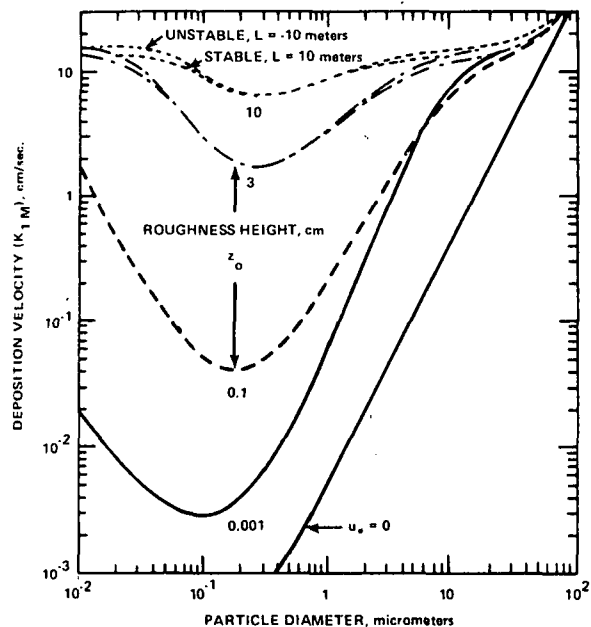


Figure 6-17. Predicted deposition velocities of particles at 1 m for $u_* = 200$ cm/sec.⁵⁵

Louis on each of 11 days during the period July 1 through July 18, 1975. The results indicated typical number concentrations of airborne particles larger than 10 μ m in diameter of 7,500 particles/ m^3 upwind and 11,000 particles/ m^3 downwind. Particles larger than 30 μ m in diameter were found in concentrations of 200 particles/ m^3 upwind and 425 particles/ m^3 downwind of the city. For the downwind particle number densities of >10 μ m and >30 μ m particles, and with the assumed density of 2 g/ m^3 , the mass concentrations would be about 0.01 ng/ m^3 and 0.012 ng/ m^3 , respectively. The results reported indicate that particles >30 μ m can be transported to altitudes of 300 m by convective currents; therefore, all large particles are not removed by sedimentation in the immediate vicinity of sources. Assuming a sedimentation velocity of 0.3 cm/sec for a 10 μ m-diameter particle and an initial height of 300 m, the particle could remain airborne for approximately 27 hr and be transported about 200 km with a uniform wind of 2 m/sec. This type of long distance transport has been observed by Gillette and Winchester¹⁵ over Lake Michigan. The actual concentrations observed are very small, however, and would contribute little to ambient air loading or dustfall accumulation in regions remote from the source.

Lynam⁵⁸ studied the atmospheric diffusion of carbon monoxide and lead from an expressway (I-75, north of Cincinnati, Ohio). The significant results are shown in Figures 6-18 through 6-20. Approximately 50 percent of the lead emitted from the automobile traffic was removed from the atmosphere by

dry deposition within 640 ft of the edge of the roadway (Figure 6-18). The size distribution of the lead particles was not significantly altered between 20 and 640 ft (~6 and ~195 meters). Wind speeds ranged from approximately 0.5 to 3.8 m/sec. Assuming a mean wind speed of 2 m/sec, the 50-percent reduction within 640 ft would correspond to about 1.5 min of travel time. The concentration of lead decreased from about $7 \mu\text{g}/\text{m}^3$ at 20 ft to about $1.5 \mu\text{g}/\text{m}^3$ at 640 ft, a decrease by a factor of about 5. The data were not sufficient to determine the relative efficiency of sedimentation versus impaction in the total removal process; however, Figures 6-19 and 6-20 indicate that the removal mechanism was not strictly limited to sedimentation. Daines et al.,³¹ in their study of the relationship of atmospheric lead to traffic volume and distance from a highway, found a 50-percent reduction in lead between 10 and 150 ft of the edge of the roadway.

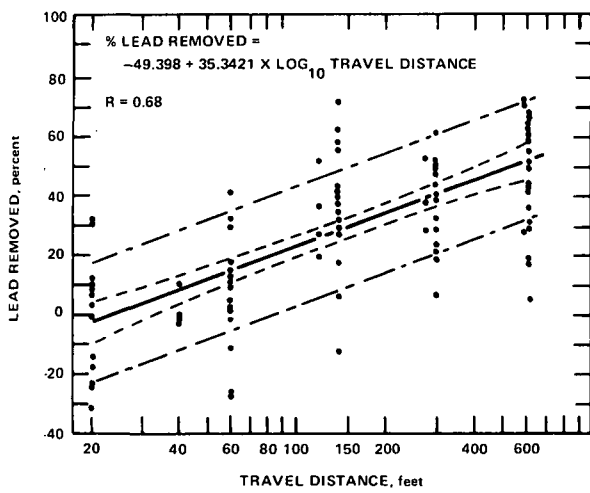


Figure 6-18. Regression of percentage lead particulates removed by dry deposition with distance from roadway.⁶⁸ (Legend: —= regression line; ---= 95% confidence limits for regression line; - - - = 95% confidence limits for single value; R = correlation coefficient.)

Smith⁵⁹ investigated lead contamination of white pine growing along an east-west section of Interstate 95 in Connecticut. He found that lead contamination decreased regularly with increasing distance from the road and was greatest on the sides of the trees nearest the highway. Based on the much higher concentration of lead deposited on the needles nearest the roadway, Smith concluded that pine trees may serve as rather efficient air filters.

6.3.2.2 PRECIPITATION

Precipitation, or wet deposition, removal processes include rainout and washout. Rainout occurs

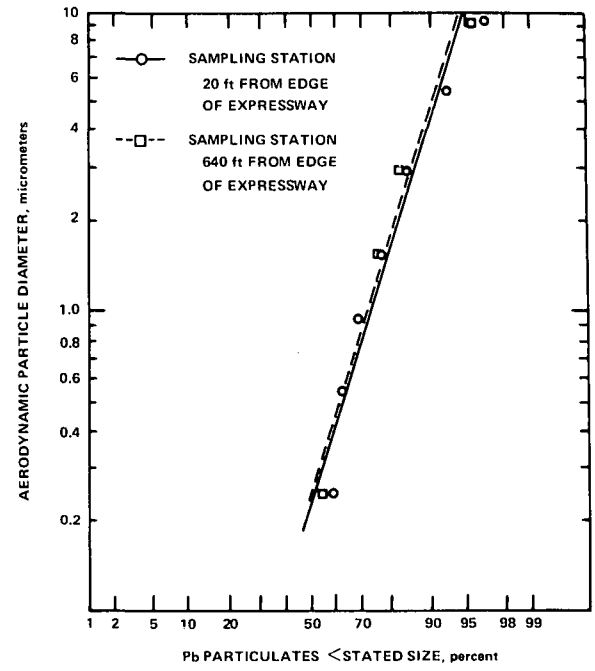


Figure 6-19. Comparison of size distribution of lead particulates collected at 20 and 640 ft from an expressway north of Cincinnati, Ohio. Determined by seven-stage Andersen sampler.⁵⁸

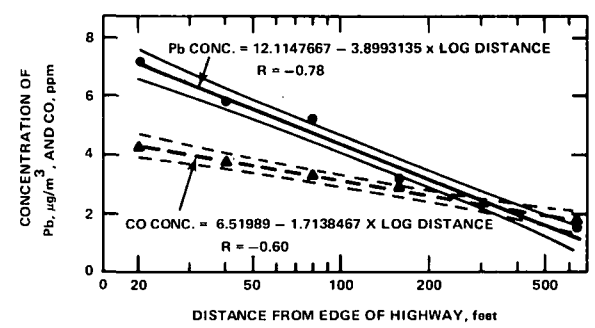


Figure 6-20. Atmospheric concentration of lead and carbon monoxide as a function of log of distance from edge of highway (R = correlation coefficient).⁵⁸

when particulate matter is present in the super-saturated environment of a growing cloud. The small particles (0.1 to $0.2 \mu\text{m}$) act as nuclei for the formation of small droplets, which grow into raindrops.⁴⁹ Droplets also collect particles under $0.1 \mu\text{m}$ by Brownian motion and by the water-vapor gradient. The nucleation process may also occur on particulate matter present below cloud level, producing droplets large enough to be affected by sedimentation. These processes are referred to as rainout. A second process (washout) occurs when falling raindrops collect particles by diffusion and impaction on the way to the ground. Rainout and

washout together are known as wet deposition. Although data on the lead content of precipitation are rather limited, those that do exist indicate a high variability. Lazrus et al.⁶⁰ sampled precipitation at 32 U.S. stations and found a correlation between gasoline use and lead concentration in rainfall in each area. Similarly, there is probably a correlation between lead concentration in rainfall and distance from large stationary point sources of lead emissions in the vicinity of such sources. The authors pointed out that at least twice as much lead is found in precipitation as in water supplies, inferring the existence of a process by which lead is depleted after precipitation reaches the ground. Russian studies⁶¹ point to the insolubility of lead compounds in surface waters and acknowledge this removal by natural sedimentation and filtration.

The intensity of rainfall appears to be negatively correlated with the amount of lead washed out of the atmosphere. Ter Haar et al.⁶² found that showers had lower concentrations than slow, even rainfall. Data presented by Jaworowski⁴⁴ show that in recent years, the lead content in rainwater ranged from 0 to 1858 $\mu\text{g/liter}$.

A laboratory study in which simulated rainfall was used to determine the efficiency with which automotive lead particulates could be washed out indicated that the efficiency was less than 1 percent.⁶³

Concentrations of ^{210}Pb in rainwater have also been reported by Jaworowski⁴⁴ as highly variable (as much as two orders of magnitude in the same locality) and not related to season or amount of precipitation. Values ranged from 0.2 to 300 pCi/liter.⁴⁴ High concentrations were found in samples collected from northern continental localities, and low concentrations were found in samples from oceanic and Antarctic locations. Jaworowski suggests that the differences might be attributed in part to artificial contamination by nuclear explosions.

6.3.2.3 FIELD STUDIES

Atkins and Kruger⁶⁴ conducted a field sampling program in Palo Alto, California, to determine the effectiveness of sedimentation, impaction, rainout, and washout in removing lead contaminants from the atmosphere. Rainfall in the area averages approximately 33 cm (13 in)/year and occurs primarily during the late fall and winter months. Airborne concentrations at a freeway site varied from 0.3 $\mu\text{g}/\text{m}^3$ to a maximum of 19 $\mu\text{g}/\text{m}^3$ in the fall and winter seasons, and were a maximum of 9.3 $\mu\text{g}/\text{m}^3$ in the spring. During periods of light rainfall in the

spring, the maximum concentration observed was 7.4 $\mu\text{g}/\text{m}^3$. A typical daily concentration profile observed is shown in Figure 6-21. More than 90 percent of the lead pollutants reaching the surface during the 1-year sampling period were collected in dry fallout. Dry deposition as a function of distance from the freeway is shown in Figure 6-22. Approximately 1 percent of the total dry fallout collected near the expressway was lead. Wet deposition (approximately 33 cm or 13 in of rain per year) accounted for 5 to 10 percent of the lead removal at the sampling sites. A summary of the field data is shown in Table 6-10.

