UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Environmental Criteria and Assessment Office (MD-52)
Research Triangle Park, North Carolina 27711

December 3, 1982

Dr. Ron Snee
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Dear Dr. Snee:

Enclosed you will find copies of the most recent draft versions of those chapters of the Air Quality Criteria Document for Lead which deal with air quality and ecosystem effects. These are: Chapter 3 (physical and chemical properties), Chapter 4 (sampling and analytical methods), Chapter 5 (sources and emissions), Chapter 6 (transport and transformation) and Chapter 8 (ecosystem effects). Each of these chapters has undergone two rounds of peer-review during workshops held here at RTP on May 18-20 and August 2-4, as well as editing, text-to-reference checks, and rigorous reading conducted by ECAO staff. Although there still remains a fair amount of work to be done on the bibliographies, these chapters will be released in essentially the same form as you see them here in the External Review Draft of the Lead Document, projected for completion in March, 1983. There will be a 90-day public comment following the release of the External Review Draft, during which time we will welcome your comments on these materials. We do request, however, that you withhold those comments until then, as these chapters have been provided to you as background information only. Your cooperation in this matter will be greatly appreciated.

Please note that my letter of October 25th contained a typographical error with regard to the dates of our January peer-review workshop on the health effects chapters. This meeting will be held on Tuesday, January 18 through Thursday, January 20. May I remind you to make your hotel reservations now, if you have not already done so.

The draft versions of Chapters 7, 9, 10, 11, 12 and 13 (to be discussed at the January meeting) will be mailed to you in mid-December. There is, however, a possibility that Chapter 13 (risk evaluation) will not be mailed until early January; the remaining chapters should give you enough to read over the Christmas holidays, though!

Best wishes,

David E. Weil, Ph.D.
Project Manager

DEW/jr

Enclosures

TABLE OF CONTENTS
Chapter 3
Chemical and Physical Properties

LIST OF TABLES

3. CHEMICAL AND PHYSICAL PROPERTIES

3.1 INTRODUCTION

Lead is a gray-white metal of bright luster that, because of its easy isolation and low melting point (327.5°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, and it was used extensively by the Egyptians; the British Museum contains a lead figure found in an Egyptian temple which possibly dates from 3000 B.C. The most abundant ore is galena, in which lead is present as the sulfide (PbS), and from which metallic lead is readily smelted. The metal is soft, malleable, and ductile, a poor electrical conductor, and 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. Its alloys are used as solder, type metal, and various antifriction materials. The metal and the dioxide are used in storage batteries, and much metal is used in cable covering, plumbing and ammunition. Because of its high nuclear cross section, lead is extensively used as a radiation shield around X-ray equipment and nuclear reactors.

3.2 ELEMENTAL LEAD

In comparison with the most abundant metals in the earth's crust (aluminum and iron), lead is a rare metal; even copper and zinc are more abundant by factors of five and eight, respectively. Lead is, however, more abundant than the other toxic heavy metals; its abundance in the earth's crust has been estimated (Moeller, 1952) to be as high as 1.6×10^{-3} percent, although some other authors (Heslop and Jones, 1976) suggest a lower value of 2×10^{-4} percent. Either of these estimates suggests that the abundance of lead is more than 100 times that of cadmium or mercury, two other significant systemic metallic poisons. More important, since lead occurs in highly concentrated ores from which it is readily separated, the availability of lead is far greater than its natural abundance would suggest. The great environmental significance of lead is the result both of its utility and of its availability. Lead ranks fifth among metals in tonnage consumed, after

iron, copper, aluminum and zinc; it is, therefore, produced in far larger quantities than any other toxic heavy metal (Dyrssen, 1972). The properties of elemental lead 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	327.5 °C
Boiling point	1740 °C
Covalent radius (tetradehral)	1.44 Å
Ionic radii	1.21 Å (+2), 0.78 Å (+4)
Resistivity	21.9×10^{-6} ohm/cm

Natural lead is a mixture of four stable isotopes: ^{204}Pb (1.5 percent), ^{206}Pb (23.6 percent), ^{207}Pb (22.6 percent), and ^{208}Pb (52.3 percent). There is no radioactive progenitor for ^{204}Pb, but ^{206}Pb, ^{207}Pb, and ^{208}Pb are produced by the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively. There are four radioactive isotopes of lead that occur as members of these decay series. Of these, only ^{210}Pb is long lived, with a half-life of 22 years. The others are ^{211}Pb (half-life 36.1 min), ^{212}Pb (10.64 hr), and ^{214}Pb (26.8 min). The stable isotopic compositions of naturally occurring lead ores are not identical, but show variations reflecting geological evolution (Russell and Farquhar, 1960). Thus, the observed isotopic ratios depend upon the U/Pb and Th/Pb ratios of the source from which the ore is derived and the age of the ore deposit. The $^{206}Pb/^{204}Pb$ isotopic ratio, for example, varies from approximately 16.5 to 21 depending on the source (Doe, 1970). The isotopic ratios in average crustal rock reflect the continuing decay of

uranium and thorium. The differences between crustal rock and ore bodies, and between major ore bodies in various parts of the world, often permit the identification of the source of lead in the environment.

3.3 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 (Cotton and Wilkinson, 1980). Thus, the average energy of a C-H bond is 100 kcal/mole, and it is this factor that stabilizes CH_4 relative to CH_2; for lead, the Pb-H energy is only approximately 50 kcal/mole (Shaw and Allred, 1970), and this is presumably too small to compensate for the Pb(II) → Pb(IV) promotional energy. It is this same feature 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, for lead catenation occurs only in organolead compounds. Lead does, however, form compounds like Na_4Pb_9 which contain distinct polyatomic lead clusters (Britton, 1964), and Pb-Pb bonds are found in the cationic cluster $[Pb_6O(OH)_6]^{+4}$ (Olin and Soderquist, 1972).

A listing of the solubilities and physical properties of the more common compounds of lead is given in Appendix 3A. 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, $Pb(NO_3)_2$, and lead acetate, $Pb(OCOCH_3)_2$. Inorganic lead (II) salts are, for the most part, 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 3A. The transformation of lead salts in the atmosphere is discussed in Chapter 6.

3.4 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; although a few organolead(II) compounds, such as dicyclopentadienyllead, $Pb(C_5H_5)_2$, are known, 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 (Rufman and Rotenberg, 1980).

Because of their use as antiknock agents in gasoline and other fuels, the most important organolead compounds have been the tetraalkyl compounds tetraethyllead (TEL) and tetramethyllead (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 by the reaction of the alkyl chloride with lead-sodium alloy (Shapiro and Frey, 1968):

$$4NaPb + 4C_2H_5Cl \rightarrow (C_2H_5)_4Pb + 3Pb + 4NaCl \qquad (3\text{-}1)$$

The methyl compound, TML, is also manufactured by a Grignard process involving the electrolysis of lead pellets in methylmagnesium chloride (Shapiro and Frey, 1968):

$$2CH_3MgCl + 2CH_3Cl + Pb \rightarrow (CH_3)_4Pb + 2MgCl_2 \qquad (3\text{-}2)$$

A common type of commercial antiknock mixture contains a chemically redistributed mixture of alkyllead compounds. In the presence of Lewis acid catalysts, a mixture of TEL and TML undergoes a redistribution reaction to produce an equilibrium mixture of the five possible tetraalkyllead compounds. For example, an equimolar mixture of TEL and TML produces a product with a composition as shown below:

Component	Mol percent
$(CH_3)_4Pb$	4.6
$(CH_3)_3Pb(C_2H_5)$	24.8
$(CH_3)_2Pb(C_2H_5)_2$	41.2
$(CH_3)Pb(C_2H_5)_3$	24.8
$(C_2H_5)_4Pb$	4.6

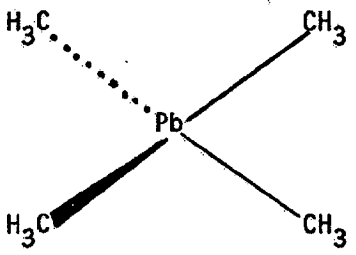
These lead compounds are removed from internal combustion engines by a process called lead scavenging, in which they react in the combustion chamber with halogenated hydrocarbon additives (notably ethylene dibromide and ethylene dichloride) to form lead halides, usually bromochlorolead(II). Mobile source emissions are discussed in detail in Chapter 6.

Several hundred other organolead compounds have been synthesized, and the properties of many of them are reported by Shapiro and Frey (1968). The continuing importance of organolead chemistry is demonstrated by a variety of recent publications investigating the syntheses (Hager and Huber, 1980, Wharf et al., 1980; and structures Barkigia, et al., 1980) of organolead complexes, and by recent patents for lead catalysts (Nishikido, et al., 1980).

3.5 FORMATION OF CHELATES AND OTHER COMPLEXES

The bonding inorganometallic derivative 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.

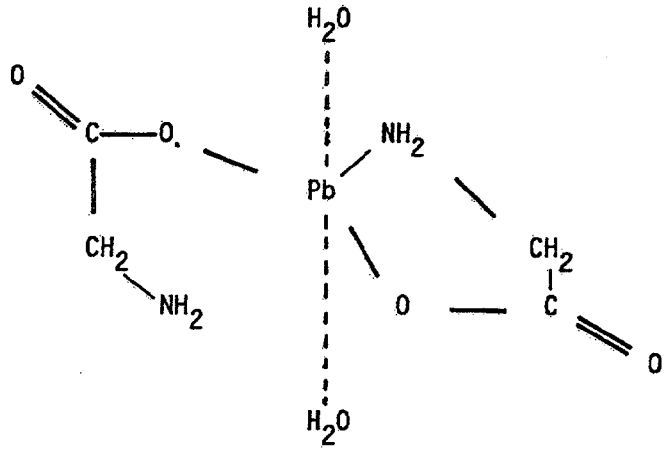
The donor atoms in a metal complex could be almost any basic atom or molecule; the only requirement is that a donor, usually called a ligand, must have a pair of electrons available for bond formation. In general, the metal atom occupies a central position in the complex, as exemplified by the lead atom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



(a)

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 ligands or chelating agents. In the chemistry of lead, chelation normally involves Pb(II), leading to kinetically

quite labile (although thermodynamically stable) octahedral complexes. 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 occurs with the amino acid glycine, as represented in (b) for a 1:2 (metal:ligand) complex.



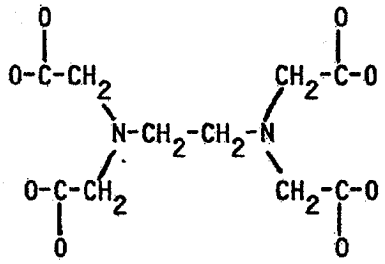
(b)

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

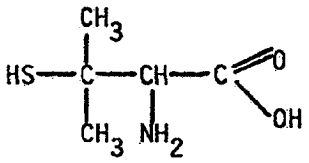
Since Pb(II) is a relatively soft (or class b) metal ion (Ahrland, 1966, 1968, 1973; Pearson, 1963, 1968; Basolo and Pearson, 1968), it forms strong bonds to soft donor atoms like the sulfur atoms in the cysteine residues of proteins and enzymes; it also coordinates strongly with the imidazole groups 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 substrate's approach to the active site of the protein. As has been demonstrated in several studies (Jones and Vaughn, 1978; Williams and Turner, 1981; Williams et al., 1982), there is a correlation between the LD_{50} values of metal complexes and the chemical softness parameter σp (Pearson and Mawby, 1967). Thus, for both mice and Drosophila, soft metal ions like lead(II) have been found to be more toxic than hard metal ions (Williams et al., 1982). This classification of metal ions according to their toxicity has been discussed in detail by Nieboer and Richardson (1980). Lead(II) has a higher

softness parameter than either cadmium(II) or mercury(II), so lead(II) compounds would not be expected to be as toxic as their cadmium or mercury analogues.

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 be 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 lead poisoning are ethylenediaminetetraacetate ions (EDTA), D-penicillamine [(c) and (d), respectively], and their derivatives. EDTA is known to act as a hexadentate ligand toward metals (Lis, 1978; McCandlish et al., 1978). X-ray diffraction studies have demonstrated that D-penicillamine is a tridentate ligand binding through its sulfur, nitrogen and oxygen atoms to cobalt (de Meester and Hodgson, 1977a; Helis, et al., 1977), chromium (de Meester and Hodgson, 1977b), cadmium (Freeman et al., 1976), and lead itself (Freeman et al., 1974), but both penicillamine and other cysteine derivatives have been shown to act as only bidentate ligands (Carty and Taylor, 1977; de Meester and Hodgson, 1977c). Moreover, penicillamine binds to mercury only through its sulfur atoms (Wong et al., 1973; Carty and Taylor, 1976).



EDTA (c)



PENICILLAMINE (d)

It should be noted that both the stoichiometry and structures of metal chelates depend upon pH, and that structures different from those manifest in solution may occur in crystals. 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 permit their use in the effective treatment of lead poisoning.

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TABLE OF CONTENTS

Chapter 4
Sampling and Analytical Methods for Environmental Lead

LIST OF TABLES

LIST OF FIGURES

4. SAMPLING AND ANALYTICAL METHODS FOR ENVIRONMENTAL LEAD

4.1 INTRODUCTION

Lead, like all criteria pollutants, has a designated Reference Method for monitoring and analysis as required in State Implementation Plans for determining complicance with the lead National Ambient Air Quality Standard. The Reference Method (40 CFR Part 50, Appendix G) uses a high volume sampler (hi-vol) for sample collection and atomic absorption spectrometry for analysis. The reference method may be revised to require collection of a specific size fraction of atmospheric particles. Size specific inlets will be discussed in sections 4.2.3.

Airborne lead originates principally from man-made sources, about 75 to 90 percent from automobile exhausts, and is transported through the atmosphere to vegetation, soil, water and animals. Knowledge of environmental concentrations of lead and the extent of its movement among various media is essential in order to control lead pollution and to assess its effects on human populations.

The collection and analysis of environmental samples for lead requires a rigorous quality assurance program (44 FR 27574). It is essential that the investigator recognize all sources of contamination and use every precaution to eliminate them. Contamination occurs on the surfaces of collecting containers and devices, on the hands and clothing of the investigator, in the chemical reagents, in the laboratory atmosphere, and on the labware and tools used to prepare the sample for analysis. General procedures for controlling contamination in trace metal analysis are described by Zief and Mitchell (1976). Specific details for the analysis of lead are given in Patterson and Settle (1976). In the following discusssions of methods for sampling and analysis, it is the underlying assumption that all procedures should be carried out with precise attention to contamination control.

In the following sections, the specific operations, procedures and instrumentations involved in monitoring and analyzing environmental lead are discussed. Site selection criteria are treated briefly due to the lack of verifying data. Much remains to be done in establishing valid criteria for sampler location. The various types of samples and substrates used to collect airborne lead are described. Methods for collecting dry deposition, wet deposition, aqueous, soil and vegetation samples are also reviewed along with current

sampling methods specific for mobile and stationary sources. Finally, advantages and limitations of techniques for sample preparation and analysis are discussed.

4.2 SAMPLING

The purpose of sampling is to determine the nature and concentration of lead in the environment. Sampling strategy is dictated by research needs. This strategy encompasses site selection, choice of instrument used to obtain representative samples and choice of method used to preserve sample integrity.

4.2.1 Regulatory Siting Criteria for Ambient Aerosol Samplers

In September of 1981, EPA promulgated regulations establishing ambient air monitoring and data reporting requirements for lead (46 FR 44159) comparable to those already established in May of 1979 for the other criteria pollutants. Inherent in these promulgations was the establishment of State and Local Air Monitoring Stations (SLAMS), certain of which comprise the National Air Monitoring Stations network (NAMS). The NAMS network is designed to serve national monitoring needs, including assessment of national ambient trends. Such monitoring stations are located in areas where pollutant concentrations and populations densities are the greatest. Whereas sampling for lead is accomplished when sampling for TSP, the designs of lead and TSP monitoring stations must be collated to insure compliance with the NAMS criteria for each pollutant as presented in Table 4-1, Table 4-2, and Figure 4-1.

In general, the criteria with respect to monitoring stations designates that there must be at least two SLAMS sites for lead in any area which has a population greater than 500,000 and/or any area where lead concentrations currently exceed the ambient lead standard (1.5 $\mu g/m^3$) or have exceeded it since January 1, 1974. In such areas, the SLAMS sites designated as part of the NAMS network must include a microscale or middlescale site located near a major roadway (≧30,000 ADT), as well as a neighborhood scale site located in a highly populated residential sector with high traffic density (≧30,000 ADT).

With respect to the criteria developed for the siting of monitors for lead and other criteria pollutants, there are standards for elevation of the monitors above ground level, setback from roadways and setback from obstacles. A summary of the specific siting criteria for lead is presented in Table 4-1 and summarized below:

- Samples must be placed between 2 and 15 meters from the ground and greater than 20 meters from trees.

Table 4-1. Design of National Air Monitoring Stations

Criteria	TSP (Final Rule)[1]	Air Pb (Final Rule)[2]			
Stations					
Spatial Scale					
Category (a)	Neighborhood Scale	Microscale or Middle Scale			
Category (b)	-	Neighborhood Scale			
Number Required	As per Table 4-2	Minimum 1 each Category where population >500,000			
Siting					
Category (a)	High Traffic and Population Density Neighborhood Scale	Major Roadway Microscale	or	Major Roadway Middle Scale	
ADT	>3000	≧30,000		≧10,000	20,000 ≧40,000
M from Edge of Roadway	As per Figure 4-1	5-15		>15-50	>15-75 >15-100
M above Ground Level	2-15	2-7		2-15	2-15 2-15
Category (b)		High Traffic and Population Density Neighborhood Scale			
ADT		≦10,000	20,000	≧40,000	
M from Edge of Roadway		>50	>75	>100	
M above Ground Level		2-15	2-15	2-15	

[1]Federal Register, Vol. 44, No. 92, pp. 27558-27604, May 10, 1979.

[2]Federal Register, Vol. 46, No. 171, pp. 44159-44172, September 3, 1981.

Table 4-2. TSP NAMS Criteria

Approximate Number of Stations per Area[1]			
	Concentration		
Population Category	High[2]	Medium[3]	Low[4]
High -- >500,000	6-8	4-6	0-2
Medium -- 100-500,000	4-6	2-4	0-2
Low -- 50-100,000	2-4	1-2	0

[1]Reproduced from Federal Register, Volume 44, No. 92, p. 27590, May 10, 1979.

[2]When TSP Concentration exceeds by 20% Primary Ambient Air Standard of 75 $\mu g/m^3$ annual geometric mean.

[3]TSP Concentration > Secondary Ambient Air Standard of 60 $\mu g/m^3$ annual geometric mean.

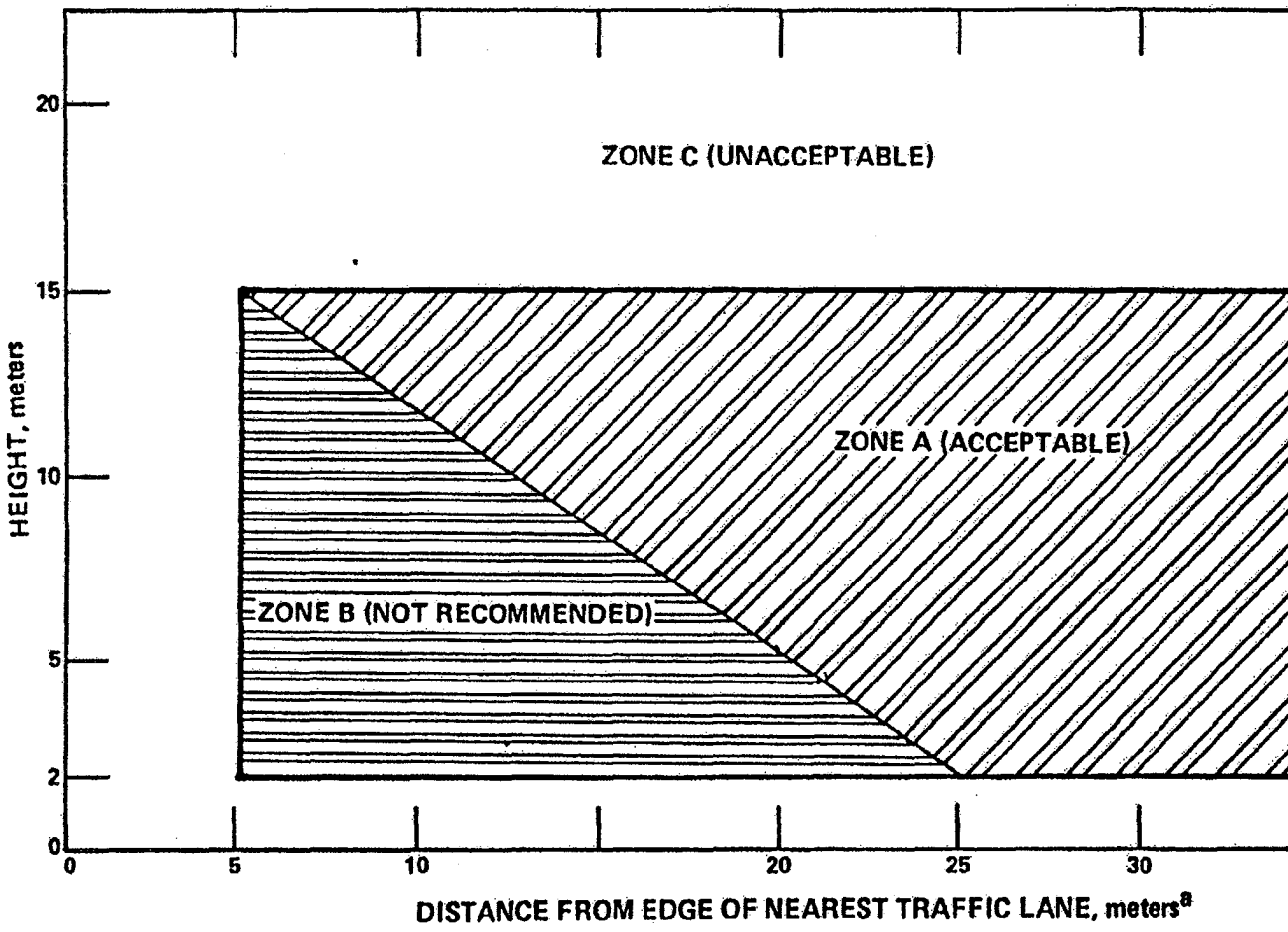
[4]TSP Concentration < Secondary Ambient Air Standard.

- Spacings of samplers from roads should vary with traffic volume; a range of 5 to 100 meters from the roadway is suggested.

- Distances from samplers to obstacles must be at least twice the height the obstacle protrudes above the sampler.

- There must be a 270° arc of unrestricted air flow around the monitor to include the prevailing wind direction that provides the maximum pollutant concentration to the monitor.

- No furnaces or incineration flues should be in close proximity to the monitors.



[a]APPLIES WHERE ADT >3,000

Figure 4-1. Acceptable zone for siting TSP monitors.

Zone A: Recommended for neighborhood, urban, regional and most middle spatial scales.
Zone B: SLAMS placed in Zone B have middle scale of representativeness.
(All NAMS in Zone A)

Source: Environment Reporter, Federal Regulations, 121-2322(121 AIR), January

To clarify the relationship between monitoring objectives and the actual siting of a monitor, the concept of a spatial scale of representativeness was developed. The spatial scales are discribed in terms of the physical dimensions of the air space surrounding the monitor throughout which pollutant concentrations are fairly similar. Table 4-3 describes the scales of representativeness while Table 4-4 relates monitoring objectives to the appropriate spatial scale.

The time scale may also be an important factor. A study by Lynam (1972) illustrates the effect of set back distance on short term (15 minutes) measurements of lead concentrations directly downwind from the source. They found sharp reductions in lead concentrations with increasing distance from the roadway. A similar study by PEDCO Environmental (1981) did not show the same pronounced reductions when the data were averaged over monthly or quarterly time periods. The apparent reason for this effect is that windspeeds and directions are not consistent. Therefore, siting criteria must include sampling times sufficiently long enough to include average windspeed and direction, or a sufficient number of samples must be collected over short sampling periods to provide an average value consistent with a 24-hour exposure.

4.2.2 Ambient Sampling for Lead Aerosol and Gases

Airborne lead is primarily inorganic particulate matter but may occur in the form of organic gases. Devices used for collecting samples of ambient atmospheric lead include the standard hi-vol and a variety of other collectors employing filters, impactors, impingers or scrubbers, either separately or in combination. Some samplers measure total particulate matter gravimetrically and the lead data is usually expressed in $\mu g/g$ PM or $\mu g/m^3$ air. Other samplers do not measure PM gravimetrically and the lead data can only be expressed as $\mu g/m^3$. One sampler measures dry deposited lead expressed in $\mu g/cm^2/day$. Some instruments separate particles by size. As a general rule, particles <2.5 µm are considered fine, and particles >2.5 µm are considered coarse.

Table 4-3. Description of Spatial Scales of Representativeness

Microscale	Defines ambient concentrations in air volumes associated with areas ranging from several to 100 meters in size.
Middle Scale	Defines concentrations in areas from 100 to 500 meters (area up to several city blocks).
Neighborhood Scale	Defines concentrations in an extended area of uniform land use, within a city, from 0.5 to 4.0 kilometers in size.
Urban Scale	Defines citywide concentrations, areas from 4-50 kilometers in size. Usually requires more than one site.
Regional Scale	Defines concentrations in a rural area with homogeneous geography. Range of tens to hundreds of kilometers.
National and Global Scales	Defines concentrations characterizing the U.S. and the globe as a whole.

Based on descriptions in the Federal Register, Volume 44, No. 92, p. 27586, May 10, 1979.

Table 4-4. Relationship Between Monitoring Objectives and Appropriate Spatial Scales

Monitoring Objective	Appropriate Spatial Scale for Siting Air Monitors
Highest Concentration	Micro, Middle, Neighborhood (sometimes Urban).
Population	Neighborhood, Urban
Source Impact	Micro, Middle, Neighborhood
General (Background)	Neighborhood, Regional

Reproduced from Federal Register, Volume 44, No. 92, p. 27586, May 10, 1979.

In a typical sampler, the ambient air is drawn down into the inlet and deposited on a collection substrate after one or more stages of particle size separation. Inlet effectiveness, internal wall losses and retention efficiency of the collection surface may bias the collected sample by attenuating particles of certain sizes.

4.2.2.1 High Volume Sampler. The present State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) employ the standard hi-vol sampler (Robson and Foster, 1962; Silverman and Viles, 1948; U.S. Environmental Protection Agency, 1971) as part of their sampling networks. As a Federal Reference Method Sampler, the hi-vol operates with a specific flow rate range of 1.13 to 1.70 m^3/min drawing air through a 200 x 250 mm glass fiber filter. At these flow rates, 1600 to 2500 m^3 of air per day are sampled. Many hi-vol systems are presently equipped with mass flow sensors to control the total flow rate through the filter.

The present hi-vol approach has been shown, during performance characterization tests, to have a number of deficiencies. First, wind tunnel testing by Wedding et al. (1977) has shown that the inlet characteristics of the hi-vol sampler are strongly affected by particle size, windspeed and wind direction. However, since most lead aerosols have been shown to have a mass medium diameter (MMD) in the range of 0.25 to 1.4 μm (Lee et al., 1972), the hi-vol sampler should present reasonably good estimates of ambient lead concentrations. However, for particles >5 μm, the hi-vol system is unlikely to collect representative samples (McFarland et al., 1979; Wedding et al., 1977). In addition, Lee and Wagman (1966) and later Stevens et al. (1978), have documented that the use of glass fiber filters leads to the formation of sulfate artifact. Spicer et al. (1978) suggested a positive nitrate artifact while Stevens et al. (1980) showed both a positive and negative artifact may occur with glass or quartz filters when using a hi-vol sampler.

4.2.2.2 Dichotomous Sampler--The dichotomous sampler collects two particle size fractions, typically 0 to 2.5 μm and 2.5 μm to the upper cutoff of the inlet employed. The impetus for the dichotomy of collection, which approximately separates the fine and coarse particles, was provided by Whitby et al. (1972) to assist in the identification of particle sources. A 2.5 μm cutpoint for the separator was also recommended by Miller et al. (1979) because it satisfied the requirements of health researchers interested in respirable

particles, provided adequate separation between two naturally occurring peaks in the size distribution, and was mechanically practical. Because the fine and coarse fractions collected in most locations tend to be acidic and basic, respectively, this separation also minimizes potential particle interaction after collection.

The particle separation principle used by this sampler was described by Haunam and Sherwood (1965) and Conner (1966). A recent version now in use by EPA was developed by Loo et al. (1966). The separation principle involves acceleration of the particles through a nozzle. Ninety percent of the flow-stream is diverted to a small particle collector, while the larger particles, due to their inertia, continue toward the large particle collection surface. The inertial virtual impactor design causes 10 percent of the fine particles to be collected with the coarse particle fraction. Therefore, the mass of fine and coarse particles must be adjusted to allow for their cross contamination. This mass correction procedure has been described by Dzubay (1981).

Teflon® membrane filters with pore sizes as large as 2.0 μm can be used (Dzubay, 1981; Stevens, 1981) in the dichotomous sampler and have been shown to have essentially 100 percent collection efficiency down to particles aerodynamic diameter of 0.03 μm (Liu et al., 1978). See section 4.2.5. Because the sampler operates at a flowrate of 1 m^3/hr (167 l/min) and collects submilligram quantities of particles, a microbalance with a 1 μg resolution is recommended for filter weighing (Shaw, 1981). Removal of the fine particles via this fractionation technique causes the collected coarse particles to have a greater tendency to fall off the filter if care is not taken during filter handling and shipping (Shaw, 1979). However, Dzubay and Barbone (1983) have developed a filter coating procedure which eliminates particle loss during transport. A study by Wedding et al. (1980) has shown that the Sierra Inlet to the dichotomous sampler was sensitive to windspeed. The 50 percent cut-point (D_{50}) was found to vary from 10 to 22 μm over the windspeed range of 0 to 15 km/h.

Automated versions of the sampler allow timely and unattended changes of the sampler filters. Depending on atmospheric concentrations, short-term samples of as little as 4 hours can provide diurnal pattern information. The mass collected during such short sample periods, however, is extremely small and high variability of the results may be expected.

4.2.2.3 Impactor Samplers--Impactors provide a means of dividing an ambient particle sample into subfractions of specific particle sizes for possible use in determining size distributions. A jet of air is directed toward a collection surface, which is often coated with an adhesive or grease to reduce particle bounce. Large, high-inertia particles are unable to turn with the airstream and consequently hit the collection surface. Smaller particles follow the airstream and may be directed either to another impactor stage or collected on a filter. Use of multiple stages, each with a different particle size cutpoint, provides collection of particles in several size ranges.

Removable impaction surfaces may be weighed for particle mass before and after exposure. The particles collected may be removed and analyzed for individual elements. The selection and preparation of these substrates have significant effects on the impactor performance. Improperly coated or overloaded surfaces can cause particle bounce to lower stages resulting in substantial cutpoint shifts (Dzubay et al., 1976). Additionally coatings may cause contamination of the sample. Marple and Willeke (1976) showed the effect of various impactor substrates on the sharpness of the stage cutpoint. Glass fiber substrates can also cause particle bounce or particle interception and are subject to the formation of artifacts, due to reactive gases interacting with the glass fiber, similar to those on hi-vol sampler filters (Liu, 1980).

Cascade impactors typically have 2 to 10 stages, and flowrates for commercial low-volume versions range from about 0.01 to 0.10 m^3/min. Lee and Goranson (1972) modified a commercially available 0.03 m^3/min low-volume impactor and operated it at 0.14 m^3/min to obtain larger mass collections on each stage. Cascade impactors have also been designed to mount on a high-vol sampler and operate at flowrates as high as 0.6 to 1.1 m^3/min.

Particle size cutpoints for each stage are dependent primarily on sampler geometry and flowrate. The smallest particle size cutpoint routinely used is approximately 0.3 μm, although special low-pressure impactors such as that described by Hering et al. (1978) are available with cutpoints as small as 0.05 μm. However, due to the low pressure, volatile organics and nitrates are lost during sampling. A membrane filter typically is used after the last stage to collect the remaining small particles.

4.2.2.4 Dry Deposition Sampling--Dry deposition may be measured directly with surrogate or natural surfaces, or indirectly using micrometeorological techniques. The earliest surrogate surfaces were dustfall buckets placed upright and exposed for several days. The HASL wet-dry collector is a modification which permits one of a pair of buckets to remain covered except during rainfall. These buckets do not collect a representative sample of particles in the small size range where lead is found because their rim perturbs the natural turbulent flow of the main airstream (Hicks et al., 1980). They are widely used for other pollutants, especially large particulates, in the National Atmospheric Deposition Program.

Other surrogate surface devices with smaller rims or no rims have been developed recently (Elias et al., 1976; Lindberg et al., 1979; Peirson et al., 1973). Peirson et al. (1973) used horizontal sheets of filter paper exposed for several days with protection from rainfall. Elias et al., (1976) used teflon disks held rigid with a 1 cm teflon ring. Lindberg et al. (1979) used petri dishes suspended in a forest canopy. In all of these studies, the calculated deposition velocity (Chapter 6.3.1) was within the range expected for small aerosol particles.

A few studies have measured direct deposition on vegetation surfaces using chemical washing techniques to remove surface particles. These determinations are generally 4 to 10 times lower than comparable surrogate surface measurements (Elias et al., 1976; Lindberg et al., 1979), but this difference could be that natural surfaces represent net accumulation rather than total deposition. Lead removed by rain or other processes would show an apparently lower deposition rate.

There are several micrometeorological techniques that have been used to measure particle deposition. They overcome the major deficiency of surrogate surfaces, the lack of correlation between the natural and artificial surface, but micrometeorological techniques require expensive equipment and skilled operators. They measure instantaneous or short-term deposition only and this deposition is inferred to be to a plane projected surface area only, not necessarily to vegetation surfaces.

Of the five micrometeorological techniques commonly used to measure particle deposition, only two have been used to measure lead particle deposition. Everett et al. (1979) used the profile gradient technique where lead

concentrations are measured at two or more levels within 10 m above the surface. Parallel meteorological data are used to calculate the net flux downward. Droppo (1980) used eddy correlation which measures fluctuations in the vertical wind component with adjacent concentration measurements of lead. The calculated differences of each can be used to determine the turbulent flux. These two micrometeorological techniques and the three not yet used for lead, modified Bowen, variance, and eddy accumulation, are described in detail in Hicks et al. (1980).