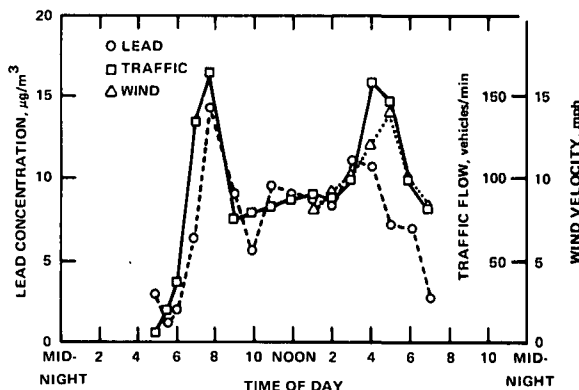


Figure 6-21. Atmospheric lead concentration at freeway site in Palo Alto, California, on August 15, 1966.⁶³

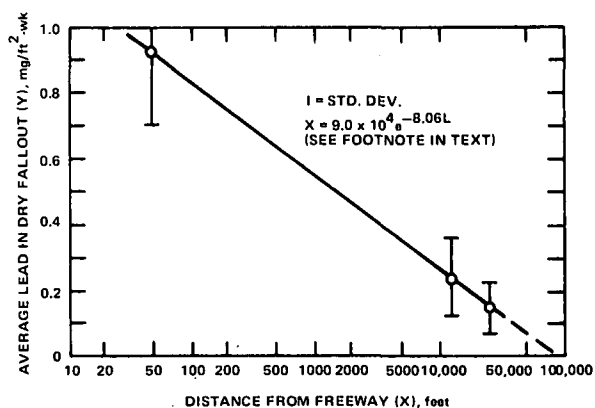


Figure 6-22. Average lead in dry fallout as a function of distance from the freeway.⁶³

*Figure 6-22 is a semi-log plot of the three average lead values as a function of distance from the freeway. The data appear to fall along a straight line, suggesting that the relationship between lead in fall out, L , and distance from the freeway, X , can be described by $X = ae^{bL}$ where a and b are constants. From the semi-plot, the appropriate values for a and b are $a = 9.0 \times 10^4$; $b = -0.06$, if L is expressed in $\text{mg}/\text{ft}^2\text{-wk}$ and X is expressed in feet. Therefore $X = 9.0 \times 10^4 e^{-0.06L}$. The area under this curve, from $X_1 = 50$ ft to $X_3 = 26,900$ ft, should represent the total amount of lead deposited in the Palo Alto area for each 1-ft section of freeway. This value is 7.85 g/ft. The area under the curve from $L = 0.95$ $\text{mg}/\text{ft}^2\text{-wk}$ to $L = 0$ should represent the total amount of lead that was removed by sedimentation, assuming that the data can be extrapolated past 26,900 ft. This value is 11.1 g/ft. This indicated that an average of 70 percent of the lead that was removed by sedimentation was removed within 5 miles of the source.

TABLE 6-10. SUMMARY OF FIELD DATA FROM PALO ALTO, CALIFORNIA⁶⁴

Item	Freeway ^a (Bayshore)	Resi- dential	Foot- hills
Lead in dry fallout:			
Average, mg/ft ² -wk	0.92	0.24	0.153
Amount removed, mg/ft ² -yr	49.4	11.7	8.3
Lead in rainfall:			
Average, mg/liter	0.181	0.149	0.035
Amount removed, mg/ft ² -yr	3.25	3.66	0.92
Average air concentration,			
$\mu\text{g}/\text{m}^3$	7.30	2.28	1.90
Pb/total solids in air	0.042	0.018	0.016
Pb/nonvolatile solids in dry fallout	0.0112	0.0102	0.0049

Andren et al.⁶⁵ evaluated the contribution of wet and dry deposition of lead in a study of the Walker Branch Watershed, Oak Ridge, Tennessee, during the period June 1973 to July 1974. The mean precipitation in the area is approximately 130 cm/year (51 in/year). The major atmospheric emissions in the vicinity of Oak Ridge are derived primarily from three coal-fired steam plants. A foundry and ferroalloy plant approximately 64.5 km (40 miles) to the west were assumed to have a minor impact because of orographic barriers. Results reported for the period January through June of 1974 are presented in Table 6-11. Rainfall, or wet deposition, contributed approximately 67 percent of the total deposition for the period.

TABLE 6-11. DEPOSITION OF LEAD AT THE WALKER BRANCH WATERSHED, 1974⁶⁵

Period	Lead deposition (g/ha)	
	Wet ^a	Dry
January	34.1	< 16.7
February	6.7	< 3.3
March	21.6	< 10.6
April	15.4	< 7.5
May	26.5	< 13.0
June	11.1	< 5.4
Total	115.4	56.5
Average	19.2	9.4

^aTotal deposition ~ 172 g/ha. Wet deposition ~ 67 percent of total.

Huntzicker et al.¹⁰ estimated the flow of automobile-emitted lead in the Los Angeles Basin based on measurements of particle size, atmospheric concentrations, and surface deposition of lead at various sites around the Basin. A flow diagram based on the study and modified by Schuck and Morgan⁶⁶ is shown in Figure 6-23. Of the lead emitted from automobile exhaust in the Basin (estimated to be about 18 tons per day), the investigators calculated that about 56 percent was deposited near the source (near deposition), 12 percent was deposited in the Basin

but in areas removed from the source (far deposition), and about 32 percent was transported out of the Basin by the wind. The values presented for deposition and wind removal were for dry weather only (i.e., dry deposition only).

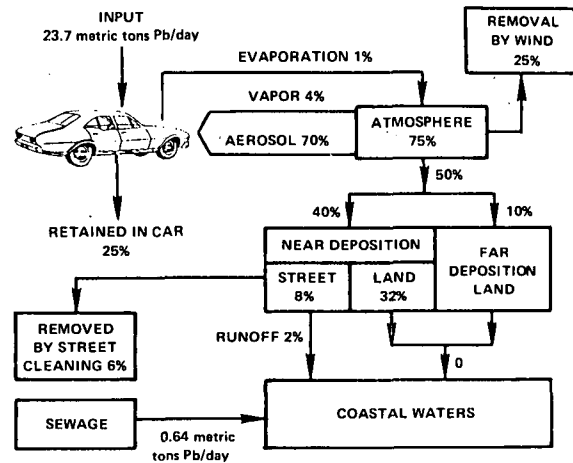


Figure 6-23. Fate of lead contributed from automotive traffic in Los Angeles Basin.⁶⁵

Roberts et al.⁶⁷ found an exponential decrease in dustfall with distance around two secondary smelters (Figure 6-24). The authors concluded that the high rate of fallout around the smelters originated from episodal large-particulate emissions from low-level fugitive sources rather than from the stack. This being the case, sedimentation would be the principal removal process. The lead in dustfall values decreased well over 90 percent within a distance of 300m.

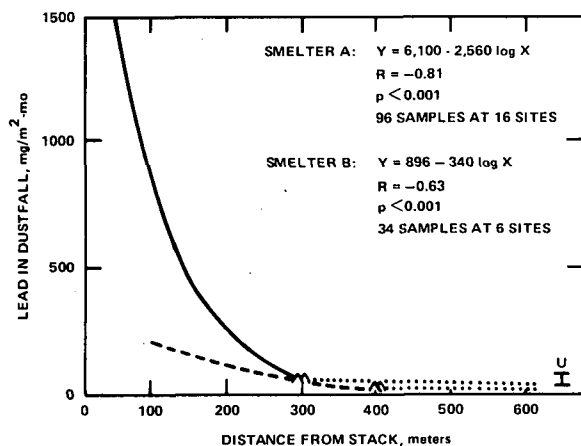


Figure 6-24. Contamination of dust by lead emissions from two secondary smelters. Solid and dashed lines are fitted curves corresponding to the regression equations; dotted lines are an extrapolated fit; U indicates corresponding values found in urban control areas.⁶⁶

Studies such as those described above clearly indicate that lead is effectively removed from the atmosphere by dry and wet deposition processes, and that atmospheric concentrations are significantly influenced by these removal mechanisms even in the immediate vicinity of the source. The rate of removal is highly dependent, however, on the size distribution of the particles, the nature and characteristics of the deposition surfaces, airborne concentrations, and atmospheric conditions including stability, winds, and precipitation. In dry weather, the lead will be deposited on surfaces in the form of dustfall by sedimentation, diffusion, or inertial mechanism, depending primarily on the size of the particles. Mass deposition near the sources will be controlled primarily by sedimentation of large particles, whereas the smaller particles will remain airborne longer, be transported further by the wind, and be removed primarily by diffusion and inertial mechanisms.

The characteristics of the surfaces on which the lead is deposited will significantly influence the deposition and retention. Deposition will be greater in a wooded area than on paved surfaces or short grass. Buildings also will influence the dry deposition, although there are few data available to quantify the effect. In areas with higher annual rainfall, removal by precipitation (wet deposition) becomes more important and may be the dominant process.

All of these factors substantially influence potential human lead-exposure patterns — both inhalation of airborne lead and possible ingestion of dust containing lead. The dry deposition removal mechanisms deplete the airborne concentrations but deposit the material in the form of dust. The factors controlling dry deposition then become extremely important from the standpoint of potential exposure patterns for dust, since they may strongly influence temporal and spatial variations. Because of sedimentation of large particles, dustfall rates (mass) will be highest immediately adjacent to roadways with dense automobile traffic and near stationary sources of all types where lead may be emitted. These rates will diminish to a rather low value in areas remote from sources and where the small particles are removed primarily by diffusion and inertial mechanisms.

The accumulation on the deposition surfaces will depend on the rate of deposition and the rate at which the material is cleaned from the surfaces by precipitation or by mechanical means such as street sweeping or vacuuming. Dust entering buildings or homes by air transport will usually be deposited on

flat surfaces such as floors or furniture. The same physical processes will control the rate of deposition. The potential exposure level, particularly for young children, will depend on the accumulation, which again will be influenced by the deposition rate and the frequency and methods of cleaning. In occupational environments where fugitive dust emissions are high, accumulation will be rapid if surfaces are not frequently cleaned. Significant amounts of this dust may be carried on clothing into the homes of workers and contribute further to the total lead-dust loading in the home environment.