4.2.2.5 Gas Collection--When sampling ambient lead with systems employing filters, it is likely that vapor-phase organolead compounds will pass through the filter media. The use of bubblers downstream of the filter containing a suitable reagent or absorber for collection of these compounds has been shown to be effective (Purdue et al., 1973). Organolead may be collected on iodine crystals, adsorbed on activated charcoal, or absorbed in an iodine monochloride solution (Skogerboe et al., 1977a).

In one experiment, Purdue et al. (1973) operated two bubblers in series containing iodine monochloride solution. One hundred percent of the lead was recovered in the first bubbler. It should be noted, however, that the detection sensitivity was poor. In general, use of bubblers limits the sample volume due to losses by evaporation and/or bubble carryover.

4.2.3 Source Sampling

Sources of lead include automobiles, smelters (lead and other nonferrous metals), coal-burning facilities, battery manufacturing plants, chemical processing plants, facilities for scrap processing, and welding and soldering operations. A potentially important and unquantified secondary source is fugitive dust from mining operations and from soils contaminated with automotive emissions (Olson and Skogerboe, 1975). Chapter 5 contains a complete discussion of sources of lead emissions. The following sections discuss the sampling of stationary and mobile sources.

4.2.3.1 Stationary Sources--Sampling of stationary sources for lead requires the use of a sampling train at the source of the effluent stream. 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. A sampling probe is inserted directly in the stack or exhaust stream. In the tentative ASTM method for sampling for atmospheric

lead, air is pulled through a 0.45 μm membrane filter and an activated carbon adsorption tube (ASTM, 1975). In a study of manual methods for measuring emission concentrations of lead and other toxic materials (Coulson et al., 1973), 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 ? .

4.2.3.2 Mobile Sources--Three principle procedures have been used to obtain samples of auto exhaust aerosols for subsequent analysis for lead compounds: a horizontal dilution tunnel, plastic sample collection bags and a low residence time proportional sampler. In each procedure, samples are air diluted to simulate roadside exposure conditions. In the most commonly used procedure, a large horizontal air dilution tube segregates fine combustion-derived particles from larger lead particles ablated from combustion chamber and exhaust deposits. In this procedure, hot exhaust is ducted into a 56-cm diameter, 12-m long, air dilution tunnel and mixed with filtered ambient air in a 10-cm diameter mixing baffle in a concurrent flow arrangement. Total exhaust and dilution airflow rate is 28 to 36 m^3/min. which produces a residence time of approximately 5 sec. in the tunnel. At the downstream end of the tunnel, samples of the aerosol are obtained by means of isokinetic probes using filters or cascade impactors (Habibi, 1970).

In the bag technique, auto emissions produced during simulated driving cycles are air-diluted and collected in a large plastic bag. The aerosol sample is passed through a filtration or impaction sampler prior to lead analysis (Ter Haar et al., 1972). This technique may result in errors of aerosol size analysis due to condensation of low-vapor-pressur organic substances onto the lead particles.

To minimize condensation problems, a third technique, a low-residence-time sampling system, has been used. It is based on proportional sampling of raw exhaust, again diluted with ambient air followed by filtration or impaction (Ganley and Springer, 1974; Simpson and Springer, 1973). Since the sample flow must be a constant proportion of the total exhaust flow, 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.

In recent years, various configurations of the horizontal air dilution tunnel have been developed. Several dilution tunnels have been made of polyvinyl chloride with a diameter of 46 cm, but these are subject to wall losses due to charge effects (Gertel et al., 1973; Moran et al., 1972; Trayser et al., 1975). Such tunnels of varying lengths have been limited by exhaust temperatures to total flows above approximately 11 m^3/min. Similar tunnels have been used in which a centrifugal fan located upstream is used rather than a positive displacement pump located downstream (Trayser et al., 1975). This geometry produces a slight positive pressure in the tunnel and expedites transfer of the aerosol to holding chambers for studies of aerosol growth. However, turbulence from the fan may affect the sampling efficiency. Since the total exhaust plus dilution airflow is not held constant in this system, potential errors can be reduced by maintaining a very high dilution air/exhaust flow ratio (Trayser et al., 1975).

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 (Habibi, 1973; Hirschler et al., 1957; Hirschler and Gilbert, 1964; Sampson and Springer, 1973). The cylindrical filtration unit used in these studies is better than 99 percent efficient in retaining lead particles (Habibi, 1973). Supporting data for lead balances generally confirm this conclusion (Kunz et al., 1975).

4.2.4 Sampling for Lead in Other Media

Other primary environmental media that may be affected by airborne lead include precipitation, surface water, soil and vegetation. The sampling plans and the sampling methodologies used in dealing with these media depend on the purpose of the experiments, the types of measurements to be carried out, and the analytical technique to be used. General recommended approaches are given below in lieu of specific procedures associated with the numerous possible special situations.

4.2.4.1 Precipitation--The investigator should be aware that dry deposition occurs continuously, that lead at the start of a rain event is higher in concentration than at the end, and that rain striking the canopy of a forest may rinse dry deposition particles from the lead surfaces. Rain collection systems should be designed to collect precipitation on an event basis and to collect sequential samples during the event. They should be tightly sealed

from the atmosphere before and after sampling to prevent contamination from dry deposition, falling leaves, and flying insects. Samples should be acidified to pH 1 with HNO_3 and refrigerated immediately after sampling. All collection and storage surfaces should be thoroughly cleaned and contamination-free.

Two automated systems have been in use for some time. The Sangamo Precipitation Collector, Type A, collects rain in a single bucket exposed at the beginning of the rain event (Samant and Vaidya, 1982). These authors reported no leaching of lead from the bucket into a solution of 0.02% HNO_3. A second sampler described by Coscio et al. (1982) also remains covered between rain events; it can collect a sequence of 8 samples during the period of rain and may be fitted with a refrigeration unit for sample cooling. No reports of lead analyses were given. Recommendation of either system is not intended and should not be inferred.

4.2.4.2 Surface Water--Atmospheric lead may be dissolved in water as hydrated ions, chemical complexes and soluble compounds, or it may be associated with suspended matter. Because the physico-chemical form often influences the environmental effects, there is a need to differentiate among the various chemical forms of lead. Complete differentiation among all such forms is a complex task that has not yet been fully accomplished. The most commonly used approach is to distinguish between dissolved and suspended forms of lead. All lead passing through a 0.45 μm membrane filter is operationally defined as dissolved while that retained on the filter is defined as suspended (U.S. Environmental Protection Agency, 1979).

When sampling water bodies, flow dynamics should be considered relative to the purpose of the sample collection. Water at the convergence point of two flowing streams, for example, may not be well mixed for several hundred meters. Similarly, the heavy metal concentrations above and below the thermocline of a lake may be very different. Thus, several samples should be selected in order to define the degree of lateral, longitudinal, or depth variation and the final sampling plan should be based on the results of pilot studies. In cases where the average concentration is of primary concern, sampling can be based on collection at several points and then mixed to obtain a composite.

Containers used for sample collection and storage should be clean and fabricated from essentially lead-free plastic or glass, e.g., Teflon® or quartz. Even these containers must often be leached with hot acid for several hours to ensure lead-free status. If only the total lead is to be determined, the sample may be collected without filtration in the field. Nitric acid should be added immediately to reduce the pH to less than 2 (U.S. Environmental Protection Agency, 1979). The acid will normally dissolve the suspended lead. Otherwise, it is recommended that the sample be filtered upon collection to separate the suspended and dissolved lead and the latter preserved by acid addition as above. It is also recommended that water samples be stored at 4°C until analysis (Fishman and Erdmann, 1973; Kopp and Kroner, 1967; Lovering, 1976; National Academy of Sciences, 1972; U.S. Environmental Protection Agency, 1979).

4.2.4.3 Soils--The distance and depth gradients associated with lead in soil from emission sources must be considered in designing the sampling plan. Beyond that, actual sampling is not particularly complex (Skogerboe et al., 1977a). Vegetation, litter, and large objects such as stones should not be included in the sample. Depth samples should be collected so their vertical integrity can be preserved. The samples should be air dried and stored in sealed containers until analyzed.

4.2.4.4 Vegetation--Because most soil lead is in forms unavailable to plants, and because lead is not readily transferred from roots to shoots, plant roots typically contain very little lead and shoots even less (Zimdahl, 1976, 1977). Before analysis, a decision must be made as to whether or not the plant material should be washed to remove surface contamination from dry deposition and soil particles. If the plants are sampled for total lead content (e.g., if they serve as animal food sources) they cannot be washed. If the effect of lead on internal plant processes is being studied, the plant samples should be washed. In either case, the decision must be made at the time of sampling, as washing cannot be effective after the plant materials have dried. Fresh plant samples cannot be stored for any length of time in a tightly closed container before washed 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.

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 to arrest enzymatic reactions and render the plant tissue amenable to grinding. Subsequent storage in sealed containers is required. For analysis of surface lead, fresh, intact plant parts are agitated in dilute nitric acid or EDTA solutions for a few seconds.

4.2.4.5 Foodstuffs--In 1972, lead was added to 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 (Kolbye et al., 1974). Various food items from the several food classes are purchased in local markets and made up into meal composites 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. Other sampling programs may be required for different investigative purposes. For those foods where lead may be deposited on the edible portion, the question of whether or not to use typical kitchen washing procedures before analysis should be considered in the context of the experimental purpose.

4.2.5 Filter Selection and Sample Preparation

In sampling for airborne lead, air is drawn through filter materials such as glass fiber, cellulose acetate, or porous plastics (Skogerboe et al., 1977a, Stern, 1968). These materials often include contaminant lead that can interfere with the subsequent analysis (Gandrud and Lazrus, 1972; Kometani et al. 1972; Luke et al., 1972; Seeley and Skogerboe, 1974). If the sample collected is large, then the effects of these trace contaminants may be negligible (Witz and MacPhee, 1976). Procedures for cleaning filters to reduce the lead blank rely on washing with acids or complexing agents (Gandred and Lazrus, 1972). The nature of the filter and the analytical method to be used often determines the ashing technique. In some methods, e. g., X-ray fluorescence, analysis can be performed directly on the filter if the filter material is suitable (Dzubay and Stevens, 1975). A general review of filter materials is available (Skogerboe, 1974).

The main advantages of glass fiber filters are low pressure drop and high particle collection efficiency at high flow rates. The main disadvantage is variable inherent lead content which makes their use inadvisable in many cases (Komentani et al., 1972; Luke at al., 1972). This has placed a high priority on the standardization of a suitable filter for high-volume samples (Witz and MacPhee, 1976). Other investigations have indicated, however, that glass-fiber filters are now available that do not present a lead interference problem (Scott et al., 1976a). Teflon® filters have been used since 1975 by Dzubay (1982) and Stevens (1978) and they have shown these filters to have very low lead blanks (<2 ng/cm^2). The collection efficiencies of filters, and also of impactors, have been shown to be dominant factors in the quality of the derived data (Liu and Pui, 1976; 1980; Skogerboe et al., 1977b).

Sample preparation usually involves conversion to a solution through wet ashing of solids with acids or through dry ashing in a furnace followed by acid treatment. Either approach works effectively if used properly (Kometani et al., 1972; Skogerboe et al., 1977a). In one investigation of porous plastic Nuclepore filter, examples were found in which the lead blanks were too high to allow measurements of ambient air lead concentrations (Skogerboe et al., 1977a).

4.3 ANALYSIS

The choice of analytical method 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 widely used and recommended (40 CFR Part 50). Optical emission spectrometry (Scott et al., 1976a) and X-ray fluorescense (Dzubay and Stevens, 1975; Hammerle and Pierson, 1975; Jaklevic et al., 1973; and Stevenson et al., 1978) are rapid and inexpensive methods for multielemental analyses. X-ray fluorescence can measure lead concentrations reliably to 1 ng/m^3 using samples collected with commercial dichotomous samplers. Other analytical methods have specific advantages appropriate for special studies. Only those analytical techniques receiving widespread current use in lead analysis are described below. More complete reviews are available in the literature (American Public Health Association, 1971; Lovering, 1976; Skogerboe et al., 1977a; National Academy of Sciences, 1980).

With respect to measuring lead without sampling or laboratory contamination, several investigators have shown that the magnitude of the problem is quite large (Patterson and Settle, 1974; Patterson et al., 1976; Pierre et al., 1976; Patterson et al., 1982; Skogerboe, 1982). It appears that the problem may be caused by failure to control adequately the blank or failure to standardize instrument operation (Patterson, 1982; Skogerboe, 1982).

Data have been presented indicating that the laboratory atmosphere, collecting containers, and the labware used may be primary contributors to the lead blank problem (Murphy, 1974; Patterson, 1982; Skogerboe, 1982). Failure to recognize this and other sources such as reagents and hand contact is very likely to result in the generation of artificially high analytical results.

4.3.1 Atomic Absorption Analysis

Atomic absorption spectrometry (AAS) is a widely accepted method for the measurement of lead in environmental sampling (Skogerboe et al., 1977a). A variety of lead studies using AAS have been reported (Kometani et al., 1972; Zoller et al., 1974; Huntzicker et al., 1975; Scott et al., 1976a; Lester et al., 1977; Hirao et al., 1979; Compton and Thomas, 1980; Bertenshaw et al., 1981).

The lead atoms in the sample must be vaporized either in a precisely controlled flame or in a furnace. Furnace systems in atomic absorption offer high sensitivity as well as the ability to analyze microsamples (Lester et al., 1977; Rouseff and Ling, 1980; Stein et al., 1980; Bertenshaw et al., 1981). These enhanced capabilities are offset in part by greater difficulties in analytical calibration and by losses in analytical precision.

A notable application involves the use of graphite cups as particle filters with the subsequent analysis of the cups directly in the furnace system (Seeley and Skogerboe, 1974; Torsi et al., 1981). Pachuta and Lone (1980) collected particles on cellulose acetate filters. Disks (0.5 cm^2) were punched from these filters and analyzed by insertion of the nichrome cups containing the disks into a flame. These two procedures offer the ability to determine particulate lead directly with minimal sample handling.

In an analysis using AAS and high-volume samplers, atmospheric concentrations of lead were found to be 0.63 ± 0.3 ng/m^3 at the South Pole (Zoller et al., 1974). Lead analyses of 995 particulate samples from the NASN were accomplished by AAS with an indicated precision of 11 percent (Scott et al.,

1976a). More specialized atomic absorption methods for the determination of tetraalkyl lead compounds in water and fish tissue have been described by Chau et al. (1979) and in air by Birnie and Noden (1980) as well as Rohbock et al. (1980).

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 AAS is that it has become so popular that untrained operators are using it in many laboratories without adequate quality control.

Techniques for AAS are still evolving. Improved nonflame atomization systems, electrodeless discharge lamps, and other equipment refinements and technique developments have been reported (Skogerboe et al. 1977a).

4.3.2 Emission Spectroscopy

Optical emission spectroscopy is based on the measurement of the light emitted by elements when they are excited in an appropriate energy medium. The technique has been used to determine the lead content of soils, rocks, and minerals at the 5- to 10 µg/g level with a relative standard deviation of 5 to 10 percent (anonymous, 1963); this method has also been applied to the analysis of a large number of air samples (Edwards, 1974; Scott et al., 1976a; Suginae and Skogerboe, 1978). The primary advantage of this method is that it allows simultaneous measurement of a large number of elements in a small sample (Ward and Fishman, 1976).

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 (Copeland et al., 1973; Seeley and Skogerboe, 1974). Lead concentrations of 1 to 10 µg/m^3 could be detected after a half-hour flow at 800 to 1200 ml/min through the filter.

Scott et al. (1976b) analyzed composited particulate samples obtained with hi-vols for about 24 elements, including lead, using a direct-reading emission spectrometer. 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 particles.

More recent activities have focused attention on the inductively coupled plasma (ICP) as a valuable means of excitation and analysis (Garbarino and Taylor, 1979; Winge et al., 1977). The ICP system offers a higher degree of sensitivity with less analytical interference problems than typical of many of the other emission spectrometric systems. Optical emission methods are placed at a disadvantage when they are used for analysis of a single element since the equipment is expensive and a high level of operator training is required. This problem is largely offset when the analysis for several elements is required as is often the case for atmospheric aerosols.

4.3.3 X-Ray Fluorescence

X-ray emissions that characterize the elemental content of a sample also occur when atoms are irradiated at sufficient energy to remove an inner-shell electron (Hammerle and Pierson, 1975; Jaklevic et al., 1973; Skogerboe et al., 1977a; Stevens et al., 1978). This fluorescence allows simultaneous identification of a range of elements, including lead.

X-ray fluorescence may require a high-energy irradiation source. But with the X-ray tubes coupled with fluoresors (Jakelvic et al., 1973; Dzubay and Stevens, 1975; Paciga and Jervis, 1976) very little energy is transmitted to the sample, thus sample degradation is kept to a minimum (Shaw et al., 1980). Electron beams (McKinley and Heinrich, 1966), and radioactive isotope sources (Kneip and Lauer 1972) have been used extensively (Birks et al., 1971; Birks, 1972) as energy sources for XRF analysis. To reduce background, secondary fluorescers have been employed (Birks et al., 1971; Dzubay and Stevens, 1975). The fluorescent X-ray emission from the sample may be analyzed with a crystal monochromator and detected with scintillation or proportional counters (Skogerboe et al., 1977a) or with low-temperature semiconductor detectors that discriminate the energy of the fluorescence. The latter technique requires a very low level of excitation (Dzubay and Stevens, 1975; Toussaint and Boniforti, 1979).