Emission rates from automobile traffic and from stationary sources are highly variable in time, even on an hourly basis. Since the residence time of large particles in the atmosphere is on the same order or less, the dustfall rates in the immediate vicinity of sources should also be highly variable. This is reflected in airborne concentrations measured very near the source.

As a consequence of the number of variables involved and of the temporal and spatial variations occurring, it is not possible to quantify human exposure in uncontrolled cases without the use of personal monitors. Estimates of such exposure may vary by an order of magnitude or greater. For a given emission pattern, one can generally conclude that potential exposure from lead in dust should be greatest (1) in dry seasons, (2) in areas with sparse vegetation, (3) within a few hundred meters of the sources, (4) under conditions of stable atmospheres, (5) during the morning and afternoon traffic rush hours in the vicinity of freeways, and (6) during peak production periods of stationary sources (usually during the day).

6.3.2.4 RESUSPENSION

The threshold stress, which must be exceeded before a particle is resuspended from a surface, is a function of the particle properties, particle size, and the surface properties. A particle of a given size and density will resuspend more easily from a smooth surface than from an irregular surface such as an asphalt road. Particles on a dirt road or other soil surfaces may become attached to soil particles and behave quite differently from an inert free particle. This process of weathering tends to reduce resuspension. Moisture, influenced by atmospheric variables such as wind, precipitation, humidity, and solar radiation, may inhibit resuspension.

Data in the literature on resuspension show that this process is not well understood, and hence resuspension rates cannot yet be predicted to any degree

of accuracy. For example, Mishima⁶⁸ indicates that reported resuspension factors* vary over 10 orders of magnitude from 10^{-2} to 10^{-11} . (The resuspension factor, in m^{-1} , equals the airborne concentration, in ng/m^3 , divided by the ground source concentration, in ng/m^2 .) It is useful, however, to examine data from more controlled resuspension experiments in order to obtain a qualitative idea of expected lead resuspension rates.

Sehmel⁶⁹ has examined the resuspension of ZnS particles smaller than 25 microns from an asphalt road surface. He found that when a car was driven across the recently applied tracer, 0.001 percent to 1.0 percent of the material was resuspended. However, the fraction resuspended decreased by 2 to 3 orders of magnitude when a 30-day period elapsed between application of the tracer and the car passage.

The fraction resuspended per vehicle passage increased as a function of vehicle speed and was independent of wind velocities for the test conditions. The fraction resuspended per vehicle passage was greater for a drive through the tracer test lane than on the adjacent lane and greater for a 3/4-ton truck than for a car. These results suggest that resuspension of lead from roadways may play a significant role in the overall transport of lead away from automotive sources. This may be important considering the conclusions of Huntzicker et al.¹⁰ that a considerable fraction of the emitted lead deposits directly on the roadways.

In another experiment, Sehmel and Lloyd⁷⁰ examined the resuspension of $10\text{-}\mu\text{m}$ monodisperse uranine particles from a smooth surface in the laboratory. They found that the fraction of material resuspended per second varied from 10^{-6} to 10^{-3} for wind speeds of 16.5 to 18.3 m/sec. They also measured the resuspension of CaMo_4 over sandy soil.⁷⁰ The fraction of material resuspended per second ranged from 2×10^{-10} to 2.2×10^{-8} for winds of 1.3 to 20 m/sec.

A limited amount of data on lead resuspension is also available. Figure 6-25 shows the deposition of lead found as a function of height above a roof surface.⁷² The lead was deposited on flat Teflon plates mounted at various heights. The greater depositions close to the roof are believed by the investigators to be due to resuspended roof dust.

The environmental consequence of salt particle resuspension from roads has been reported by Smith.⁷³ Needles from white pine planted adjacent to an interstate highway in Connecticut showed excessive sodium and calcium content resulting from

airborne salt resuspension from the highway. The deposition of airborne salt appears to be similar to that of lead from automobile exhaust.⁶⁹

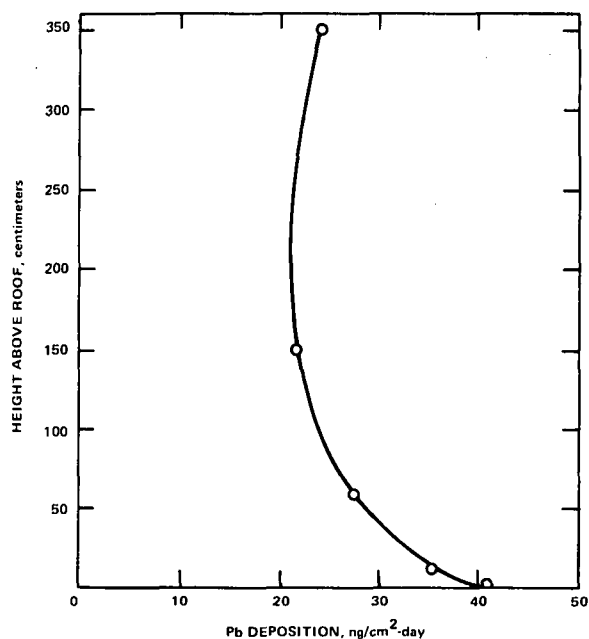


Figure 6-25. Total deposition of lead on Teflon plates at various heights above the roof of Keck Laboratories, California Institute of Technology, Pasadena.⁷¹

Baum et al.⁷⁴ sampled airborne particulate for a period of about 2 years at several locations in Portland, Oregon, using paraffin-coated Mylar films with four- and five-stage Lundgren impactors. Soil and dust samples, both surface and subsurface, were also taken at the air-sampling sites. Samples were analyzed for lead and other elements. Chemical elemental balance methods were used to calculate soil and dust burdens in the air. The authors report that greater than 90 percent of the submicrometer-sized airborne particles were associated with automotive emissions. The larger particles were reported to be contributed about equally by resuspended street dust and direct emissions from automobiles.

These data suggest that lead resuspension may play an important role in the transport of lead. At present, however, it is not possible to reach quantitative conclusions about this mechanism. Size distribution measurements of ambient lead presented here and elsewhere in the literature represent airborne data that have been influenced by the combined factors of atmospheric transport, deposition, and resuspension.

6.3.3 Models

There is an extensive body of literature on at-

atmospheric transport and diffusion models.⁷⁵⁻⁷⁹ A detailed discussion is beyond the scope of this document. The mathematical models are usually based on the basic Gaussian plume model emanating from the early work of Sutton⁴⁶ and Pasquill⁴⁷ and well described by Gifford.⁷⁶ Stern⁷⁷ provided an excellent review of air quality modeling techniques for both rural and urban modeling situations. Experimental data describing the pollutant concentrations from point sources show that, in spite of wide variations, these plumes exhibit a strong tendency toward a Gaussian or normal distribution as a statistical average. In simple terms, parameters reflecting the turbulent component define the horizontal and vertical dimensions of a pollutant cloud in a vertical plane perpendicular to the mean wind velocity.

Cermack et al.⁸⁰ have used the wind tunnel to model physically the atmospheric boundary layer over urban areas to determine the pollutant transport characteristics.

6.4 TRANSFORMATION AND TRANSPORT IN OTHER ENVIRONMENTAL MEDIA

6.4.1 Soils

Numerous studies have shown significant contamination of soils by the emission of lead from mobile and stationary sources and through the disposal of waste products. Excellent reviews of the early literature, as well as reports on more recent research, have been published by members of a joint research staff from Colorado State University and the Universities of Missouri and Illinois.^{20,29} Many of the studies of lead before 1973 were limited to analysis for elemental lead and did not include analysis for associated ions. Such information is not sufficient to permit a thorough examination and understanding of (1) transformation and transport processes that occur among the environmental media, (2) mobility of lead in soils, (3) uptake and distribution of lead in plants, and (4) the overall impact of lead on human health and ecosystems. Information on the chemical forms of lead is needed.

Soil is a complex matrix composed of several hundred different compounds, only a small fraction of which are lead. Most analytical techniques are not capable of providing positive identification of specific compounds unless separation methods are used that do not alter the lead compounds. Recently, nondestructive separation/preconcentration techniques have been developed and used by the Colorado State University research group to determine lead compounds in soil and plants.¹⁰

Lead contaminants are deposited on soil by dry and wet deposition processes. Present understanding of the chemical reactions involving these particles once they are deposited into or on the soil is incomplete.⁸¹ Early work indicates that lead probably reacts with soil anions, e.g., $\text{SO}_4^{=}$, $\text{PO}_4^{=}$, or $\text{CO}_3^{=}$, or with some organic or clay complex.⁸² These reactions would tend to make the Pb insoluble, thus inhibiting rapid mobility in the soil or plant as well as microbial uptake. Direct evidence supporting these reactions is limited. In a study by Lagerwerff and Brower,⁸³ lead was precipitated in Na^+ -treated, alkalized soils. The solubility of the precipitate increased with decreasing pH and concentration of NaCl. Furthermore, absorption of soil lead by hydrous oxides of iron and manganese, and its consequent immobilization, has been reported by Gadde and Laitinen.⁸⁴

Studies have identified cation exchange capacity, organic matter content, pH, soil type, and soil drainage as the important factors influencing the mobility of lead in soils.⁸⁵ Santillan-Medrano and Jurinak⁸⁶ conducted batch equilibrium studies to obtain solubility data for lead and cadmium in soil. Lead solubility decreased in the soils as pH increased. The lowest values were obtained in calcareous soil. In noncalcareous soil, the solubility of lead appears to be regulated by $\text{Pb}(\text{OH})_2$, $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_4(\text{PO}_4)_2$, $\text{Pb}_5(\text{PO}_4)_3\text{OH}$, and even PbCO_3 , depending on the pH.

The creation of organic chelating agents by biologic activity serves as one of the most effective processes of metal mobilization or immobilization in the soil. These agents are either plant products, microbial metabolites, or humic compounds (humic acids). The latter are capable of precipitating lead. The amounts and types of organic matter present appear to provide an important control mechanism for the movement of heavy-metal ions in soil systems. The association of lead and organic matter, however, is not always empirically consistent.⁸⁷

Olson and Skogerboe²⁹ preconcentrated lead compounds in roadside soil samples and used X-ray powder diffraction techniques for compound identification. The lead compounds in each soil fraction examined are shown in Table 6-12. The most abundant lead salt found was the relatively insoluble PbSO_4 . The authors note that generally 70 percent or more of the total lead in the soils examined was contained in the dense fractions and that the majority (>50 percent) of this lead was present as sulfate. The results indicate that oxides present in the soil

were minor constituents compared to the sulfate concentrations. Since lead bromochloride compounds are the principal constituents of fresh automobile exhaust emissions, conversion to lead sulfate must have occurred either in the atmosphere or in the soil. The authors suggest that sulfuric acid formed from SO_2 in the atmosphere or at the soil interface may react with the lead particulate to form lead sulfate. Reaction with the sulfate ion also may occur in the soil in contact with groundwater.²⁴ The results of Lee et al.⁹ (Section 6.2.2.1) support these general contentions.

Data are limited regarding the chemical composition of lead in soil contaminated by emissions from stationary sources. Lead sulfide and lead chloride are thought to be the major constituents in soils in the vicinity of mining industries, and lead oxide is the chief one in the vicinity of smelters. The presence of lead sulfide as the primary compound in soils along a mine-access road in Missouri has been reported, (Table 6-12). Analytical data confirming the other compounds mentioned above are not available.

6.4.2 Water

6.4.2.1 INORGANIC

The chemistry of lead in an aqueous solution is highly complex because the element can be found in a multiplicity of forms. Hem and Durum have reviewed the chemistry of lead in water in detail,⁸⁸ and the aspects of aqueous lead chemistry that are germane to this document are discussed in Chapter 3.

Natural concentrations of lead in lead-ore deposits do not normally move appreciably in ground or surface water. Any lead dissolved from primary lead sulfide ore tends to combine with carbonate or sulfate ions to (1) form insoluble lead carbonate or lead sulfate, or (2) be absorbed by ferric hydroxide.⁸⁷ An outstanding characteristic of lead is its tendency to form compounds of low solubility with the major anions of natural water. The hydroxide, carbonate, sulfide, and more rarely the sulfate may act as solubility controls. The amount of lead that can remain in solution in water is a function of the pH of the water and the dissolved salt content. Equilibrium calculations show that the total solubility of lead in hard water (pH > 5.4) is about 30 $\mu\text{g/liter}$ and about 500 $\mu\text{g/liter}$ in soft water (pH < 5.4).⁸⁹ Lead sulfate (PbSO_4) is present in soft water and limits the lead concentration in solution. Above pH 5.4, PbCO_3 and $\text{Pb}_2(\text{OH})_2\text{CO}_3$ limit the

TABLE 6-12. LEAD COMPOUNDS IDENTIFIED IN ROADSIDE SOILS BY X-RAY POWDER DIFFRACTION TECHNIQUES²⁹

Location and soil fraction	Compounds found	Estimated concentrations ^a
Fort Collins:		
Magnetic	PbSO_4	Major
Nonmagnetic	PbSO_4	Major
	$\text{PbO}\cdot\text{PbSO}_4$	Minor
	PbO_2	Trace
	PbO^b	Trace
Denver:		
Magnetic	PbSO_4	Major
Nonmagnetic	PbSO_4	Major
Chicago:		
Magnetic	PbSO_4	Major
Nonmagnetic	PbO	Major
	PbSO_4	Minor
Chicago:		
Magnetic	PbSO_4	Major
Nonmagnetic	PbSO_4	Major
Missouri:		
Magnetic	None ^c	—
Nonmagnetic	PbS	Major
	PbSO_4	Minor

^aMajor indicates the principal portion of lead present in the soil fraction indicated and, therefore, the principal portion of the soil sample. Minor refers to approximately 1 to 10 percent of the lead in the respective fractions. Trace quantities are less than approximately 1 percent of the total in each fraction.

^bAssignment is based on the presence of only the most intense d-spacing and is therefore questionable.

^cComplex d-spacing pattern obtained with all intensities low; positive assignment of any one compound or group of compounds is questionable.

concentration. The carbonate concentration is in turn dependent on the partial pressure of CO_2 as well as the pH. Calculations by Hem and Durum⁸⁸ show that many river waters in the United States have lead concentrations near the solubility limits imposed by their pH levels and contents of dissolved CO_2 species. Because the influence of changing temperature and pH may be substantial, observed lead concentrations may vary significantly from theoretically calculated ones.

Lazrus et al.⁶⁰ calculated that as much as 138 g/ha-mo of lead may be deposited by rainfall in some parts of the northeastern United States. Assuming an average annual rainfall runoff of 50 cm (~20 in), the average concentration of lead in the runoff would have to be about 330 $\mu\text{g/liter}$ to remove the lead at the rate of 138 g/ha-mo. Concentrations as high as 330 $\mu\text{g/liter}$ could be stable in water with pH near 6.5 and an alkalinity of about 25 ng bicarbonate ion/liter of water. Water having these properties is common in runoff areas of New York State and New England; hence, the potential for high lead concentrations exists there. In other areas, the average pH and alkalinity are so high that less than 1 $\mu\text{g/liter}$ of lead could be retained in solutions at equilibrium.⁸⁷

A significant fraction of the lead carried by river water may be in an undissolved state. This nonsolute lead can consist of colloidal particles in suspension or larger undissolved particles of lead carbonate, oxide, hydroxide, or other lead compounds incorporated in other components of particulate lead from runoff, either as sorbed ions or surface coatings on sediment mineral particles or carried as a part of suspended living or nonliving organic matter.⁸⁷ A laboratory study by Hem⁹⁰ of sorption of lead by cation exchange indicated that a major part of the lead in stream water may be adsorbed on suspended sediment. Figure 6-26 illustrates the distribution of lead outputs between filtrate and solids in stream water from both urban and rural compartments, as reported by Rolfe and Jennett.⁹¹ The majority of lead output is associated with suspended solids in both urban and rural compartments with very little dissolved in the filtrate. The ratio of lead in suspended solids to lead in filtrate varies from 4:1 in the rural compartment to 27:1 in the urban compartment.

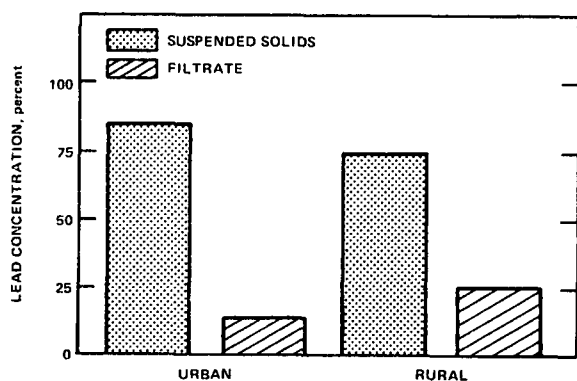


Figure 6-26. Lead distribution between filtrate and suspended solids in stream water from urban and rural compartments.⁹⁰

The concentration of lead usually reported represents a somewhat arbitrarily defined solute fraction, separated from the nonsolute fraction by filtration. Most filtration techniques cannot be relied on to remove all colloidal-sized particles. Upon acidification of the filtered sample, which is usually done to preserve it before analysis, the colloidal material that passes through is dissolved and reported in that form. Usually the solids removed from a surface water sample by filtration are not analyzed for lead. But even the lead in rainfall can be mainly particulate, and thus it will be necessary to obtain more information on the amounts of lead transported in nonsolute form⁸⁷ before a valid estimate can be obtained of the effectiveness of runoff in transporting lead away from areas where it has been deposited by atmospheric fallout and rain.

6.4.2.2 ORGANIC

The organic components of soil-water system are an extremely diverse group of compounds that includes carbohydrates, amino acids, phenolic and quinonic compounds, organic acids, nucleic acids, enzymes, porphyrins, and humic materials.⁸⁷ In addition to the natural organic compounds present in soils, streams and lakes contain organic sediments and suspended solids that have been derived from municipal, agricultural, and industrial wastes. These wastes include carbohydrates, proteins, nucleic acids, enzymes, lipids, and many other organic compounds found in living systems. In addition, oils, plasticizers, polymers, and many other organic compounds are discharged to natural waterways by manufacturing and chemical industries. The interaction of lead with these organic compounds is still not well understood, but most of these organic materials can confidently be expected to form complexes with lead (and other metals), since they all contain available donor sites for complexation. A discussion of metal complexation is presented in Chapter 3 and Appendix B.

The presence of fulvic acid (a constituent of soil humic materials) in water has been shown to increase the rate of solution of lead sulfide 10 to 60 times over that of a water solution at the same pH that did not contain fulvic acid.^{87,92} At pH values near 7, soluble lead-fulvic acid complexes were present in solution. At initial pH values between 7.4 and about 9, the lead-fulvic complexes partially decomposed, and lead hydroxide and carbonate were precipitated. At initial pH values of about 10, the lead-fulvic acid complexes again increased. This increase was attributed to dissociation of phenolic groups at high pH values, which increases the complexing capacity of the fulvic acid. But it may also have been due to the formation of soluble lead-hydroxyl complexes.

In summary, the complexing of lead by most of the common sulfur-, phosphorus-, oxygen-, and nitrogen-containing ligands means that lead will accumulate in living and nonliving organic components of soil-water and sediment-water systems. The living and nonliving organic components are not independent, of each other, but they are constantly interacting as the living components metabolize the nonliving components of the system and then die, contributing their remains to the pool of nonliving compounds in the system. The fate of heavy metals in this process has not been elucidated; but the sediment in a contaminated surface-water body will serve as a large reservoir that can provide lead and other metals to the biota of the system even after

heavy-metal pollutants have ceased to be introduced. Most attention has been given to the heavy metals dissolved in the water phase of surface water rather than to the complexed metals in the sediment phase, though sediments probably contain a higher amount of lead.⁸⁷

The biotransformation of lead to volatile tetramethyl lead constitutes one mechanism by which lead may leave sediment-water systems. The direct, biological methylation of certain inorganic lead compounds by lake sediment microorganisms has been reported.^{93,94} All the lake sediments tested were able to transform trimethyl lead to tetramethyl lead,⁹³ but only some of the sediments were able to transform lead nitrate and lead chloride into tetramethyl lead. No biotransformation occurred when the lake sediments were incubated with lead oxide, lead hydroxide, lead bromide, lead cyanide, or lead palmitate.⁹³ Certain pure bacterial isolates (see Chapter 8) from these lake sediments were shown to transform trimethyl lead to tetramethyl lead in the anaerobic incubation system used.⁹³

The conversion of the tri- to the tetramethyl lead salt was subsequently postulated to be chemical rather than biological, proceeding via formation and then decomposition of an organic sulfide intermediate, $(\text{Me}_3\text{Pb})_2\text{S}$.⁹⁵ Using a system containing no sulfides, however, other workers showed the production by microorganisms of Me_4Pb from Me_3Pb^+ much in excess of yields expected from the stoichiometry of redistribution reactions of lead alkyl compounds in aqueous solutions.⁹⁴ Thus, the alkylation appears to be direct and biological. The alkylation of lead, unlike that of mercury, was not mediated by methylcobalamin, as shown when equimolar amounts of Me_3PbOAc , Me_3PbCl , Me_2PbCl_2 , and $\text{Pb}(\text{NO}_3)_2$ were substituted for inorganic mercury in an aqueous test system ($\sim\text{pH}$ 7).⁹⁵ Taylor and Hanna,⁹⁶ however, have recently demonstrated that prolonged incubation of methylcobalamin with a fine suspension of lead oxide (Pb_3O_4) in an aqueous medium results in partial demethylation of the corrinoid. This chemical demethylation of MeB_{12} by Pb_3O_4 was shown to be highly pH dependent, with no demethylation occurring at pH 7, and 61 percent occurring at pH 2. Tracer studies with [^{14}C]-methyl-labeled methylcobalamin indicated that demethylation of MeB_{12} by $\text{Pb}(\text{IV})$ was accompanied by a proportional volatilization of the label. These results are in agreement with the known instability of monoalkyl lead compounds in aqueous media as described by Wood.⁹⁷

The alkylation of lead, then, unlike that of mercury, does not appear to result in nonvolatile, toxic organolead that could undergo biomagnification in the food chain. Volatile TML generated *in situ* would be expected to escape from a body of water. The possible uptake of tetramethyl lead by aquatic organisms during its passage to the surface of a body of water is unknown.