X-ray emission induced by charged-particle excitation (proton-induced X-ray emission or PIXE) offers an attractive alterative to the more common techniques (Barfoot et al., 1979; Hardy et al., 1976; Johansson et al., 1970). Recognition of the potential of heavy-particle bombardment for excitation was demonstrated by Johansson et al. (1970), who reported an interference-free

signal in the picogram (10^{-12} gm) range. 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 high particle fluxes obtainable from accelerators also contribute to the sensitivity of the PIXE method. Literature reviews (Folkmann et al., 1974; Gilfritch et al., 1973; Herman et al., 1973; Walter et al., 1974) 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 (Johansson et al., 1975) and papers involving the use of PIXE for aerosol analysis have appeared (Hardy et al., 1976; Johansson et al., 1975). The use of radionuclides to excite X-ray fluorescence and to determine lead in air particles has also been described (Havranek and Bumbalova, 1981; Havranek et al., 1980).

X-radiation is the basis of the electron microprobe method of analysis. When an intense electron beam is incident on a sample, it produces several forms of radiation, including X-rays whose wavelengths depend on the elements present in the material and whose intensities depend on the relative quantities of these elements. An electron beam that gives a spot size as small as 0.2 μm is possible. The microprobe is often incorporated in a scanning electron microscope that allows precise location of the beam and comparison of the sample morphology with its elemental composition. Under ideal conditions, the analysis is quantitative, with an accuracy of a few percent. The mass of the analyzed element may be in the 10^{-14} to 10^{-16} g range (McKinley and Heinrich, 1966).

Electron microprobe analysis is not a widely applicable monitoring method. It requires expensive equipment, complex sample preparation procedures, 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.

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, low detection limits (2 ng/m^3) and the availability of automated analytical equipment. Disadvantages are that the X-ray analysis requires liquid nitrogen (e.g. for energy-dispersive models), and highly trained analysts.

The detection limit for lead is approximately 9 ng/cm^2) of filter area (Jaklevic and Walter, 1977) which is well below the quantity obtained in normal sampling periods with the dichotomous sampler (Dzubay and Stevens, 1975).

4.3.4 Mass Spectrometry

Isotope dilution mass spectrometry (IDMS) is an absolute measurement technique. It serves as the standard against which other analytical techniques are compared. No other techniques serve more reliably as a comparative reference. Its use for analyses at subnanogram concentrations of lead and in a variety of sample types has been reported (Chow et al., 1969; Chow et al., 1974; Facchetti, 1979; Hirao and Patterson, 1974; Murozumi et al., 1969; Patterson et al., 1976; Rabinowitz et al., 1973).

The unique isotopic composition of lead from various ore body and crustal sources may also be used as a means of tracing the origin of the lead. Other examples of IDMS application are found in several reports cited above, and in those by Rabinowitz and Wetherill (1972); Stacey and Kramers (1975); and Machlon et al. (1976).

4.3.5 Colorimetric Analysis

Colorimetric or spectrophotometric analysis for lead using dithizone (diphenylthiocarbazone) as the reagent has been used for many years (Anonymous, 1963; Horowitz et al., 1970; Sandell, 1944). It was the primary method recommended by a National Academy of Sciences (1972) report on lead, and the basis of the tentative method of testing for lead in the atmosphere by the American Society for Testing and Materials (1975). Prior to the development of the IDMS method, colorimetric analysis has served as the reference by which other methods have been tested.

The procedures for the colorimetric analysis require a skilled analyst if reliable results are to be obtained. The American Society of Testing and Materials conducted a collaborative test of the method (Foster et al., 1975) and concluded that the procedure gave satisfactory precision in the determination of particulate lead in the atmosphere. In addition, the required apparatus is simple and relatively inexpensive, the absorption is linearly related to the lead concentration, large samples can be used, and interferences can be removed (Skogerboe et al., 1977a). Realization of these advantages depends on meticulous attention to the procedures and reagents.

4.3.6 Electrochemical Methods (Anodic Stripping Voltammetry, Differential Pulse Polarography)

Analytical methods based on electrochemical phenomena are found in a variety of forms (Sawyer and Roberts, 1974; Willard et al., 1974). They are characterized by a high degree of sensitivity, selectivity, and accuracy derived from the relationship between current, charge, potential, and time for electrolytic reactions in solutions. The electrochemistry of lead is based primarily on Pb(II), which behaves reversibly in ionic solutions having a reduction potential near -0.4 volts versus the standard calomel electrode (Skogerboe et al., 1977a). Two electrochemical methods generally offer sufficient analytical sensitivity for most lead measurement problems. Differential pulse polarography (DPP) relies on the measurement of the faradaic current for lead as the voltage is scanned while compensating for the nonfaradaic (background) current produced (McDonnell, 1981). Anodic stripping voltammetry (ASV) is a two step process in which the lead is first preconcentrated onto a mercury electrode by an extended but selected period of reduction. After the reduction step, the potential is scanned to oxidize the lead and allow measurement of the oxidation (stripping) current. The preconcentration step allows development of enhanced analytical signals; when used in combination with the differential pulse method lead concentrations at the subnanogram level can be measured (Copeland et al., 1973; Willard et al., 1974; Zirino and Healy, 1972).

The ASV method has grown rapidly in popularity. It has been applied to the analysis of atmospheric lead (Harrison et al., 1971; Khandekar et al., 1981; MacLeod and Lee, 1973). Landy (1980) has shown the applicability to the determination of Cd, Cu, Pb, and Zn in Antarctic snow while Nguyen et al. (1979) have analyzed rain water and snow samples. Green et al. (1981) have used the method to determine Cd, Cu and Pb in sea water. The ASV determination of Cd, Cu, Pb and Zn in foods has been described by Jones et al., (1977) and the general accuracy of the method summarized by Holak (1980). Current practice with commercially available equipment allows lead analyses at subnanogram concentrations with precision at the 5 to 10 percent on a reasonably routine basis (Skogerboe et al., 1977a).

4.3.7 Methods for Compound Analysis

The majority of analytical methods are restricted to measurement of total lead and cannot directly 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 (Ter Haar and Bayard, 1971). Gas chromatography (GC) using the electron capture detector has been demonstrated to be useful for organic lead compounds (Shapiro and Frey, 1968). The use of atomic absorption as the GC detector for organolead compounds has been described by DeJonghe et al. (1981), while a plasma emission detector has been used by Estes et al. (1981). In addition, Messman and Rains (1981) have used liquid chromatography with an atomic absorption detector to measure organolead compounds. Mass spectrometry may also be used (Mykytieck et al., 1980).

Powder X-ray diffraction techniques have been applied to the identification of lead compounds in soils by Olson and Skogerboe (1975) and by Linton et al., (1980). X-ray diffraction techniques were used (Harrison and Perry, 1977; Foster and Lott, 1980; Jacklevic et al., 1981) to identify lead compounds collected on air filters.

4.4 CONCLUSIONS

To monitor lead particles in air, collection with the hi-vol and dichotomous samplers and analysis by atomic absorption spectrometry and X-ray fluorescence methods have emerged as the most widely used methods. Sampling with the hi-vol has inherent biases in sampling large particles and does not provide for fractionation of the particles according to size, nor does it allow determination of the gaseous (organic) concentrations. Sampling with a dichotomous sampler provides size information but does not allow for gaseous lead measurements. The size distribution of lead aerosol particles is important in considering inhalable particulate matter. 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 multi-element analysis. Other analytical techniques find application for specific purposes. The paucity of data base on the types of lead compounds at subnanogram levels in the ambient air is currently being addressed through development of improved XRO analyzer procedures.

4.5 REFERENCES FOR CHAPTER 4

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TABLE OF CONTENTS
Chapter 5
Sources and Emissions

LIST OF TABLES

LIST OF FIGURES

5. SOURCES AND EMISSIONS

5.1 HISTORICAL PERSPECTIVE

The history of global lead emissions has been assembled from chronological records of deposition in polar snow strata, marine and freshwater sediments, and the annual rings of trees. These records are important for two reasons. They aid in establishing natural background levels of lead in air, soils, plants, animals, and humans. They also place current trends in atmospheric lead concentrations in the perspective of historical changes. Most chronological records document the sudden increase in atmospheric lead at the time of the industrial revolution, and a later burst during the 1920's when lead-alkyls were first added to gasoline.

Tree ring analyses are not likely to show the detailed year-by-year chronological record of atmospheric lead increases. In situations where tree species that retain the nutrient solution only in the most recent annual rings are growing in heavily polluted areas where soil lead has increased 100-fold, significant increases in the lead content of tree rings over the last several decades have been documented. Rolfe (1974) found 4-fold increases in both rural and urban tree rings using pooled samples from the period of 1910-20 and comparing these to samples from the period from 1963-73. Symeonides (1979) found a 2-fold increase during a comparable interval at a high-lead site but no increase at a low lead site. Baes and Ragsdale (1981) found significant post-1930 increases in oak (Quercus) and hickory (Carya) with high lead exposure, but only in hickory with low lead exposure.

Pond sediment analyses (Shirahata, et al. 1980) have shown a 20-fold increase in lead deposition during the last 150 years, documenting not only the increasing use of lead since the beginning of the industrial revolution in western United States, but also the relative fraction of natural vs. anthropogenic lead inputs. Other studies have shown about the same magnitude of increasing deposition in freshwater sediments (Christensen and Chien, 1981; Galloway and Likens, 1979; Edgington and Robbins, 1976), and marine sediments (Ng and Patterson, 1979). The pond and marine sediments also document the shift in isotopic composition caused by the recent opening of the New Lead Belt in Missouri, where the ore body has an isotopic composition substantially different from other ore bodies of the world.

Perhaps the best and certainly the most controversial chronological record is that of the polar ice strata of Murozumi et al. (1969), which extends nearly three thousand years back in time (Figure 5-1). The data of Jaworowski et al. (1981) and Herron et al. (1977) do not agree with the value found by Murozumi et al. (1969) for the early period around 800 B.C. Ng and Patterson (1981) have shown that the ice cores of Herron et al. (1977) were contaminated with industrial greases. Patterson (1982) has also discussed the probable errors made by Jaworowski et al. (1981) in their determination of manmade lead in glacial ice samples. In summary, it is likely that atmospheric lead emissions have increased 2000-fold since the pre-Roman era, and that even at this early time, the atmosphere may have been contaminated by a factor of three over natural levels (Murozumi et al. 1969).

The history of global emissions may also be determined from total production of lead, if the fraction of that lead released to the atmosphere during the smelting process, the fraction released during industrial consumption and the amount of lead emitted from non-lead sources are known. The historical picture of lead production has been pieced together from many sources by Settle and Patterson (1980) (Figure 5-2). They used records of coin production accumulated silver stocks to estimate the lead production needed to support this industry. Until the industrial revolution, lead production was determined largely by the ability or desire to mine lead for its silver content. Since that time, lead has been used as an industrial product in its own right, and efforts to improve smelter efficiency, including control of stack emissions and fugitive dusts, have made lead production more economical. This improved efficiency is not reflected in the chronological record because of atmospheric emissions of lead from many other anthropogenic sources, especially gasoline combustion (see Table 5-2). From this knowledge of the chronological record, it is possible to sort out contemporary emissions from natural and manmade sources.

5.2 NATURAL SOURCES

Lead enters the biosphere from lead-bearing minerals in the lithosphere through both natural and man-made processes. Measurements of soil materials taken at 8-in. depths in the continental United States (Loverling, 1976; Schacklette et al. 1971) show a median lead concentration of 15 to 16 μg Pb/g soil. Ninety-five percent of these measurements show 30 μg/g of lead or less, with a maximum sample concentration of 700 μg/g.

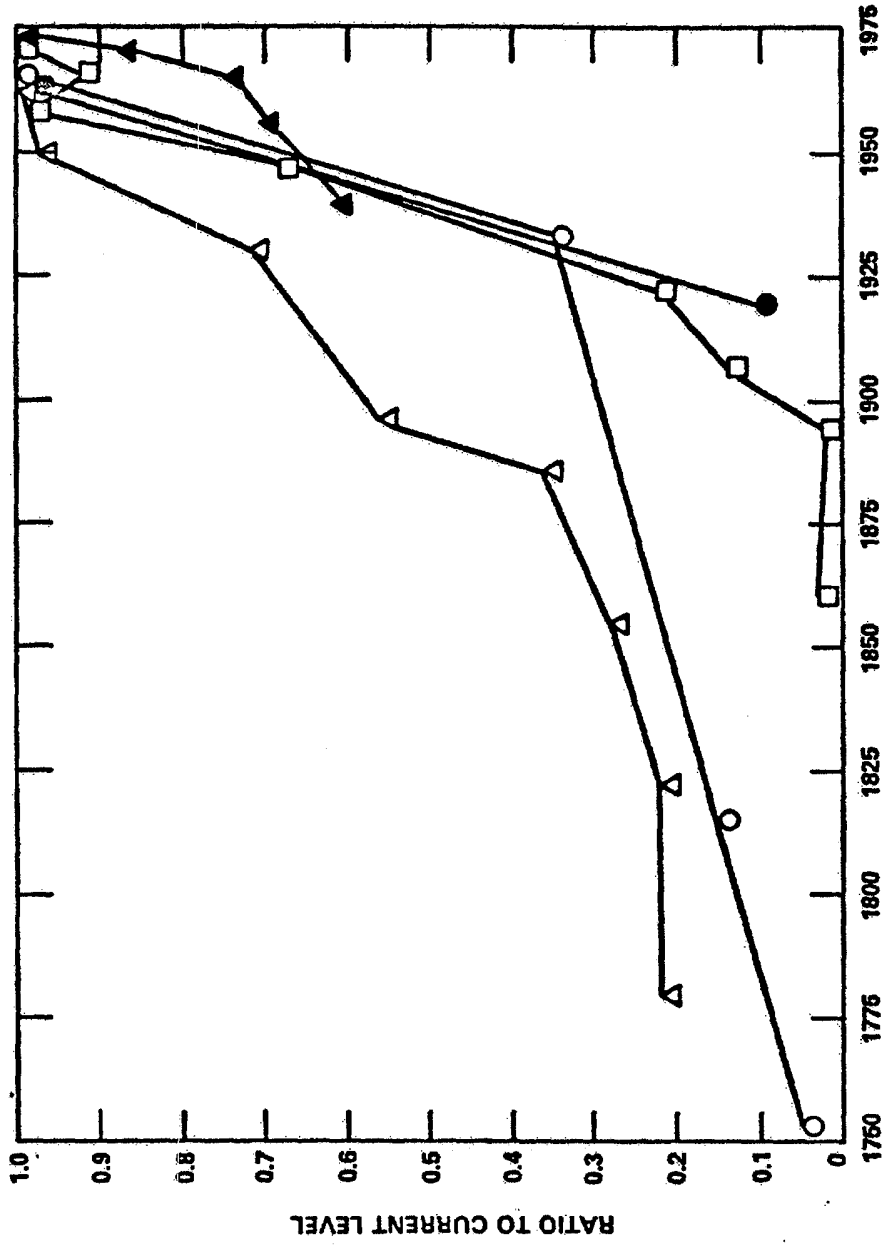

Figure 5-1. Chronological record of the relative increase of lead in snow strata, pond and lake sediments, marine sediments, and tree rings. The data are expressed as a ratio of the latest year of the record and should not be interpreted to extend back in time to natural or uncontaminated levels of lead concentration.

Source: Adapted from Murozumi et al. (1969) (○), Shirahata et al. (1980) (□), Edington and Robbins (1976) (△), Ny and Patterson (1979) (▲), and Rolfe (1974) (●).

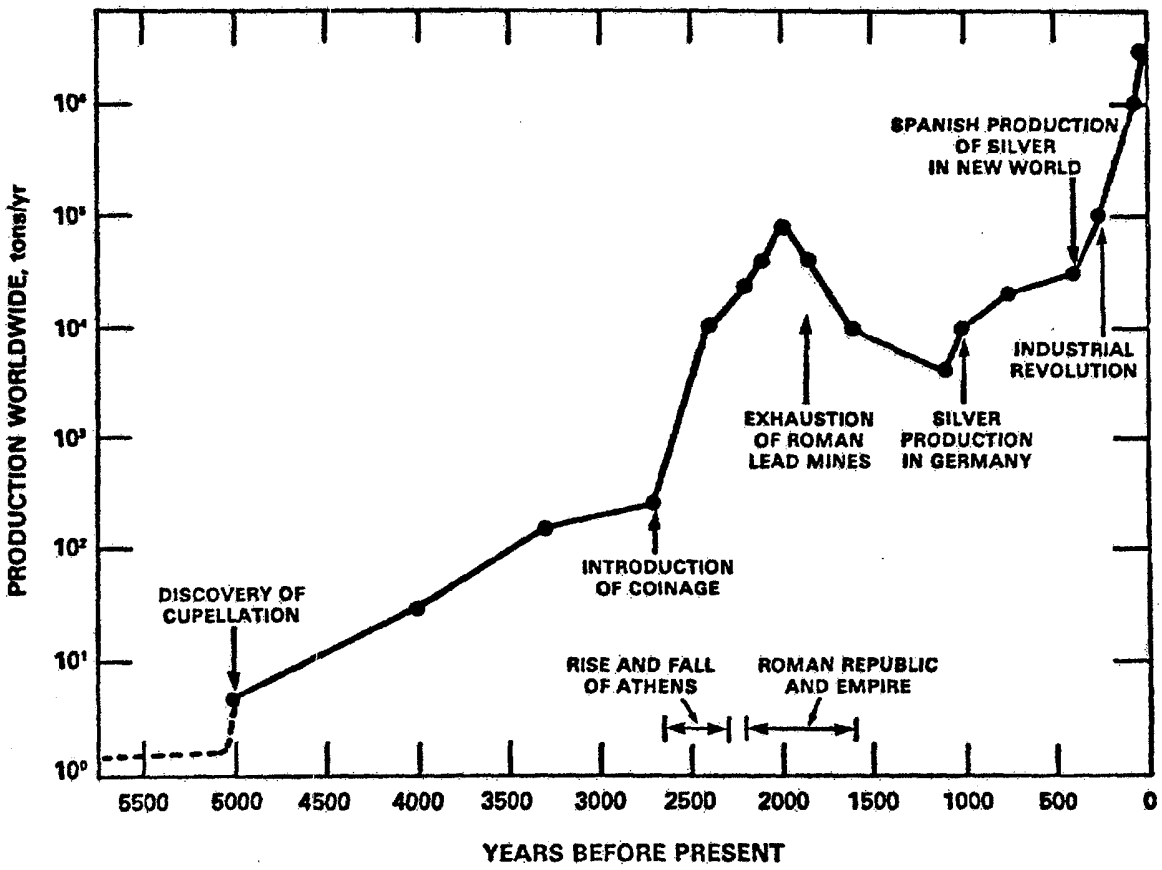

Figure 5-2. The global lead production has changed historically in response to major economic and political events. Increases in lead production (note log scale) correspond approximately to historical increases in lead emissions shown in Figure 5-1.

Source: Adapted from Settle and Patterson (1980).

In natural processes, lead is first incorporated in soil in the active root zone, from which it may be absorbed by plants, leached into surface waters, or eroded into windborne dusts (National Academy of Sciences, 1980; Chamberlain, 1970; Patterson, 1965; Chow and Patterson, 1962).

Calculations of natural contributions using geochemical information indicate that natural sources contribute a relatively small amount of lead to the atmosphere. For example, if the typical 25 to 40 $\mu g/m^3$ of rural airborne particulate matter consisted solely of wind-entrained soils containing 15 $\mu g/g$, and rarely more than 30 μg of lead/g, as cited above, then the natural contribution to airborne lead would range from 0.0004 to 0.0012 $\mu g/m^3$. It has been estimated from geochemical evidence that the natural particulate lead level is less than 0.0005 $\mu g/m^3$ (National Academy of Sciences, 1980; United Kingdom Department of the Environment, 1974). In fact, levels as low as 0.000076 $\mu g/m^3$ have been measured at the South Pole in Anarctica (Boutron and Lorius, 1979). In contrast, average lead concentrations in urban suspended particulate matter (Akland, 1976; U.S. Environmental Protection Agency, 1979, 1978) range as high as 6 $\mu g/m^3$. Evidently, most of this urban particulate lead stems from man-made sources.

5.3 MANMADE SOURCES

5.3.1 Production

Lead occupies an important position in the U.S. economy, ranking fifth among all metals in tonnage used. Approximately 85 percent of the primary lead produced in this country is from native mines, although often associated with minor amounts of zinc, cadmium, copper, bismuth, gold, silver, and other minerals (U.S. Bureau of Mines, 1975). Missouri lead ore deposits account for approximately 80 to 90 percent of the domestic production. Approximately 40 to 50 percent of annual lead production is recovered and eventually recycled.

5.3.2 Utilization

The 1971-1980 uses of lead are listed by major product category in Table 5-1. (U.S. Bureau of Mines, 1981; 1976). Total utilization averaged approximately 1.36×10^6 metric tons/yr (MT/yr) over the 10-year period, with storage batteries and gasoline additives accounting for ~ 70 percent of total use. The gasoline antiknocks listed in Table 5-1 include additives for both domestic and import markets. The additive fraction of total lead utilization has decreased from greater than 18 percent in 1971-1973

TABLE 5-1. U.S. UTILIZATION OF LEAD BY PRODUCT CATEGORY (1971-1980), METRIC TONS/YEAR
(U.S. BUREAU OF MINES, 1981)

Product category	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980
Storage batteries	616,581	661,740	697,888	772,656	634,368	746,085	858,099	879,274	814,332	645,357
Gasoline antiknock additives[a]	239,666	252,545	248,890	227,847	189,369	217,508	211,296	178,473	186,945	127,903
Pigments and ceramics	73,701	80,917	98,651	105,405	71,718	95,792	90,704	91,642	90,790	78,430
Ammunition	79,423	76,822	73,091	78,991	68,098	66,659	62,043	55,776	53,236	48,662
Solder	63,502	64,659	65,095	60,116	52,011	57,448	58,320	68,390	54,278	41,366
Cable coverings	47,998	41,659	39,006	39,387	20,044	14,452	13,705	13,851	16,393	13,408
Caulking lead	27,204	20,392	18,192	17,903	12,966	11,317	8,725	9,909	8,017	5,684
Pipe and sheet lead	41,523	37,592	40,529	34,238	35,456	34,680	30,861	23,105	27,618	28,393
Type metal	18,876	18,089	19,883	18,608	14,703	13,614	11,395	10,795	10,019	8,997
Brass and bronze	18,180	17,963	20,621	20,172	12,157	14,207	15,148	16,502	18,748	13,981
Bearing metals	14,771	14,435	14,201	13,250	11,051	11,851	10,873	9,510	9,630	7,808
Other	56,958	63,124	61,019	62,106	54,524	68,181	64,328	75,517	68,329	50,314
TOTAL	1,298,383	1,349,846	1,397,876	1,450,679	1,176,465	1,351,794	1,435,497	1,432,744	1,358,335	1,070,303

[a]Includes additives for both domestic and export markets.

to less than 12 percent in 1980. 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 only 0.5 to 0.8 million MT are recovered annually. Lead in pigments, gasoline additives, ammunition, foil, solder, and steel products is widely dispersed and therefore is largely unrecoverable.

5.3.3 Emissions

Lead or its compounds may enter the environment at any point during mining, smelting, processing, use, recycling, or disposal. 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 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 5-3 shows the approximate locations of major lead mines, primary and secondary smelters and refineries, and alkyl lead plants (Lead Industries Association, 1982).

5.3.3.1 Mobile Sources--The majority of lead compounds found in the atmosphere result from leaded gasoline combustion (U.S. Environmental Protection Agency, 1973). Transportation sources, which include light-duty, heavy-duty, and off-highway vehicles, contribute over 80 percent of the total atmospheric lead (NEDS, 1980, 1979; U.S. Environmental Protection Agency, 1977). Other mobile sources, including aviation use of leaded gasoline and diesel and jet fuel combustion, contribute insignificant lead emissions to the atmosphere. Lead is added to gasoline as an antiknock additive to enhance engine performance in the form of two tetralkyl lead compounds, tetraethyl and tetramethyl lead (see Chapter 3). Lead is emitted from vehicles primarily in the form of inorganic particles, although a very small fraction (<10% of lead emissions are released as volatile organic compounds, i.e., lead alkyls (National Academy of Sciences, 1972).

The factors which affect both the rate of particulate lead emissions and the physicochemical properties of the emissions are: lead content of the fuel, other additives, vehicle fuel economy, the driving speed or conditions, and type of vehicle, as well as design parameters, maintenance, ages of the engine, exhaust, and emission control systems. The major types of vehicles

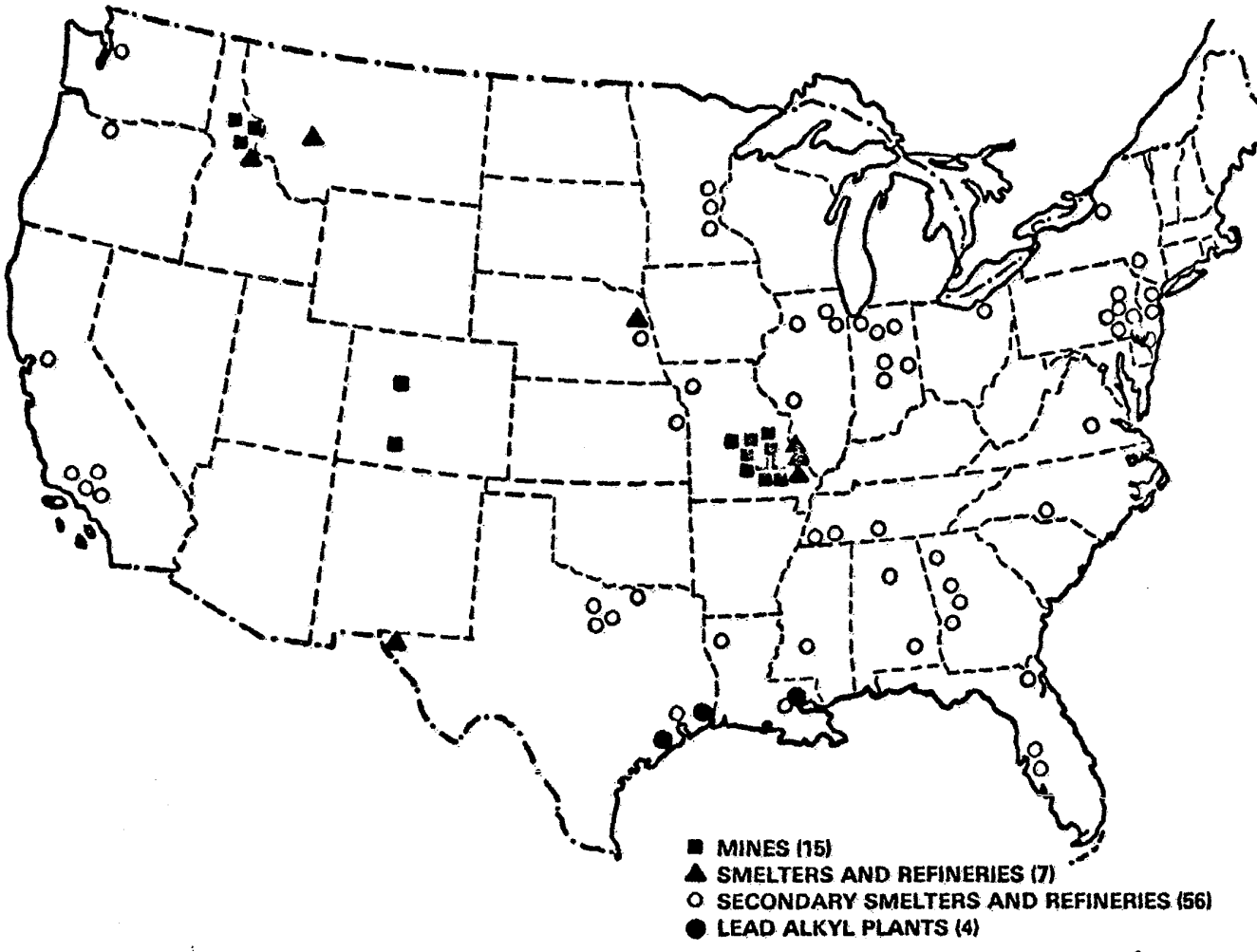

Figure 5-3. Locations of major lead operations in the United States.

TABLE 5-2. ESTIMATED ATMOSPHERIC LEAD EMISSIONS FOR THE UNITED STATES, 1975[a] (U.S. Environmental Protection Agency, 1977) AND THE WORLD (Nriagu, 1979)

Source Category	Annual U.S. Emissions MT/yr	Emissions as Percentage of U.S. Total Emissions	Emissions as Percentage of Global Emissions
Mobile subtotal	142,000[b]	--[b]	273,000
Gasoline combustion	142,000	88.1	273,000
Stationary subtotal	19,225	--	
Waste oil combustion	10,430	6.5	8,900
Solid waste disposal	1,630	1.0	
Coal combustion	400	0.2	14,000
Oil combustion	100	0.1	6,000
Wood combusion	--	--	4,500
Gray iron production	1,079	0.7	50,000
Iron and steel production	844	0.5	
Secondary lead smelting	755	0.4	770
Primary copper smelting	619	0.4	27,000
Ore crushing and grinding	493	0.3	8,200
Primary lead smelting	400	0.2	31,000
Other metallurgical	272	0.2	
Zn smelting			16,000
Ni smelting			2,500
Lead alkyl manufacture	1,014	0.6	
Type metal	436	0.3	7,400
Portland cement production	313	0.2	
Pigments	112	0.1	
Miscellaneous	328	0.2	5,900
Total	161,225	100	449,170

[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.

[b] An update of these data is underway.

TABLE 5-3. LIGHT-DUTY VEHICULAR PARTICULATE EMISSION RATE AND COMPOSITION ESTIMATES USING 1.8 g Pb/gallon FUEL
(Hare and Black, 1981)

Rate or property	Data by vehicle category	
	Pre-1970	1970 & later without catalyst
Exhaust particulate emissions, g/mi	0.29	0.13
Particle mass median equivalent diameter, μm	<0.25	<0.25
Percent of particulate mass as:		
Lead (Pb)	22 or greater	36 or greater
Bromine (Br)	11 or greater	18 or greater
Chlorine (Cl)	4 or greater	6 or greater
Trace metals	1	1 or greater
Carbon (C), total	33 or greater	33 or less
Sulfate ($SO_4^{=}$)	1.3	1.3 or greater
Soluble organics	~30 or less	~10

TABLE 5-4. HEAVY-DUTY VEHICULAR PARTICULATE EMISSION RATE ESTIMATES USING 1.8 g Pb/gallon FUEL
(Hare and Black, 1981)

Heavy-duty category	Particulate emissions by model year, g/mi	
	Pre-1970	1970 and later
Medium-duty trucks (6,000 to 10,000 lb GVW)	0.50	0.40
Heavy-duty trucks (over 10,000 lb GVW)	0.76	0.60

TABLE 5-5. AVERAGE LEAD CONTENT OF U.S. GASOLINES IN GRAMS/GALLON, 1975-1982
(DuPont, 1982)

	1975	1976	1977	1978	1979	1980	1981	1982[a]
Leaded fuel	1.81	1.97	2.12	2.04	1.90	1.37	1.19	1.44
Unleaded fuel	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Sales-weighted total gasoline pool	1.62	1.60	1.53	1.35	1.16	0.75	0.60	0.60
EPA's proposed lead reduction schedule, g/gal[b]	1.7	1.4	1.0	0.8	0.5	0.5	0.5	0.5

[a]Forecasted.

[b]Prior to 1979, compliance with the proposed lead reduction schedule was not enforced and the standard for 0.5 g/gal was delayed until October 1980.

are light-duty (predominantly cars) and heavy-duty (trucks and buses). The important properties of the particulate emissions include the total amount emitted, the size distribution of the particles, and the chemical composition of these particles as a function of particle size. The most commonly used index of particle size is the mass median equivalent diameter (MMED), which is defined as the point in the size distribution of particles such that half the mass lies on either side of the MMED (U.S. Public Health Service, 1970). Table 5-3 summarizes a recent study estimating the particulate emission rates and particle composition for light-duty vehicles operated on a leaded fuel of 1.8 g Pb/gallon (Hare and Black, 1981). Table 5-4 estimates particulate emission rates for heavy-duty vehicles (trucks) operated on a leaded fuel of 1.8 g Pb/gallon (Hare and Black, 1981). The lead content of 1.8 g Pb/gallon was chosen to approximate the lead concentration of leaded gasoline during 1979 (Table 5-5). Another recent study utilizing similar composite emission factors provides estimates of motor vehicle lead emissions for large areas (Provenzano, 1978).

Lead occurs, on the average, as PbBrCl in fresh exhaust particles (Hirschler et al., 1957). This lead compound is 64.2 percent lead by mass and is a common form of lead emitted due to the presence of the scavengers ethylene dichloride and ethylene dibromide in normal leaded fuel. PbBrCl has theoretical mass ratios for lead, bromine, and chlorine of 0.64, 0.25, and 0.11, respectively. The particle compositional data in Table 5-3 indicate that mass ratios for lead, bromine, and chlorine are approximately 0.60, 0.30, and 0.10, respectively, from both pre- and post-1970 vehicles. Data from another study (Lang et al., 1981), involving 1970-1979 vehicles, indicated that mass ratios for lead, bromine, and chlorine were 0.62, 0.30, and 0.08, respectively.