6.4.3 Plants

Lead is transferred from the atmosphere to the soil and vegetative compartments of the environment by dry and wet deposition. Considerable attention has been devoted to determining the amount and localization of lead in roadside and smelter areas, but little information is available regarding its chemistry and effects in those areas. Motto et al.⁹⁸ suggested that plant uptake is probably related better to soluble rather than total lead in soils. Wilson and Cline⁹⁹ concluded that only 0.003 to 0.005 percent of total lead in soil is available for plant uptake. The soil solution is affected by all the reactions that occur as the constituents are changed through addition to or depletion from the soil. Ultimately, the composition of the soil solution is controlled by the solubility of the various mineral phases in the soil. The long-term effects of lead in soils are uncertain. Only recently has attention been given to the solubility relationships of PbSO_4 , $\text{Pb}_3(\text{PO}_4)_2$, and PbCO_3 as possible controlling mechanisms for the amount of lead in soils.⁴⁴ If PbCO_3 is involved as a reaction product, there is the possibility that soils of high pH, upon becoming acidic, could release lead at some future time.¹⁰⁰ The question of chemical identity of lead in plants is still largely unanswered. Hamp and Ziegler¹⁰¹ have suggested that lead associated with plant surfaces in nature may be largely lead phosphate. Zimdahl,¹⁰² citing studies conducted at Colorado State University and the University of Illinois, reported the identification of lead pyrophosphate in bean roots and lead orthophosphate in soybean root. The results of later solubility studies of the two compounds suggested that lead pyrophosphate should be the dominant form in plants.

The process by which lead is taken up by plants, which may be passive,^{85,103} is favored under conditions of low soil pH.¹⁰⁴ MacLean et al.¹⁰⁵ have suggested that soil management practices such as the addition of organic matter, lime, and phosphate may be appropriate in contaminated soils to reduce the availability of lead for plant uptake. They found that the concentration in oats and alfalfa varied inversely

with pH and organic matter, and that addition of phosphate reduced the uptake of lead; they suggested that the pH effect was due to repression of lead solubility at the higher pH values. John and Van Laerhoven¹⁰⁶ found little difference in uptake by oats and lettuce when lead was derived from water-insoluble lead carbonate as opposed to the more water-soluble lead chloride or nitrate. Hence the formation of lead carbonate as a result of liming would not explain the pH effect.

Work at the University of Illinois and at Colorado State University, cited by Zimdahl,¹⁰² has shown that uptake by several plant species is inversely proportional to soil lead content and is greatest under conditions of low pH and low phosphorus. The binding or exchange capacity of soils, related to organic content, is extremely important as a determinant of lead availability to plants. Chelating agents can modify the uptake and possibly the movement of heavy metals by plants, but the relative importance of natural chelating substances is hard to evaluate at this time.¹⁰² Zimdahl,¹⁰² citing a number of studies regarding chelation of lead with EDTA, concludes that the extent of lead movement within the plant is still unresolved. He questions whether studies with synthetic and highly ionized chelating agents such as EDTA actually reflect what is happening in nature.

In a study conducted at the University of Illinois¹⁰⁷ (cited by Zimdahl¹⁰²), it was shown that the roots of hydroponically grown corn acquired a surface lead precipitate and slowly accumulated crystalline lead in the cell walls. The surface precipitate formed quickly and independently of plant activity. Two compounds were postulated but not identified. The lead entering the root was concentrated in some but not all dictyosome vesicles. After precipitation had occurred in the dictyosome vesicle, cell-wall precursors were added to the vesicle by apposition of vesicles or by internal secretion. As the lead-containing crystals grew, more cell-wall material was added, so that the entire vesicle eventually moved to the periphery of the cell to achieve fusion with the cell wall. Lead deposits were thereby concentrated at the cell wall and not within mitochondria or other organelles.¹⁰² Although this sequence of events was observed in the root tips, deposits were observed throughout the plant, and it was suggested that a similar process occurred in all plant tissues.¹⁰²

The deposition of lead on the leaf surfaces of plants where the particles are often retained for long time periods must also be considered.^{32,108,109} Several studies have shown that plants near roadways

exhibit considerably higher levels of lead than those farther away. In most instances, the higher concentrations were due to lead particle deposition on plant surfaces.³² Studies have shown that particles deposited on plant surfaces are often very difficult to remove completely by simple washing techniques considered characteristic of the treatment that would be used in a household kitchen.^{108,110,111} Leaves with hairy surfaces seem able to retain (and attract) particles via an electrostatic mechanism. Other types of leaves are covered with a cuticular wax sufficiently sticky to preclude the removal of particles. Thus rainfall does not serve as a particularly effective means of removing the deposited particles.¹¹⁰ Animals or humans consuming the leafy portions of such plants can certainly be exposed to higher than normal levels of lead. Fortunately, a major fraction of lead emitted by automobiles is deposited inside a typical highway right-of-way, so at least part of this problem is alleviated.

The particle deposition on leaves has led some investigators to stipulate that lead may enter plants through the leaves. This would typically require, however, that the lead particles be dissolved by constituents of the leaf surface and/or converted to the ionic form via contact with water. The former possibility is not considered likely, since cuticular waxes are relatively inert chemically. Zimdahl and Arvik⁸⁵ have shown in a rather elegant set of experiments that entry of ionic lead through plant leaves is of minimal importance. By using the leaf cuticles of several types of plants essentially as membranes, they found that even high concentrations of lead ions would not pass through the cuticles into distilled water on the opposite side.

The results of the studies discussed above generally indicate the following:

1. The uptake of lead by plants from soil is highly dependent on the chemical equilibria prevalent in the soil in question. The uptake can probably be controlled through treatment of the soil with materials (e.g., lime, phosphate fertilizers, etc.) that affect these chemical equilibria.
2. Although uptake rates are enhanced at lower soil pH levels, the majority of the lead taken up remains in the plant roots; only smaller fractions are translocated to the shoots.
3. Deposition and retention of lead particles on plant surfaces can serve as a route of animal or human exposure to automotive lead. Thus crops grown near sources of high traffic

should probably be considered suspect unless appropriate safety precautions are taken.

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7. ENVIRONMENTAL CONCENTRATIONS AND POTENTIAL EXPOSURES

7.1 AMBIENT AIR EXPOSURES

Several studies on concentrations of lead in the ambient air have been undertaken. These studies were generally intended to survey the levels and distributions of lead in the general air environment and around sources. They usually were not designed in conjunction with epidemiological studies of the concurrent effects of lead on man or other organisms. Yet that is the context in which these studies must now be interpreted to shed the most light possible on the concentrations likely to be encountered in various environmental settings.

Measurements taken with high-volume samplers, dust-fall buckets, and particle size fractionators are included in these studies; however, with the exception of the NASN data from 1970 through 1974, quality control and interlaboratory comparability are unspecified. The effectiveness of some filter media in collecting very small lead-containing particles has been questioned; this subject is discussed in Chapter 4. The studies show that:

1. Lead typically occurs in urban airborne suspended particles 0.5 μm or less in mass median equivalent diameter at annual average concentrations ranging from <0.1 to $5 \mu\text{g}/\text{m}^3$, with an overall average of 1 to $2 \mu\text{g}/\text{m}^3$.
2. Urban concentrations of lead have declined somewhat since 1970.
3. Suspended particles in rural air samples contain lead at concentrations ranging from <0.01 to $1.4 \mu\text{g}/\text{m}^3$, with an overall average of about $0.2 \mu\text{g}/\text{m}^3$.
4. Monthly average concentrations of lead in urban settleable particles range from 3 to $12 \text{mg}/\text{m}^2\text{-mo}$.
5. Indoor concentrations of lead are quite variable, but are generally one- to two-thirds the concentrations of adjacent outdoor levels.

A discussion of the NASN measurements follows.

Summaries of additional studies can be found in Appendix C.

7.1.1 National Air Surveillance Network (NASN) Data

Since 1957, samples of suspended particulate matter collected at some 300 urban and 30 nonurban NASN sites have been analyzed for trace metals, including lead. Only data beginning with 1966 are summarized here, however, because the procedure used before 1966 was found to recover only about 50 percent of the lead actually present. The emission spectrographic method now employed in the analysis has sufficient sensitivity to permit detection of lead in all urban and most nonurban samples.

Summaries of the data for urban and nonurban NASN sites for 1966 through 1974 are presented in Tables 7-1 and 7-2, which categorize the sites by four successive annual average concentration ranges.^{1,2} The majority of the urban sites (91 percent of the site-years) reported annual averages below $2.0 \mu\text{g}/\text{m}^3$, and the majority of nonurban sites (86 percent of the site-years) reported annual averages below $0.2 \mu\text{g}/\text{m}^3$.