The fate of emitted lead particles depends upon their particle size (see Chapter 6). Particles initially formed by condensation of lead compounds in the combustion gases are quite small (well under 0.1 μm in diameter) (Pierson and Brachaczek, 1982). Particles in this size category are subject to growth by coagulation and, when airborne, can remain suspended in the atmosphere for 7 to 30 days and travel thousands of miles from their original source (Chamberlain et al., 1979). Larger particles are formed as the result of agglomeration of smaller condensation particles and have limited atmospheric

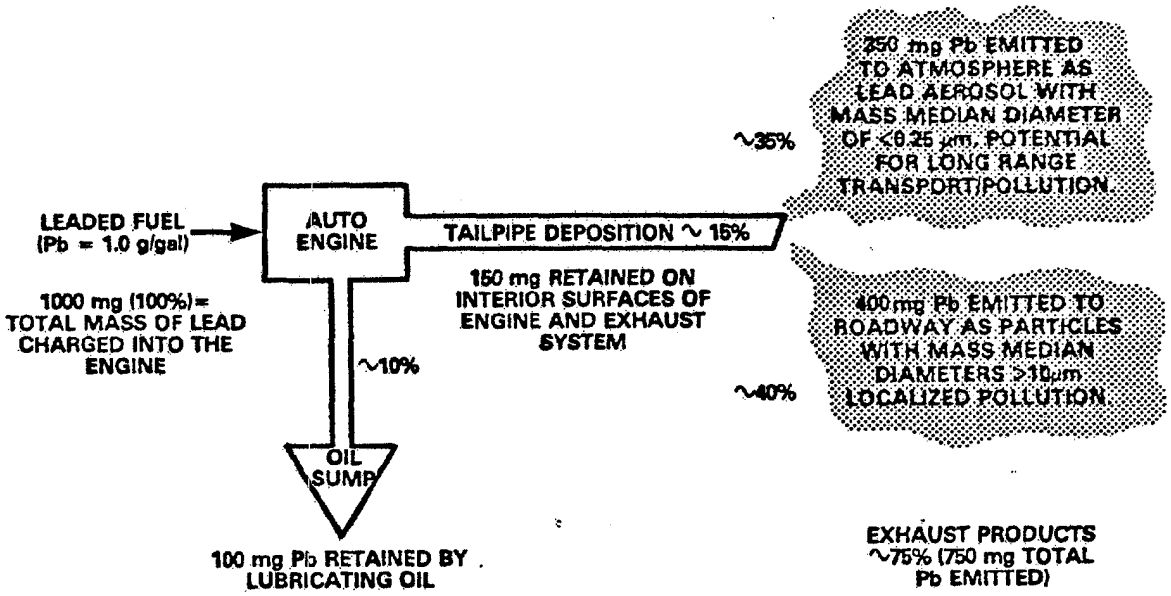

Figure 5-4. Estimated lead-only emissions distribution per gallon of combusted fuel.

lifetimes (Harrison and Laxen, 1981). The largest vehicle-emitted particles, which are greater than a hundred micrometers in diameter, may be formed by materials flaking off from the surfaces of the exhaust system. As indicated in Table 5-3, the estimated mass median equivalent diameter of leaded particles from light-duty vehicles is < 0.25 μm, suggesting that such particles have relatively long atmospheric lifetimes and the potential for long-distance transport.

The size distribution of lead exhaust particles is essentially bimodal (Pierson and Brachaczek, 1976) and depends on a number of factors, including the particular driving pattern in which the vehicle is used and its past driving history (Ganley and Springer, 1974; Habibi, 1973; 1970; Ter Haar et al., 1972; Hirschler et al., 1964; 1957). As an overall average, it has been estimated 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 small particles (< 0.25 μm MMED), and approximately 40 percent will be emitted as larger particles (> 10 μm MMED) (Ter Haar et al., 1972). 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. A flow chart depicting lead-only emissions per gallon of fuel charged into the engine is shown in Figure 5-4. It is estimated that 10 percent of the lead consumed during combustion is released into the environment via disposal of used lubricating oil (Piver, 1977). 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.

Although the majority (> 90 percent on a mass basis) of vehicular lead compounds are emitted as inorganic particles (e.g., PbBrCl), some organolead vapors (e.g., lead alkyls) are also emitted. The largest volume of organolead vapors arises from the manufacture, transport, and handling of leaded gasoline. Such vapors are photoreactive, and their presence in local atmospheres is transitory, i.e., the estimated atmospheric half-lives of lead alkyls, under typical summertime conditions, are less than half a day (Nielsen, 1982). Organolead vapors are most likely to occur in occupational settings (e.g., gasoline transport and handling operations, gas stations,

parking garages) and have been found to contribute less than 10 percent of the total lead present in the atmosphere (Gibson and Farmer, 1981; National Academy of Sciences, 1972).

The use of lead additives in gasoline, which increased in volume for many years, is now decreasing as automobiles designed to use unleaded fuel constitute the major portion of the automotive population (Table 5-1). The decline in the use of leaded fuel is the result of two regulations promulgated by the U.S. Environmental Protection Agency (F.R., 1973). The first required the availability of unleaded fuel for use in automobiles designed to meet federal emission standards with lead-sensitive emission control devices (e.g., catalytic converters); the second required a reduction or phase-down of the lead content in leaded gasoline. Compliance with the phase-down of lead in gasoline has recently been the subject of proposed rulemakings (F.R., 1982a, 1982b, 1982c, 1982d). The most recent proposed rule (F.R., 1982c) will replace the present 0.5 g/gal standard for the average lead content of all gasoline with a two-tiered standard for the lead content of leaded gasoline. Under this proposed rule, large refineries would be required to meet a standard of 1.10 g/gal for leaded gasoline while certain small refiners would be subject to a 2.50 g/gal standard.

The trend in lead content for U.S. gasolines is shown in Figure 5-5 and Table 5-5. Of the total gasoline pool, which includes both leaded and unleaded fuels, the average lead content has decreased 63 percent, from an average of 1.62 g/gal in 1975 to 0.60 g/gal in 1981 (Table 5-5, Figure 5-5). Accompanying the phase-down of lead in leaded fuel has been the increased consumption of unleaded fuel, from 11 percent of the total gasoline pool in 1975 to 50 percent in 1981 (Table 5-6 and Figure 5-6). Since 1975, when the catalytic converter was introduced by automobile manufacturers for automotive exhaust emissions control, virtually all new passenger cars have been certified on unleaded gasoline (with the exception of a few diesels and a very few leaded-gasoline vehicles). Because of the yearly turnover rate in the vehicle fleet, the demand for unleaded gasoline is forecast to increase to 58 percent in 1982 and to increase to ~75 percent of the total gasoline pool by 1985. As the demand for unleaded fuel increases, it may become uneconomical to distribute leaded gasoline for light-duty vehicles in low-volume localities.

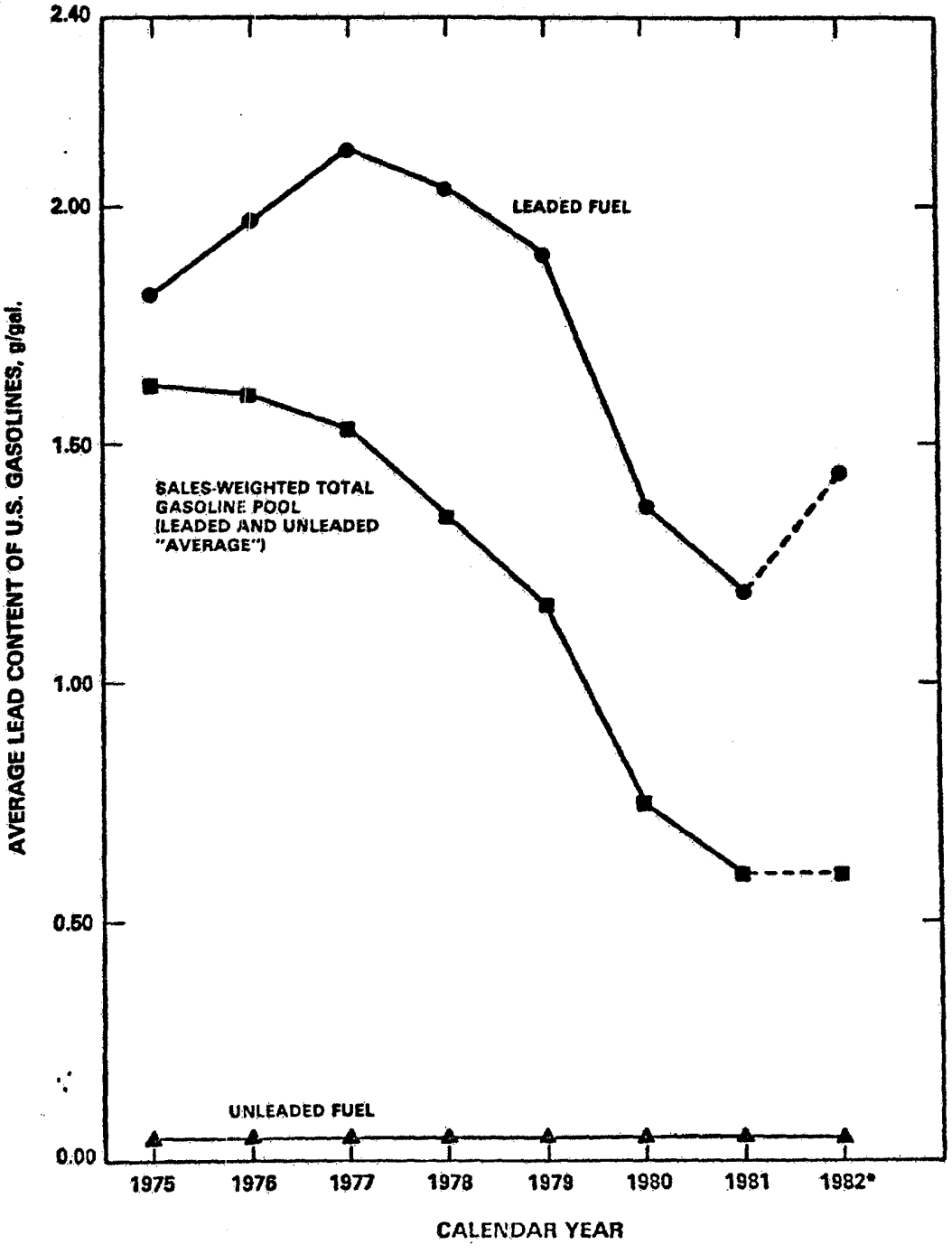

Figure 5-5. Trend in lead content of U.S. gasolines, 1975-1982. (DuPont, 1982).

*1982 DATA ARE FORECASTS.

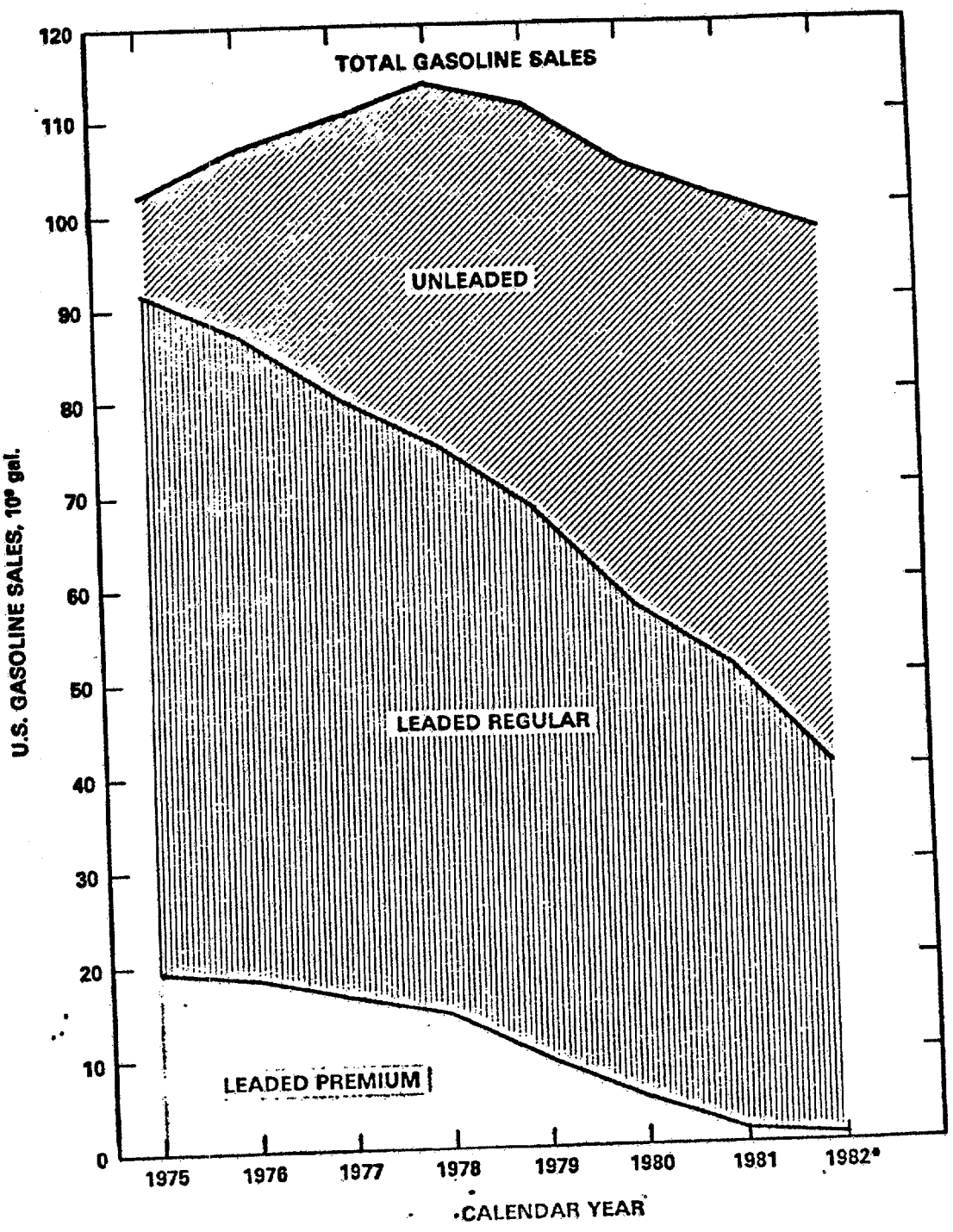

Figure 5-6. Trend in U.S. gasoline sales, 1975-1982. (DuPont, 1982).
*1982 DATA ARE FORECASTS.

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TABLE 5-6. U.S. GASOLINE SALES IN BILLIONS OF GALLONS/YEAR, 1975-1982
(DuPont, 1982)

	1975	1976	1977	1978	1979	1980	1981	1982[a]
Total sold	102.3	107.0	110.0	113.6	111.4	105.0	101.0	97.5
Leaded fuel	91.5	87.0	79.7	75.0	68.1	57.5	51.0	40.6
Regular	72.1	68.7	63.4	60.7	58.9	52.6	49.7	39.6
Premium	19.4	18.3	16.3	14.3	9.2	4.9	1.3	1.0
Unleaded fuel	10.8	20.0	30.3	38.6	43.3	47.5	50.0	56.9
(Unleaded percent of total sold)	(11%)	(19%)	(28%)	(34%)	(39%)	(45%)	(50%)	(58%)

[a]Forecasted.

The lead content of leaded gasoline (Table 5-6) is forecast to increase from 1.19 to 1.44 g/gal in 1982 (DuPont, 1982). The reason for this increase is that under the 1982 0.5 g/gal total pool standard, refiners can add ever-increasing amounts of lead to each gallon of leaded gasoline (up to the level at which it would no longer be economically justified) as the amount of unleaded gasoline produced by the refinery increases. Thus, as the amount of unleaded gasoline increases, the amount of lead in leaded gasoline can also increase under present regulations. The recent EPA proposed rulemakings (F.R., 1982a, 1982b, 1982c, 1982d) will eliminate this practice, thereby ensuring that the amount of lead used in gasoline will decline after the 1982 calendar year.

Data describing the lead consumed in gasoline and average ambient lead levels (composite of maximum quarterly values) versus calendar year are listed in Table 5-7 and plotted in Figure 5-7. The 1975 through 1979 composite quarterly lead averages are based on 105 lead-monitoring sites, primarily urban. The 1980 composite average is based on 58 sites with valid annual data. The EPA National Aerometric Data Base is still receiving the 1980 data. The linear correlation (Figure 5-8) between lead consumed in gasoline and the composite maximum average quarterly ambient average lead level is very good with $r^2 = 0.99$. The 1981 and 1982 composite averages shown in Table 5-7 and Figures 5-7 and 5-8 are derived using the linear equation of Figure 5-6. Between 1975 and 1980, the lead consumed in gasoline decreased 52 percent (from 165,577 metric tons to 78,679 metric tons) while the corresponding composite maximum quarterly average of ambient lead decreased 51 percent (from 1.23 $\mu g/m^3$ to 0.60 $\mu g/m^3$). This indicates that control of lead in gasoline over the past several years has effected a direct decrease in peak ambient lead concentrations, at least for this group of monitoring sites.

Furthermore, the equation in Figure 5-8 implies that the complete elimination of lead from gasoline might reduce the composite average of the maximum quarterly lead concentrations at these stations to 0.05 $\mu g/m^3$, a level typical of concentrations reported for nonurban stations in the U.S. (see Chapter 7). Even this level of 0.05 $\mu g/m^3$ is regarded as evidence of human activity since it is at least two orders of magnitude higher than estimates of geophysical background lead concentrations discussed at the beginning of this chapter.

TABLE 5-7. DOMESTIC CONSUMPTION OF LEAD FOR ADDITIVES IN GASOLINE IN METRIC TONS/YEAR, 1975-1982 (DuPont, 1982)

1975	1976	1977	1978	1979	1980	1981	1982[a]
165,577	171,046	168,149	153,222	129,108	78,679	60,546	58,447

[a]Forecasted.

COMPOSITE MAXIMUM QUARTERLY AVERAGE LEAD LEVELS IN $\mu g/m^3$, 1975-1982[b] (Hunt and Neligan, 1982)

1975	1976	1977	1978	1979	1980	1981[c]	1982[c]
1.23	1.22	1.20	1.13	0.93	0.60	0.47	0.45

[b]Composite averages depicted are a subset of the composite maximum quarterly averages for the 1970-1979 trend.

[c]Estimated (this work).

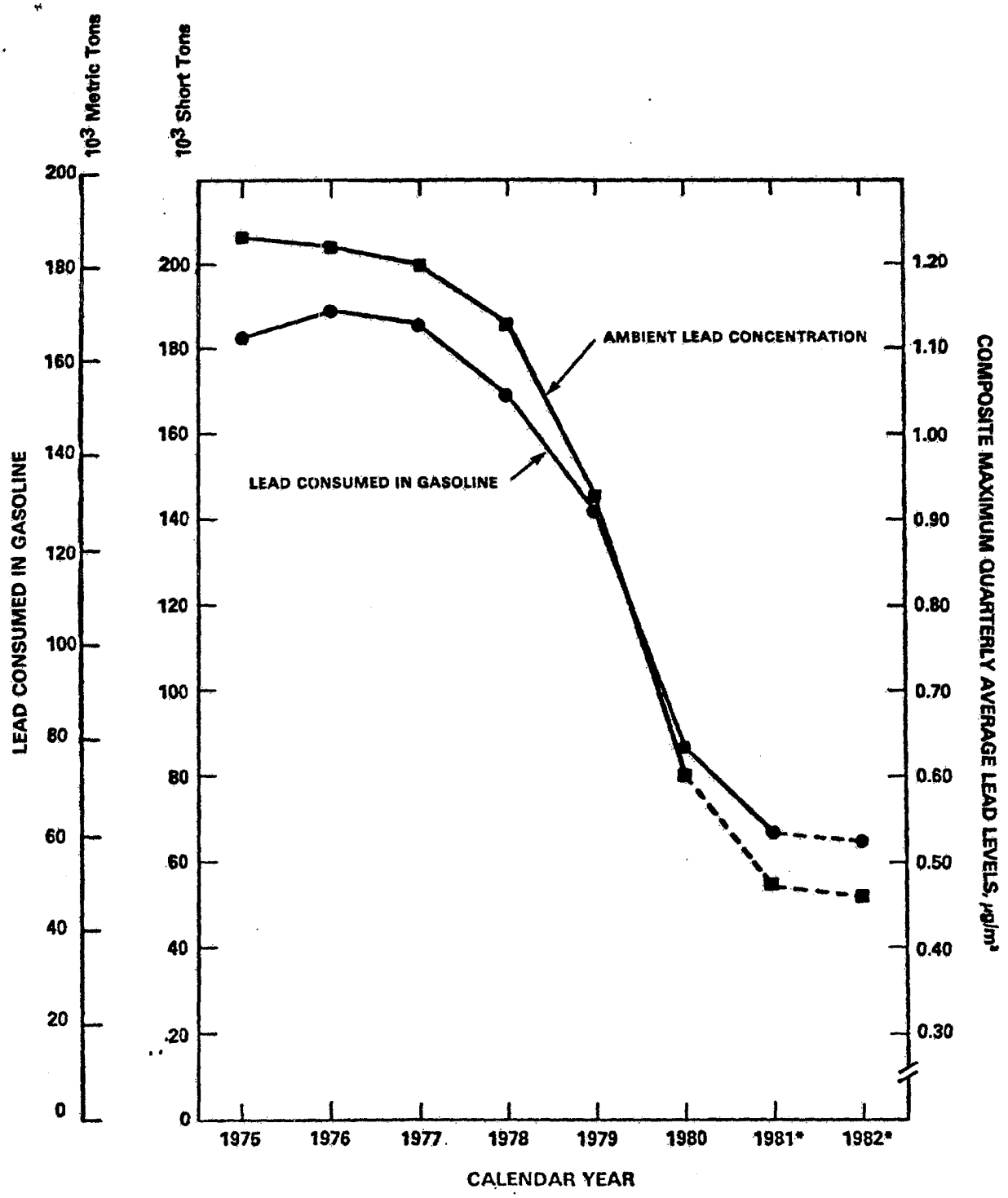

Figure 5-7. Lead consumed in gasoline (Du Pont, 1982) and ambient lead concentrations, 1975-1982. (Nunt and Neligan, 1982).
*DASHED LINES ARE ESTIMATES.

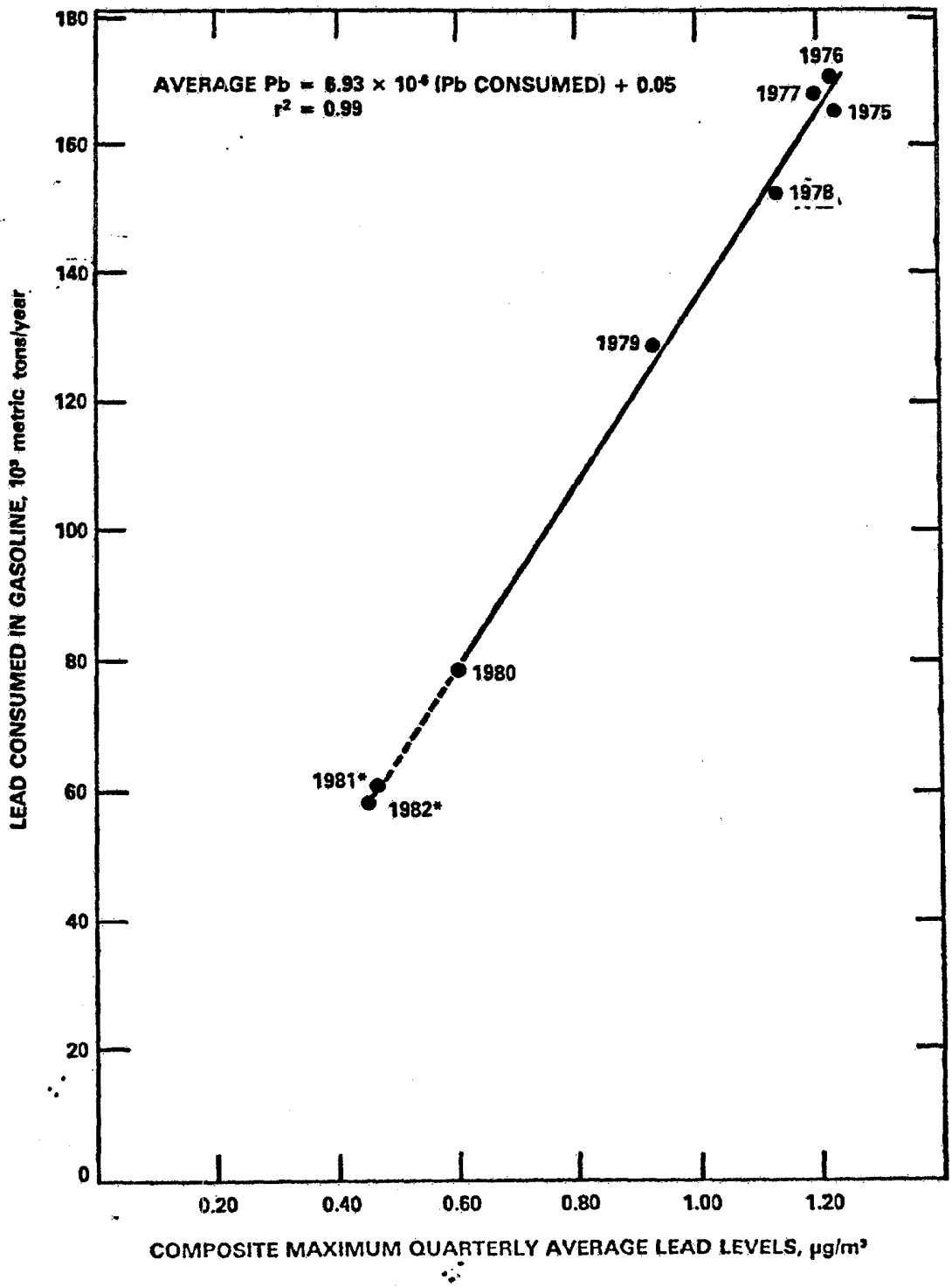

Figure 5-8. Relationship between lead consumed in gasoline and composite maximum quarterly average lead levels, 1975-1980.

*1981 AND 1982 DATA ARE ESTIMATES.

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5.3.3.2 Stationary Sources--As shown in Table 5-2 (based on 1975 emission estimates), 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 (U.S. Environmental Protection Agency, 1977). 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-1960s with the opening of the "Viburnum Trend" or "New Lead Belt" in southeastern Missouri. The presence of ten mines and three 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.

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 µg/g at the roadway, declining to a fairly constant 100 to 200 µg/g beyond about 400 ft from the roadway (Wixson et al., 1977).

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

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while the lead in the litter was chemically bound to soil organic matter. Indeed, Doelman and Haanstra (1979a) demonstrated the effects of soil lead content on delayed decomposition: sandy soils lacking organic complexing compounds showed a 30 percent inhibition of decomposition at 750 µg/g, including the complete loss of major bacterial species, whereas the effect was reduced in clay soils and non-existent in peat soils. Organic matter maintains the cation exchange capacity of soils. A reduction in decomposition rate was observed by Doelman and Haanstra (1979a) even at the lowest experimental concentration of lead, leading to the conclusion that some effect might have occurred at even lower concentrations.

When decomposition is delayed, nutrients may be limiting to plants. In tropical regions or areas with sandy soils, rapid turnover of nutrients is essential for the success of the forest community. Even in a mixed deciduous forest, a significant portion of the nutrients, especially nitrogen and sulfur, may be found in the litter reservoir (Likens et al. 1977). Annual litter inputs of calcium and nitrogen to the soil account for about 60 percent of root uptake. With delayed decomposition, plants must rely on precipitation and soil weathering for the bulk of their nutrients. Furthermore, the organic content of soil may decrease, reducing the cation exchange capacity of soil.

8.5.2 Circumvention of Calcium Biopurification

Biopurification is a process that regulates the relative concentrations of nutrient to non-nutrient elements in biological components of a food chain. In the absence of absolute knowledge of natural lead concentrations, biopurification can be a convenient method for estimating the degree of contamination. Following the suggestion by Comar (1965) that carnivorous animals show reduced Sr/Ca ratios compared to herbivorous animals which, in turn show less than plants, Elias et al. (1976,1982) developed a theory of biopurification, which hypothesizes that calcium reservoirs are progressively purified of Sr, Ba, and Pb in successive stages of a food chain. In other words, if the Sr/Ca and Ba/Ca ratios are known, the natural Pb/Ca ratio can be predicted and the observed Pb/Ca to natural Pb/Ca ratio is an expression of the degree of contamination. Elias et al. (1976, 1982) and Elias and Patterson (1980) observed continuous biopurification of calcium in grazing and detrital food chains by the progressive exclusion of Sr, Ba, and Pb (Figure 8-5). It is now believed that members of grazing and decomposer food chains are contaminated by factors

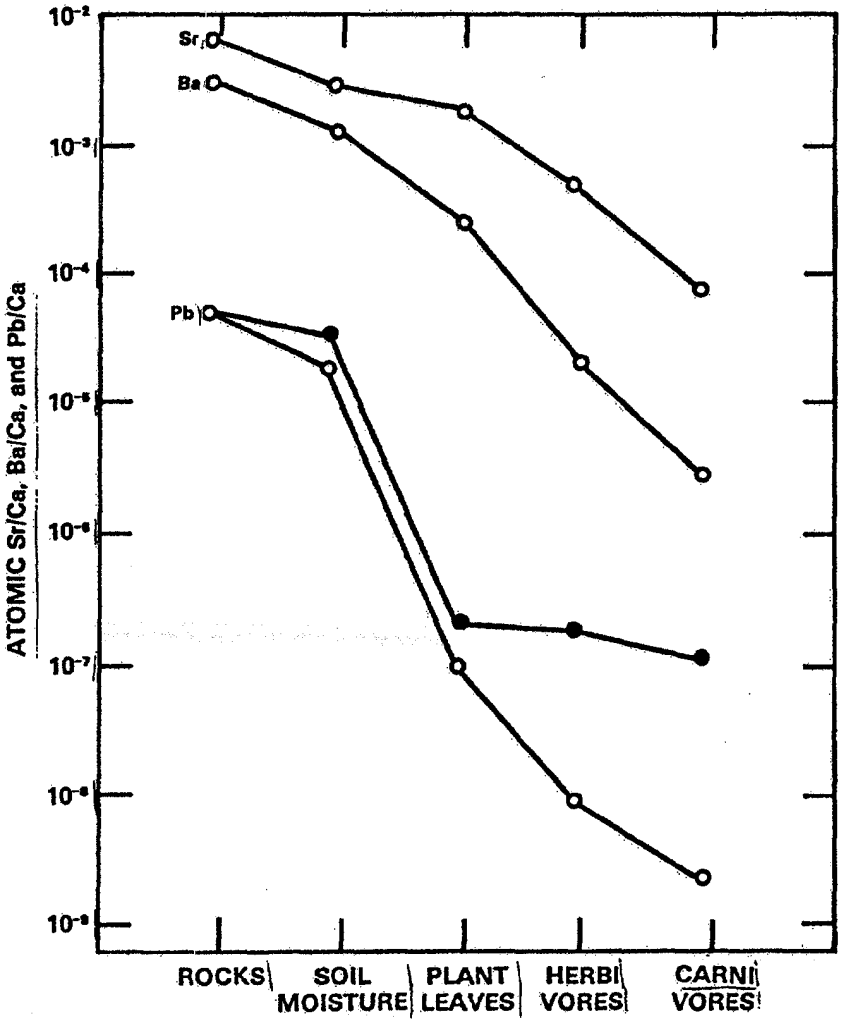

Figure 8-5. The atomic ratios Sr/Ca, Ba/Ca and Pb/Ca (O) normally decrease by several orders of magnitude from the crystal rock to ultimate carnivores in grazer and decomposer food chains. Anthropogenic lead in soil moisture and on the surfaces of vegetation and animal fur interrupt this process to cause elevated Pb/Ca ratios (●) at each stage of the sequence. The degree of contamination is the ratio of Total Pb/Ca *vs.* National Pb/Ca at any stage. Ba/Ca and Sr/Ca ratios are approximate guidelines to the expected natural Pb/Ca ratio.

Source: Adapted from Elias et al. (1982).

of 30 to 500, i.e., that 97 percent to 99.9 percent of the lead in organisms is of anthropogenic origin. Burnett and Patterson (1980) have shown a similar pattern for a marine food chain.

The mechanism of biopurification relies heavily on the selective transport of calcium across membranes, the selective retention of non-nutrients at physiologically inactive binding sites, and the reduced solubility of non-nutrient elements in the nutrient medium of plants and animals. For example, lead is bound more vigorously to soil organic complexes and is less soluble in soil moisture (Chapter 6). Lead is also adsorbed to cell walls in the root apoplast, is excluded by the cortical cell membrane, and is isolated as a precipitate in subcellular vesicles of cortical cells (Koeppe, 1981). Further selectivity at the endodermis results in a nutrient solution of calcium in the vascular tissue which is greatly purified of lead. Similar mechanisms occur in the stems and leaves of plants, in the digestive and circulatory systems of herbivores and carnivores, and in the nutrient processing mechanisms of insects.

Atmospheric lead circumvents the natural biopurification of calcium. Deposition on plant surfaces, which accounts for 90 percent of the total plant lead, increases the ratio of Pb/Ca in the diet of herbivores. Deposition on animal fur increases the Pb/Ca ratio in the diet of carnivores. Atmospheric lead consumed by inhalation or grooming, possibly 15 percent of the total intake of lead, represents sources of lead which were non-existent in prehistoric times and therefore were not present in the food chain.

8.5.3 Population Shifts Toward Lead-Tolerant Populations

It has been observed that plant communities near smelter sites are composed mostly of lead tolerant plant populations (Antonovics et al., 1971). In some cases, these populations appear to have adapted to high lead soils, since populations of the same species from low lead soils often do not thrive on high lead soils (Jowett, 1964). Similar effects have been observed for soils enriched to 28,000 µg/g dry weight with ore lead (Høiland and Oftedal, 1980) and near roadsides at soil concentrations of 1300 µg/g dry weight (Atkins et al., 1982). In these situations, it is clear that soil lead concentration has become the dominant factor in determining the success of plant populations and the stability of the ecological community. Soil moisture, soil pH, light intensity, photoperiod, and temperature are all secondary factors (Antonovics et al., 1971). Strategies for efficient use of light and water, and for

TABLE OF CONTENTS
Chapter 8
Effects of Lead on Ecosystems

LIST OF TABLES

LIST OF FIGURES

8. EFFECTS OF LEAD ON ECOSYSTEMS

8.1 INTRODUCTION

8.1.1 Scope of Chapter 8

This chapter describes the potential effects of atmospheric lead inputs on several types of ecosystems. An effect is any condition attributable to lead that causes an abnormal physiological response in individual organisms or that perturbs the normal processes of an ecosystem. A distinction is made among natural, cultivated, and urban ecosystems, and extended discussions are included on the mobility and bioavailability of lead in ecosystems.