Samples collected by the NASN from 1970 through 1974 were combined for analysis into quarterly composites. Tables 7-3 and 7-4, respectively, give the cumulative frequency distributions of urban and nonurban quarterly composite values for 1970 through 1974.¹

Urban NASN sites for which annual average concentrations have been $3.0 \mu\text{g}/\text{m}^3$ or greater are listed in Table 7-5.^{1,2} Highest concentrations for shorter intervals (quarterly and 24-hr) have been included, where available, in order to indicate the variation in concentration with averaging time and potential peak exposure conditions. A large number of Southern California cities are included in the list because of the heavy automobile traffic in these areas. Both the annual average and maximum values at Los Angeles County sites were consistently high,

TABLE 7-1. NUMBER OF NASN URBAN STATIONS WHOSE DATA FALL WITHIN SELECTED ANNUAL AVERAGE LEAD CONCENTRATION INTERVALS, 1966-1974^{1,2}

Year	Concentration interval, $\mu\text{g}/\text{m}^3$					Total
	< 0.5	0.5-0.99	1.0-1.9	2.0-3.9	4.0-5.3	
1966:						
No. stations	9	40	40	6	—	95
Percent	9	42	42	6	—	100
1967:						
No. stations	4	37	63	9	—	113
Percent	3	32	55	7	—	100
1968:						
No. stations	14	67	54	10	1	146
Percent	9	45	36	6	1	100
1969:						
No. stations	5	46	103	23	1	178
Percent	2	25	57	12	1	100
1970:						
No. stations	9	54	80	15	1	159
Percent	5	33	50	9	1	100
1971:						
No. stations	—	23	64	21	1	109
Percent	—	21	58	19	1	100
1972:						
No. stations	16	67	84	12	1	180
Percent	9	37	47	7	0	100
1973:						
No. stations	20	76	36	4	1	137
Percent	15	55	26	3	1	100
1974:						
No. stations	19	69	38	4	0	130
Percent	15	53	29	3	0	100
1966-1974:						
No. stations	96	479	562	104	6	1247
Total percent	8	38	45	8	1	100

TABLE 7-2. NUMBER OF NASN NONURBAN STATIONS WHOSE DATA FALL WITHIN SELECTED ANNUAL AVERAGE LEAD CONCENTRATION INTERVALS, 1966-1974^{1,2}

Year	Concentration interval, $\mu\text{g}/\text{m}^3$				Total
	< 0.03	0.03-0.099	0.10-0.19	0.20-0.45	
1966:					
No. stations	—	10	6	3	19
Percent	—	52	32	16	100
1967:					
No. stations	1	7	10	2	20
Percent	5	35	50	10	100
1968:					
No. stations	1	15	4	—	20
Percent	5	75	20	—	100
1969:					
No. stations	—	11	9	1	21
Percent	—	52	43	5	100
1970-1971:					
No. stations	—	—	7	3	10
Percent	—	—	70	30	100
1972:					
No. stations	10	4	9	11	34
Percent	29	12	26	33	100
1973:					
No. stations	9	7	6	1	23
Percent	39	31	26	4	100
1974:					
No. stations	3	5	6	2	16
Percent	19	31	38	12	100
1966-1974:					
No. stations	24	59	57	23	163
Total percent	15	36	35	14	100

TABLE 7-3. CUMULATIVE FREQUENCY DISTRIBUTIONS OF QUARTERLY LEAD MEASUREMENTS AT URBAN STATIONS BY YEAR, 1970 THROUGH 1974¹
($\mu\text{g}/\text{m}^3$)

Year	No. quarterly composites	Min	Percentile							Max.	Arithmetic		Geometric	
			10	30	50	70	90	95	99		Mean	Std. dev.	Mean	Std. dev.
1970	797	LD ^a	0.47	0.75	1.05	1.37	2.01	2.59	4.14	5.83	1.19	0.80	0.99	1.84
1971	717	LD ^a	0.42	0.71	1.01	1.42	2.21	2.86	4.38	6.31	1.23	0.87	1.00	1.89
1972	708	LD ^a	0.46	0.72	0.97	1.25	1.93	2.57	3.69	6.88	1.13	0.78	0.93	1.87
1973	559	LD ^a	0.35	0.58	0.77	1.05	1.62	2.08	3.03	5.83	0.92	0.64	0.76	1.87
1974	594	0.08	0.36	0.57	0.75	1.00	1.61	1.97	3.16	4.09	0.89	0.57	0.75	1.80

^a LD = limit of detection.

TABLE 7-4. CUMULATIVE FREQUENCY DISTRIBUTIONS OF QUARTERLY LEAD MEASUREMENTS AT NONURBAN STATIONS BY YEAR, 1970 THROUGH 1974¹
($\mu\text{g}/\text{m}^3$)

Year	No. quarterly composites	Min	Percentile							Max.	Arithmetic		Geometric	
			10	30	50	70	90	95	99		Mean	Std. dev.	Mean	Std. dev.
1970	124	0.003	0.003	0.003	0.003	0.003	0.267	0.383	0.628	1.471	0.088	0.190	0.040	3.72
1971	85	0.003	0.003	0.003	0.003	0.127	0.204	0.783	1.134	0.047	0.155	0.008	4.80	
1972	137	0.007	0.007	0.107	0.166	0.294	0.392	0.950	1.048	0.139	0.169	0.090	2.59	
1973	100	0.015	0.015	0.015	0.058	0.132	0.233	0.698	0.939	0.110	0.149	0.068	2.77	
1974	79	0.007	0.007	0.053	0.087	0.141	0.221	0.317	0.496	0.534	0.111	0.111	0.083	2.30

TABLE 7-5. NASN STATIONS WITH ANNUAL AVERAGE LEAD CONCENTRATIONS $\geq 3.0 \mu\text{g}/\text{m}^3$ ^{1,2}

Year and station	Average	Maximum	
		Quarterly composite	24-hr
1966:			
Phoenix, Ariz.	3.2	8.1	—
Burbank, Calif.	3.7	6.0	—
Los Angeles, Calif.	3.6	11.0	—
Pasadena, Calif.	3.6	4.3	—
1967:			
Los Angeles, Calif.	3.1	5.4	—
1968:			
Burbank, Calif.	4.4	—	14.0
Glendale, Calif.	3.0	—	7.5
Long Beach, Calif.	3.3	—	12.0
Los Angeles, Calif.	3.9	—	10.0
Pasadena, Calif.	3.5	—	8.3
1969:			
Fairbanks, Alaska	3.2	4.8	—
Phoenix, Ariz.	3.1	7.1	—
Burbank, Calif.	3.5	4.7	—
Glendale, Calif.	3.1	4.5	—
Los Angeles, Calif.	4.6	5.7	—
San Juan, Puerto Rico	3.8	4.2	—
Dallas, Tex.	3.0	5.2	—
1970:			
Burbank, Calif.	4.9	5.8	—
Glendale, Calif.	3.5	4.2	—
Los Angeles, Calif.	4.5	5.6	—
San Juan, Puerto Rico	3.7	4.1	—
Dallas, Tex.	3.2	3.8	—
1971:			
Anaheim, Calif.	3.3	4.0	—
Burbank, Calif.	5.3	6.2	—
Santa Ana, Calif.	3.5	4.6	—
Los Angeles, Calif.	4.6	6.3	—
1972:			
Burbank, Calif.	3.2	6.7	—
Glendale, Calif.	3.5	5.2	—
Los Angeles, Calif.	3.1	4.8	—
San Juan, Puerto Rico	5.0	6.9	—
1973:			
Burbank, Calif.	4.0	5.2	—

apparently because of location, topography, and meteorological conditions that favor retention of pollutants in the air over the area.

Ambient particulate lead data from NASN were studied for trends over the 10-year period from 1965 through 1974. Figure 7-1 shows the 10th, 50th, and 90th percentiles for data from 92 NASN urban sites.³ Urban lead concentrations as described by the 50th percentiles increased from 1965 until 1971 and then declined from about $1.1 \mu\text{g}/\text{m}^3$ to $0.84 \mu\text{g}/\text{m}^3$ — about a 24-percent decrease, with most of

this decline occurring between 1972 and 1973. The other percentiles exhibit a similar pattern. This general pattern describes the trend for most of the sites studied. Trends in the percentage of lead in the total particulate matter measured also follow this pattern, which indicates that the trends in lead are not just a result of general particulate controls but are a direct result of decreases in lead emissions.

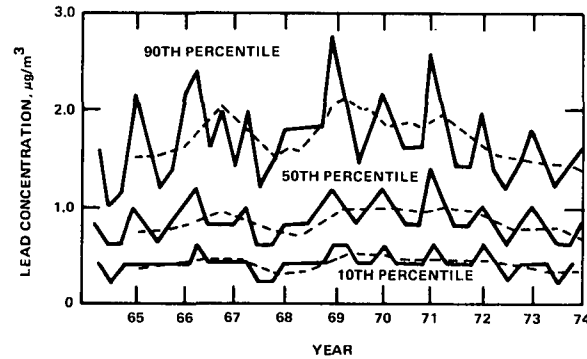


Figure 7-1. Seasonal patterns and trends in quarterly average urban lead concentrations.³

The seasonal pattern in quarterly composite values (solid lines in Figure 7-1) shows that the highest levels of airborne lead occurred in the winter quarters (first and fourth) and the lowest levels in the summer quarters (second and third). In contrast, automotive emissions of lead would be expected to be greater in the summer for two reasons: (1) gasoline usage is higher in the summer, and (2) lead content is raised in summer gasolines to replace some of the more volatile high-octane components that cannot be used in summertime gasolines. Evidently summertime meteorological conditions expedite the movement of these larger emissions more quickly and widely through the atmosphere on their way to subsequent destinations in vegetation, crops, soil, and water.

Since about the 1970 model year, automobiles have been built with lower-compression engines that can use lower-octane gasoline and thus gasoline with lower lead content. As a result of this engine modification, practically all cars built since 1970 are able to use regular gasoline instead of the more leaded premium fuels. Figures 7-2 and 7-3 show, respectively, the percentage of the total market for regular and premium gasolines and the trend in lead content of gasolines.⁴ The results of the engine modifications can be clearly seen in the lower lead content in gasoline (both in regular and premium grades) and in the subsequent increase in regular gasoline sales and decrease in premium sales. These

factors, coupled with the use of a modest amount of low-lead and no-lead gasoline introduced at about this same time, are identified as principally responsible for the observed decrease in ambient lead concentrations over this period. The increasing use of unleaded gasoline resulting from EPA regulations, which is reflected in Figure 7-2, will lead to even lower levels of atmospheric pollution in the future. The effect of these changes is enough to override the general increase in annual gasoline consumption of about 5 percent typical of recent years (except 1974). This increase in gasoline consumption probably does not proportionately affect many urban monitoring sites (which are chiefly center-city locations) because their neighborhoods are generally at or near traffic saturation. There may even be instances of a reduction in vehicle miles traveled in downtown areas because of car pooling, improved mass transit systems, and the loss of business activity to suburban shopping centers.

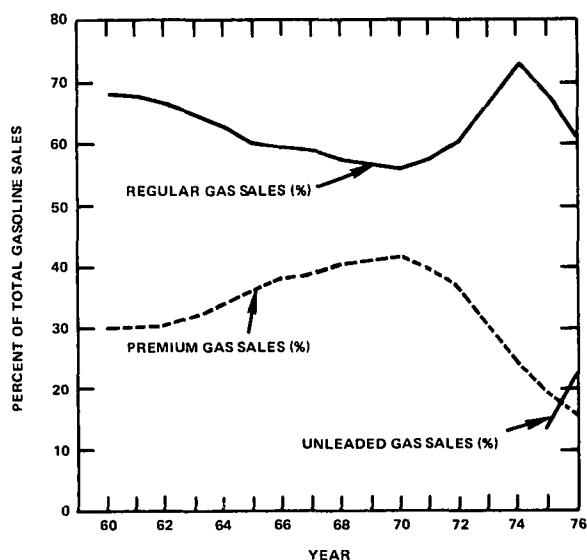


Figure 7-2. Nationwide trends in regular, premium, and unleaded gasoline sales, 1960-1976.⁴

In addition to the NASN study, a number of other studies involving major cities and rural areas have been undertaken. These data support the NASN results (see Appendix C).

7.1.2 Airborne Particle Size Distribution

In 1970, a cascade impactor network was established by EPA in six cities (Cincinnati, Chicago, Denver, Philadelphia, St. Louis, and Washington, D.C.) to collect particulates of different size ranges for subsequent analysis for lead and other metals.⁵ The samples, collected once every 2 weeks for a full

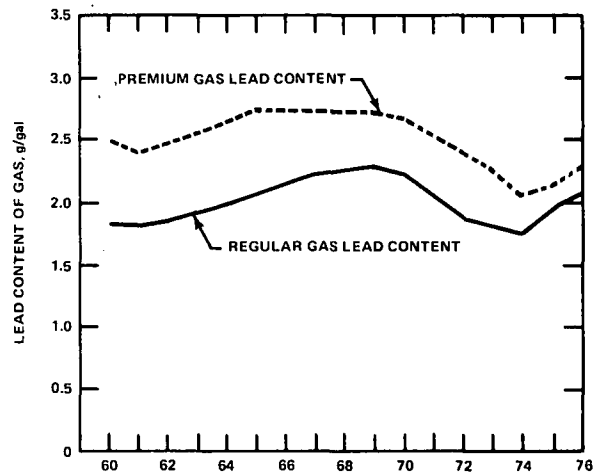


Figure 7-3. Nationwide trends in lead content of regular and premium gasoline, 1960-1976.⁴

year, were analyzed for size distribution. Samples from each city were also composited quarterly and analyzed for lead by optical emission spectroscopy.

The average annual total lead concentration as determined in this study ranged from a high quarter of $3.2 \mu\text{g}/\text{m}^3$ in Chicago to a low quarter of $1.3 \mu\text{g}/\text{m}^3$ in Washington, D.C. The average mass median diameter for lead particles ranged from $0.69 \mu\text{m}$ in St. Louis to $0.42 \mu\text{m}$ in Washington, D.C. Fifty-nine to 74 percent of the lead was associated with particles smaller than $1 \mu\text{m}$ in diameter. Quarterly and annual particle size distribution data are presented in Table 7-6.

7.1.3 Vertical Gradients of Lead in the Atmosphere

Very few studies have been conducted to determine the variation of lead concentrations with height above the ground. Of those that were found, all contained the premise, either explicitly or implicitly, that the concentrations being studied derived principally from automotive emissions. Of the studies found in the literature, none were adequately designed to establish the lead concentration versus height relationship. Such a study would require simultaneous measurement (preferably continuous) at given height intervals over a long period of time (a minimum of 1 year). Even then, the results would be valid only for a location having the same characteristics and experiencing the same atmospheric conditions. A single set of concentration values obtained over short and variable time intervals is not sufficient to draw conclusions regarding general exposure conditions.

TABLE 7-6. QUARTERLY AND ANNUAL SIZE DISTRIBUTIONS OF LEAD-BEARING PARTICLES FOR SIX CITIES. 1970⁵

City and quarter of year	Average concentration, $\mu\text{g}/\text{m}^3$	Average mass median diameter, μm	Percentage of particles $\leq \mu\text{m}$
Chicago, Ill.:			
1	2.9	1.43	41
2	3.5	0.51	65
3	3.5	0.56	65
4	2.9	0.54	64
Total year	3.2	0.68	59
Cincinnati, O.:			
1	1.0	0.25	79
2	2.2	0.41	74
3	1.9	0.54	69
4	2.1	0.65	67
Total year	1.8	0.48	72
Denver, Colo.:			
1	2.0	0.43	76
2	1.1	0.58	68
3	1.4	0.52	69
4	3.0	0.56	66
Total year	1.8	0.50	70
Philadelphia, Penn.:			
1	1.5	0.36	74
2	1.2	0.38	74
3	1.8	0.70	62
4	1.9	0.45	70
Total year	1.6	0.47	70
St. Louis, Mo.:			
1	1.9	0.46	68
2	1.6	0.63	63
3	1.8	0.78	59
4	1.8	0.95	53
Total year	1.8	0.69	62
Washington, D.C.:			
1	1.3	0.36	76
2	1.0	0.39	73
3	1.3	0.41	74
4	1.8	0.54	71
Total year	1.3	0.42	74

Darrow and Schroeder⁶ measured lead concentrations at eight heights above street level in Brattleboro, Vermont. The values found are shown in Table 7-7. The average traffic flow was reported to be 7500 cars per day. The concentration levels shown in Table 7-7 are considerably higher than those usually reported in other cities. The investigators attributed the higher values to greater collection efficiency and lower sampling heights, but this was not confirmed. The sampling times were short and variable. General conclusions regarding the relationship of concentrations versus height cannot be drawn from these data.

TABLE 7-7. LEAD IN AIR ON MAIN STREET, BRATTLEBORO, VERMONT, SEPTEMBER 12 and 13, 1972^{a,6}
($\mu\text{g}/\text{m}^3$)

Height above street, ft	Sampling times				
	8:36 a.m. 10:15 a.m.	10:20 a.m. 12:00 noon	1:20 p.m. 3:00 p.m.	3:25 p.m. 4:25 p.m.	4:35 p.m. 9/12 1:02 p.m. 9/13
1 ^b	8.94	7.84	3.85	—	—
2	—	—	5.31	17.38	—
3	8.22	4.40	—	—	—
4	—	—	7.56	21.11	—
5 ^c	7.15	8.15	—	—	—
7	—	—	—	2.40	—
8	—	—	—	—	3.01
30	—	—	—	—	4.25

^a Average air lead value for 54.38 m³ air = 8.54 μg Pb/m³.
^b 1-, 2-, 3-, and 4-ft heights: Average air lead values for 13.53 m³ air = 8.01 μg Pb/m³.
^c 5-, 7-, 8-, 30-ft heights: Average air lead values for 40.85 m³ air = 3.96 μg Pb/m³.

Edwards⁷ has reported measurements made in downtown Fort Collins, Colo. Measurements were made in a street canyon formed by two- and three-story buildings (average height, 9 m). With a 2.3 m/sec wind from the Northeast (street running north-south), lead concentrations along the east side of the street canyon ranged from 11.3 $\mu\text{g}/\text{m}^3$ at street level to 4.0 $\mu\text{g}/\text{m}^3$ at roof level. On the west side of the street, concentrations ranged from 0.9 $\mu\text{g}/\text{m}^3$ at street level to 1.3 $\mu\text{g}/\text{m}^3$ at roof level. Values for two additional sampling points above the rooftops on each side of the street were 0.4 $\mu\text{g}/\text{m}^3$ (east side) and 0.9 $\mu\text{g}/\text{m}^3$ (west side). Lead concentrations 2 to 5 blocks away ranged from 0.1 to 0.3 $\mu\text{g}/\text{m}^3$. These data reflect the wide variability that can be expected in urban traffic environments. Under moderate cross-wind conditions, concentrations within the canyon were strikingly anisotropic, and street-level concentrations along the upwind building faces were substantially higher than along the downwind face. With different wind regimes, different building configuration, and different stability conditions, the distribution of concentration values would also be different.

Barltrop and Strelow⁸ conducted an air sampling program at a proposed nursery site under an elevated motorway. The height of the motorway was 9.3 m. Air samplers were operated at five to seven sites from Monday to Friday, 8 a.m. to 6 p.m. for 1 year. The maximum individual value observed was 18 $\mu\text{g}/\text{m}^3$. The 12-month mean ranged from 1.51 $\mu\text{g}/\text{m}^3$ to 1.35 $\mu\text{g}/\text{m}^3$, with standard deviations of 0.91 and 0.66, respectively. The authors reported that the airborne concentrations were independent of height from ground level up to 7 m.

PedCo-Environmental⁹ measured lead concentrations at heights of 5 and 20 ft at sites near streets in

Kansas City, Mo. and Cincinnati, O. The sampling sites in Kansas City were described as unsheltered, unbiased by localized pollution influences, and not immediately surrounded by large buildings. The Cincinnati study area was located in a primarily residential area with one commercial street. Samplers were operated for 24-hr periods from 8 a.m. to 8 a.m.; but a few 12-hr samples were collected from 8 a.m. to 8 p.m. Data were obtained at Kansas City on 35 days and at Cincinnati on 33 days. The range and average values reported are shown in Table 7-8. In all cases except two, the measured concentrations were higher at 5 ft than at 20 ft. Note that the difference between the east side and west side of the streets was approximately the same as the difference between 5 and 20 ft in height.

TABLE 7-8. AIRBORNE LEAD CONCENTRATIONS AT 5- AND 20-FT ELEVATIONS ABOVE STREET LEVEL^a
($\mu\text{g}/\text{m}^3$)

Location	Range	Averages					
		East side of street			West side of street		
		20 ft	5 ft	Diff.	20 ft	5 ft	Diff.
Kansas City	0.8 - 4.0	1.7	2.0	0.3	1.5	1.7	0.2
Cincinnati	0.1 - 4.6	0.9	1.4	0.5	0.6	0.8	0.2

These data reflect the strong influence of the geometry of the boundary layer, wind, and atmospheric stability conditions on the vertical gradient of lead resulting from automobile emissions. The variability of concentration with height is further complicated by elevated emissions (i.e., from stacks). Concentrations measured from sampling stations on the roofs of buildings several stories high may not reflect actual human exposure conditions, but neither would a single sampling station located at ground level in a building complex. The height variation in concentration resulting from vertical diffusion of automobile emissions is likely to be small compared to temporal and spatial variations resulting from surface geometry, wind, and atmospheric conditions.

7.2 MOBILE SOURCE EXPOSURES

Several major studies have been undertaken to determine the lead levels in the air and in settled dust near busy highways that are far from any stationary lead source. Among the most intensive of these studies was the Los Angeles Catalyst Study of 1974-1975, undertaken by EPA to measure the impact of the catalytic converter on air quality near a major traffic lead source.¹⁰

Table 7-9 summarizes the 24-hr ambient concentrations of lead observed at two sites (A and C)

on opposite sides of a major freeway during the calendar year 1975. In addition to the monthly average concentration at each site, the monthly average cross-freeway difference in concentrations (C-A) and ratio of concentrations (C/A) are shown in the table. Finally, the percentage of hours in the month when winds were from the directional sector that is most favorable to the detection of cross-freeway differences is shown in the righthand column. The favorable wind direction interval is approximately 160° to 290° and was defined on the basis of concentration of carbon monoxide, which is a tracer for mobile-source pollutants.

TABLE 7-9. MONTHLY AVERAGE LEAD CONCENTRATIONS FOR 1975 LOS ANGELES CATALYST STUDY¹⁰

Month	Site A. $\mu\text{g}/\text{m}^3$	Site C. $\mu\text{g}/\text{m}^3$	Difference. C-A	Ratio. C/A	% Favorable wind direction ^B
January	6.0	6.2	0.2	1.03	28.2
February	4.1	4.8	0.5	1.18	35.2
March	3.2	5.2	2.0	1.63	43.3
April	2.8	6.0	3.3	2.14	47.6
May	1.8	7.4	5.6	4.06	65.6
June	1.4	8.1	6.8	5.68	71.2
July	1.9	8.0	6.1	4.27	68.0
August	2.8	8.4	5.7	3.00	61.6
September	3.7	8.5	5.0	2.30	59.5
October	4.2	7.3	3.3	1.74	49.4
November	4.8	6.6	1.7	1.37	31.6

^B From A to C (S + SW + W winds).

A very strong seasonal effect is observed in the data, with concentrations at Site C exceeding those at Site A by only 3 percent in January, increasing to a maximum difference of over 400 percent in June, and subsequently decreasing during the fall months (no data were collected during the month of December). As expected, there is a strong linear relationship between the occurrence of favorable wind direction and the observed cross-freeway difference in lead concentration. The correlation coefficient between the two variables is 0.96, indicating that almost all of the variation in the cross-freeway concentration of lead may be accounted for by the seasonal variation in the occurrence of favorable wind direction.

In a study conducted in London, England,¹¹ ambient air levels of organic lead were measured at urban sites. Concentrations of 0.04 to 0.11 μg organic Pb/ m^3 were found on streets of varying widths and traffic flow. These values were 0.3 to 2.6 percent of total airborne lead. The level of organic lead inside a busy tunnel was 0.02 $\mu\text{g}/\text{m}^3$, or 0.1 percent of the total airborne lead. Not surprisingly, organic lead concentrations measured at a busy service station

ranged from 0.21 to 0.59 $\mu\text{g}/\text{m}^3$, or 3.9 to 9.7 percent of total airborne lead at that site. At a less busy service station, the concentration of organic lead was 0.07 $\mu\text{g}/\text{m}^3$, or 4.2 percent of total airborne lead at that site.

Data obtained in a number of other studies on lead in dusts near roadways are summarized in Tables 7-10 and 7-11. The above data demonstrate that abnormally high concentrations of lead are found in the air and dust near major roadways, and that people who live or work (e.g., traffic policemen, service station and garage attendants) in these areas are exposed to high lead concentrations.

For comparison, Table 7-12 summarizes lead in dusts from nominally residential urban areas. These concentrations have a wider range than those in traffic-oriented dust samples. They are higher in the vicinity of an identified point source such as the El Paso smelter, but the majority of the readings are lower than those of the traffic-oriented samples.

7.3 POINT SOURCE EXPOSURES

Several studies have been undertaken to investigate lead levels in the vicinity of various point sources of lead emission such as smelters or battery plants. By far the most complete and informative studies are

TABLE 7-10. LEAD DUST ON AND NEAR HEAVILY TRAVELED ROADWAYS

Sampling site	Concentration $\mu\text{g Pb/g}$
Washington, D.C.:	
Busy intersection	12820
Many sites	(4000-8000) ¹²
Chicago:	
Near expressway	6600
Philadelphia:	
Near expressway	(3000-8000) ¹³
Brooklyn:	
Near expressway	(900-4900) ¹⁴
New York City:	
Near expressway	2000 ¹⁵
Detroit:	
Street dust	(966-1213) ¹⁶
Philadelphia:	
Gutter (low exposure)	1507
Gutter (low exposure)	(270-2626) ¹⁷
Gutter (high exposure)	3262
Gutter (high exposure)	(280-8201) ¹⁷
Miscellaneous U.S. Cities:	
Highways and tunnels	(10000-20000) ¹⁸
Netherlands:	
Heavily traveled roads	5000 ¹⁹

TABLE 7-11. LEAD CONTENT IN OR ON ROADSIDE SOIL AND GRASS AS A FUNCTION OF DISTANCE FROM TRAFFIC AND GRASS DEPTH IN PROFILE^a

Site and distance from road, m	Lead content, $\mu\text{g/g}$ dry weight			
	Grass	0-5 cm soil depth	5-10 cm soil depth	10-15 cm soil depth
West of U.S. 1, near Plant Industry Station, Beltsville, Md.:				
8	68.2	522	460	416
16	47.5	378	260	104
32	26.3	164	108	69
West of southbound lanes, Washington-Baltimore Parkway, Bladensburg, Md.:				
8	51.3	540	300	98
16	30.0	202	105	60
32	18.5	140	60	38
West of Interstate 29, Platte City, Mo.:				
8	21.3	242	112	95
16	12.5	140	104	66
32	7.5	61	55	60
North of Seymour Road, Cincinnati, O.:				
8	31.3	150	29	11
16	26.0	101	14	8.2
32	7.6	55	10	6.1

^a Adapted from Lagerwerff and Specht (cited in Reference 20).

TABLE 7-12. LEAD DUST IN RESIDENTIAL AREAS

Sampling site	Concentration, $\mu\text{g Pb/g}$
Philadelphia:	
Classroom	2000
Playground	3000
Window frames	1750 ¹⁷
Boston and New York:	
House dust	(1000-2000) ²¹
Brattleboro, Vt.:	
In home	(500-900) ⁶
Birmingham, England:	
In home	5000 ¹⁴
New York City:	
Middle class residential	(608-742) ¹⁵
El Paso, Texas, Smelertown dust at:	
0-1 mile	36853 (2800-103750) ²²
1-2 miles	2726 (100-84000) ²²
2-3 miles	2234 (100-29386) ²²
> 4 miles	2151 (200-22700) ²²
Philadelphia:	
Urban industrial	3855 (929-15680) ²³
Residential	614 (293-1030) ²³
Suburban	830 (277-1517) ²³

those carried out by Yankel et al.²⁴ and Landrigan et al.²⁵ in the neighborhood of a smelter in Silver Valley, Idaho. Consequently, the data from these studies will be described here in some detail. Other studies carried out in Solano County, Calif.; Omaha, Neb.; El Paso, Tex.; Helena Valley, Mont.; Missouri; Helsinki, Finland; Meza River Valley, Yugoslavia; and Ontario, Canada, are summarized in Appendix C. Their findings are in substantive agreement with those of the Idaho study.

Yankel and von Lindern²⁴ defined five study areas arranged concentrically around the smelter and two control areas. Area 1 consisted of homes within 1 mile of the smelter; Area 2, 1 to 2-1/2 miles from smelter; Area 3, 2-1/2 to 6 miles; Area 4, 6 to 15 miles; and Area 5, 15 to 20 miles. Environmental samples, including surface soil, house dust, paint, grass, and garden vegetables were collected at the homes in each area, as were blood samples from the resident children aged 1 to 9 years. The mean lead

levels found in the ambient air, soil, and house dust all decreased with increasing distance from the smelter. As mentioned in Chapter 12, the blood lead levels of the resident children followed a similar pattern.

Ambient air lead levels were measured by high-volume samplers stationed throughout the Silver Valley. A highly significant relationship between distance from the smelter and ambient air lead concentration was found, and this relationship was used to estimate the ambient air lead level for any location in the study area. The mean annual ambient air lead levels near a smelter for two different years (1974, 1975) are shown graphically in Figure 7-4. Similar results were obtained for the lead content of soil and house dust. As noted in Chapter 12, the children's blood lead levels correlate quite closely with ambient air lead levels, although this result should not be interpreted as suggesting that direct inhalation of lead is the principal exposure mechanism involved. One result of this pivotal study was that some specific emergency measures were taken in

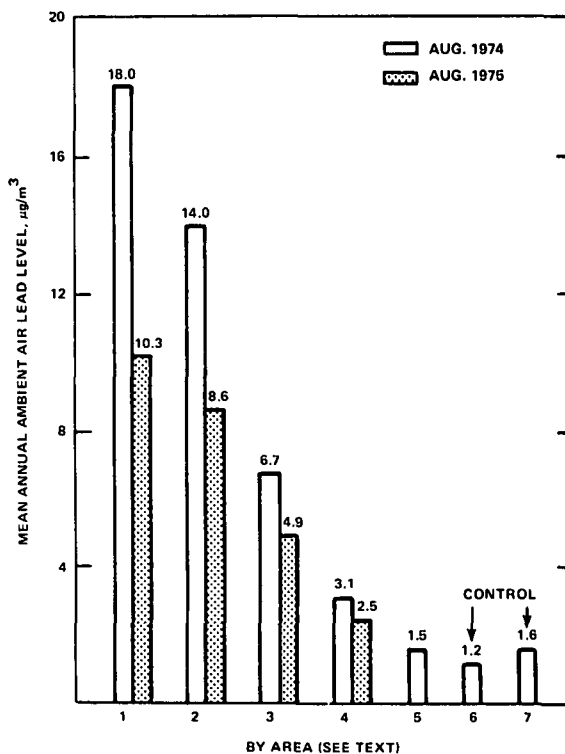


Figure 7-4. Annual ambient air lead concentration near a smelter, by area, before the August 1974 and August 1975 surveys.²⁴ Area 1 is within 1 mile of smelter; Area 2 is 1 to 1-1/2 miles from smelter; Area 3, 2-1/2 to 6 miles; Area 4, 6 to 15 miles; and Area 5, 15 to 20 miles.