There are many reports on the effects of lead on individual populations of plants and animals and a few studies on the effects of lead in simulated ecosystems or microcosms. However, the most realistic studies are those that examine the effects of lead on entire ecosystems, as they incorporate all of the ecological interactions among the various populations and all of the chemical and biochemical processes relating to lead (National Academy of Sciences, 1981). Unfortunately, these studies also include the inherent variability of natural systems and the confounding frustrations of large scale projects. Consequently, there are only a handful of ecosystem studies on which to base this report.

The principle sources of lead entering an ecosystem are: the atmosphere (from automotive emissions), paint chips, spent ammunition, the application of fertilizers and pesticides, and the careless disposal of lead-acid batteries or other industrial products. Atmospheric lead is deposited on the surfaces of vegetation as well as on ground and water surfaces. In terrestrial ecosystems, this lead is transferred to the upper layers of the soil surface, where it may be retained for a period of several years. The movement of lead within ecosystems is influenced by the chemical and physical properties of lead and by the biogeochemical properties of the ecosystem. Lead is non-degradable, but in the appropriate chemical environment, may undergo tranformations which affect its solubility (e.g., formation of lead sulfate in soils), its bioavailability (e.g., chelation with humic substances), or its toxicity (e.g., chemical methylation).

The previous Air Quality Criteria for Lead (U.S. Environmental Protection Agency, 1977) recognized the problems of atmospheric lead exposure incurred by

all organisms including man. Emphasis in the chapter on ecosystem effects was given to reports of toxic effects on specific groups of organisms, e.g. domestic animals, wildlife, aquatic organisms, vascular and nonvascular plants. Forage containing lead at 80 µg/g dry weight was reported to be lethal to horses, whereas 300 µg/g dry weight caused lethal clinical symptoms in cattle. This report will attempt to place the data in the context of sublethal effects of lead exposure, to extend the conclusions to a greater variety of domestic animals, and to describe the types and ranges of exposures in ecosystems likely to present a problem for domestic animals.

Research on lead in wildlife has traditionally fallen into the following somewhat artificial categories: waterfowl; birds and small mammals; fish; and invertebrates. In all these categories, no correlation could be made in the 1977 report between toxic effects and environmental concentrations. Some recent toxicity studies have been completed on fish and invertebrates and the data are reported below, but there is still little information on the levels of lead that can cause toxic effects in small mammals or birds.

Information on the relationship between soil lead and plants can be expanded somewhat beyond the 1977 report, primarily due to a better understanding of the role of humic substances in binding lead. Although the situation is extremely complex, it is reasonable to state that most plants cannot survive in soil containing 10,000 µg/g dry weight if the pH is below 4.5 and the organic content is below 5 percent. The specifics of this statement are discussed more extensively in Section 8.3.1.2.

Before 1977, natural levels of lead were not well known. Reports of sublethal effects of lead were sparse and there were few studies of total ecosystem effects. It is fortunate that several ecosystem studies have been completed since 1977 and many of the deficiencies in knowledge, awareness of problems, and ability to predict effects have been overcome.

In many cases it is still impossible to translate observed effects under laboratory conditions directly to predicted effects in ecosystems. Some of the known effects, which are documented in detail in the appropriate sections, are summarized here:

Plants. The basic effect of lead on plants is to stunt growth. This may be through a reduction of photosynthetic rate, inhibition of respiration, inhibition of cell elongation, or premature senescence.

Some genetic effects have been reported. All of these effects have been observed in isolated cells or in hydroponically-grown plants in solutions comparable to 1 to 2 µg/g soil moisture. These concentrations are well above those normally found in any ecosystem except near smelters or roadsides. Terrestrial plants take up lead from the soil moisture and most of this lead is retained by the roots. There is no evidence for foliar uptake of lead and little evidence that lead can be translocated in large amounts to the upper portions of the plant. Soil applications of calcium and phosphorus may reduce the uptake of lead by roots.

Animals. Lead affects the central nervous system of animals and their ability to synthesize red blood cells. Blood concentrations above 0.4 ppm (40 µg/dl) can cause observable clinical symptoms in domestic animals. Calcium and phosphorus can reduce the intestinal absorption of lead. The physiological effects of lead exposures in laboratory animals are discussed in extensive detail in Chapters 10 and 12 of this document.

Microorganisms. There is evidence that lead at concentrations normally found near roadsides and smelters (10,000 to 40,000 µg/g dw) can eliminate populations of bacteria and fungi on leaf surfaces and in soil. Many of those micoorganisms play key roles in the decomposition food chain. It is likely that the affected microbial populations are replaced by others of the same or different species, perhaps less efficient at decomposing organic matter. There is also evidence that microorganisms can mobilize lead by making it more soluble and more readily taken up by plants. This process occurs when bacteria exude organic acids that lower the pH in the immediate vicinity of the plant root.

Ecosystems. There are three known conditions under which lead may perturb ecosystem processes. At soil concentrations of 1000 µg/g or higher, delayed decomposition may result from the elimination of a single population of decomposer microorganisms. Secondly, at concentrations of 500 to 1000 µg/g, populations of plants, microorganisms, and invertebrates may shift toward lead tolerant populations of the same or different species. Finally, the normal biochemical process

which purifies and repurifies calcium in grazing and decomposer food chains may be circumvented by the addition of lead to vegetation and animal surfaces. This third effect can be measured at all ambient atmospheric concentrations of lead.

Some additional effects may occur due to the uneven distribution of lead in ecosystems. It is known that lead accumulates in soil, especially soil with high organic content. Although no firm documentation exists, it is reasonable to assume from the known chemistry of lead in soil that: 1) other metals may be displaced from the binding sites on the organic matter; 2) the chemical breakdown of inorganic soil fragments may be retarded by the interference of lead on the action of fulvic acid on iron bearing crystals; and 3) lead in soil may be in equilibrium with moisture films surrounding soil particles and thus available for uptake by plants.

To aid the reader in understanding the effects of lead on ecosystems, sections have been included that discuss such important matters as how ecosystems are organized, what processes regulate metal cycles, what criteria are valid in interpreting ecosystem effects, and how soil systems function to regulate the controlled release of nutrients to plants. The informed reader may wish to turn directly to section 8.3, where the discussion of the effects of lead on organisms begins.

8.1.2 Ecosystem Functions

8.1.2.1 Types of Ecosystems--Based on ambient concentrations of atmospheric lead and the distribution of lead in the soil profile, it is useful to distinguish among three types of ecosystems: natural, cultivated, and urban. Natural ecosystems include aquatic and terrestrial ecosystems that are otherwise unperturbed by man, and those managed ecosystems, such as commercial forests, grazing areas, and abandoned fields, where the soil profile has remained undisturbed for several decades. Cultivated ecosystems include those where the soil profile is frequently disturbed and those where chemical fertilizers, weed killers, and pest-control agents may be added. In urban ecosystems, a significant part of the exposed surface includes rooftops, roadways and parking lots from which runoff, if not channeled into municipal waste processing plants, is spread over relatively small areas of soil surface. The ambient air concentration of lead in urban ecosystems is 5 to 10 times higher

than in natural or cultivated ecosystems (See Chapter 7). Urban ecosystems may also be exposed to lead from other than atmospheric sources, such as paint, discarded batteries, and used motor oil. The effects of atmospheric lead depend on the type of ecosystems examined.

8.1.2.2 Energy Flow and Biogeochemical Cycles--Two principles govern ecosystem functions: 1) energy flows through an ecosystem; and 2) nutrients cycle within an ecosystem. Energy usually enters the ecosystem in the form of sunlight and leaves as heat of respiration. Stored chemical energy may be transported into or out of an ecosystem (e.g., leaf detritus in a stream) or be retained by the ecosystem for long periods of time (e.g., tree trunks). Energy flow through an ecosystem may give structure to the ecosystem by establishing food webs which efficiently regulate the transfer of energy. Segments of these food webs are called food chains. Energy that flows along a grazing food chain is diverted at each step to the detrital food chain.

Unlike energy, nutrient and non-nutrient elements are recycled by the ecosystem and transferred from reservoir to reservoir in a pattern usually referred to as a biogeochemical cycle (Brewer, 1979, p. 139). The reservoirs correspond approximately to the food webs of energy flow. Although elements may enter (e.g., weathering of soil) or leave the ecosystem (e.g., stream runoff), the greater fraction of the available mass of the element is usually cycled within the ecosystem.

Two important characteristics of a reservoir are the amount of the element that may be stored in the reservoir and the rate at which the element enters or leaves the reservoir. Some reservoirs may contain a disproportionately large amount of a given element. For example, most of the carbon in a forest is bound in the trunks and roots of trees, whereas most of the calcium may be found in the soil (Smith, 1980, p. 316). Some large storage reservoirs, such as soil, are not actively involved in the rapid exchange of the nutrient element, but serve as a reserve source of the element through the slow exchange with a more active reservoir, such as soil moisture. When inputs exceed outputs, the size of the reservoir increases. Increases of a single element may reflect instability of the ecosystem. If several elements increase simultaneously, this expansion may reflect stable growth of the community.

Reservoirs are connected by pathways which represent real ecosystem processes. Figure 8-1 depicts the biogeochemical reservoirs and pathways of a

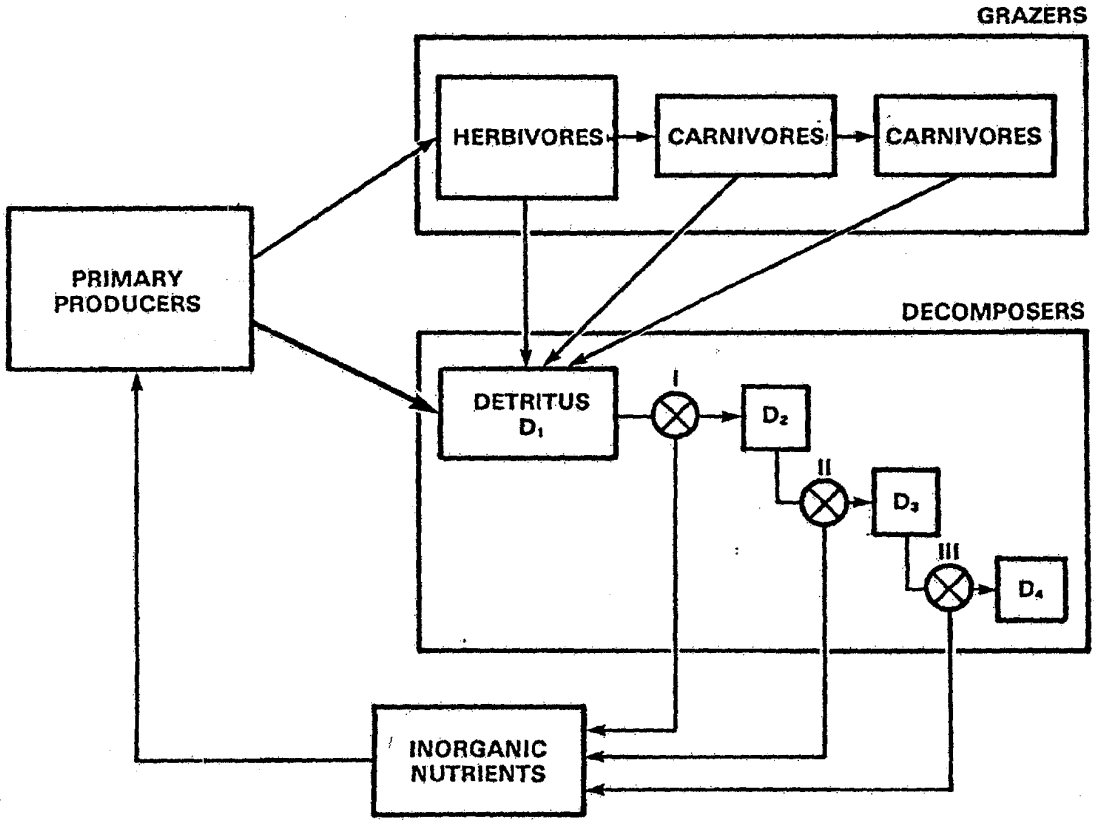

Figure 8-1. This figure depicts cycling processes within the major components of a terrestrial ecosystem, i.e. primary producers, grazers and decomposers. Nutrient and non-nutrient elements are stored in reservoirs within these components. Processes that take place within reservoirs regulate the flow of elements between reservoirs along established pathways. The rate of flow is in part a function of the concentration in the preceding reservoir. Lead accumulates in decomposer reservoirs which have a high binding capacity for this metal. It is likely that the rate of flow away from these reservoirs has increased in past decades and will continue to increase for some time until the decomposer reservoirs are in equilibrium with the entire ecosystem. Inputs to and outputs from the ecosystem as a whole are not shown.

Source: Adapted from Swift et al. (1979)

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typical terrestrial ecosystem. Most elements, especially those with no gaseous phase, do not undergo changes in oxidation state and are equally available for exchange between any two reservoirs, provided a pathway exists between the two reservoirs. The chemical environment of the reservoir may, however, regulate the availability of an element by controlling solubility or binding strengths. This condition is especially true for soils.

Ecosystems have boundaries. These boundaries may be as distinct as the border of a pond or as arbitrary as an imaginary circle drawn on a map. Many trace metal studies are conducted in watersheds where some of the boundaries are determined by topography. For atmospheric inputs to terrestrial ecosystems, the boundary is usually defined as the surface of vegetation, exposed rock or soil. The water surface suffices for aquatic ecosystems.

Non-nutrient elements differ little from nutrient elements in their biogeochemical cycles. Quite often, the cycling patterns are similar to those of a major nutrient. In the case of lead, the reservoirs and pathways are very similar to those of calcium.

The important questions are: Does atmospheric lead interfere with the normal mechanisms of nutrient cycles? How does atmospheric lead influence the normal lead cycle in an ecosystem? Can atmospheric lead interfere with the normal flow of energy through an ecosystem?

8.1.2.3 Biogeochemistry of Lead--Naturally occurring lead from the earth's crust is commonly found in soils and the atmosphere. Lead may enter an ecosystem by weathering of parent rock or by deposition of atmospheric particles. This lead becomes a part of the nutrient medium of plants and the diet of animals. More than 99 percent of the current atmospheric lead deposition is now due to human activities (National Academy of Sciences, 1980). All ecosystems receive lead from the atmosphere. In addition, lead shot from ammunition may be found in many waterways and popular hunting regions, leaded paint chips often occur in older urban regions and lead in fertilizer may contaminate the soil in agricultured regions.

In prehistoric times, the contribution of lead from weathering of soil was probably about 4g Pb/ha·yr and from atmospheric deposition about 0.02 g Pb/ha·yr, based on estimates of natural and anthropogenic emissions in Chapter 5 and deposition rates discussed in Chapter 6. Weathering rates have remained the same, but atmospheric inputs have increased to 180 g/ha·yr in natural and

some cultivated ecosystems, and 3000 g/ha·yr in urban ecosystems and along roadways (see Chapter 6). In every terrestrial ecosystem of the Northern Hemisphere, atmospheric lead deposition now exceeds weathering by a factor of at least 10, sometimes by as much as 1000.

Many of the effects of lead on plants, microorganisms, and ecosystems arise from the fact that lead from atmospheric and weathering inputs is retained by soil. Geochemical studies show that less than 3 percent of the inputs to a watershed leave by stream runoff (Siccama and Smith, 1978; Shirahata et al., 1980). In prehistoric times, stream output nearly equalled weathering inputs and the lead content of soil probably remained stable, accumulating at an annual rate of less than 0.1 percent of the original natural lead (reviewed by Nriagu, 1978). Due to human activity, lead in natural soils now accumulates on the surface at an annual rate of 5 to 10 percent of the natural lead. One effect of cultivation is that atmospheric lead is mixed to a greater depth than the 0 to 3 cm of natural soils.

Most of the effects on grazing vertebrates stem from the deposition of atmospheric particles on vegetation surfaces. Atmospheric deposition may occur by either of two mechanisms. Wet deposition (precipitation scavenging through rainout or washout) generally transfers lead directly to the soil. Dry deposition transfers particles to all exposed surfaces. Large particles (>4 μm) are transferred by gravitational mechanisms, small particles (<0.5 μm) are deposited primarily by wind-related mechanisms.

About half of the foliar dry deposition remains on leaf surfaces following normal rainfall (Elias et al., 1976; Peterson, 1978), but heavy rainfall may transfer the lead to other portions of the plant (Elias and Croxdale, 1980). Koeppe (1981) has reviewed the literature and concluded that less than 1 percent of the surface lead can pass directly into the internal leaf tissues of higher plants. The cuticular layer of the leaves is an effective barrier to aerosol particles and even to metals in solution on the leaf surface (Arvik and Zimdahl, 1974), and passage through the stomata cannot account for a significant fraction of the lead inside leaves (Carlson et al. 1976, 1977).

When particles attach to vegetation surfaces, transfer to soil is delayed from a few months to several years. Due to this delay, large amounts of lead are diverted to grazing food chains, bypassing the soil moisture and plant root reservoirs.

8.1.3 Criteria for Evaluating Ecosystem Effects

As it is the purpose of this chapter to describe the levels of atmospheric lead that may produce adverse effects in plants, animals, and ecosystems, it is necessary to establish the criteria for evaluating these effects. The first step is to determine the connection between air concentration and ecosystem exposure. If the air concentration is known, ecosystem inputs from the atmosphere can be predicted over time and under normal conditions. These inputs and those from the weathering of soil determine the concentration of lead in the nutrient media of plants, animals, and microorganisms. It follows that the concentration of lead in the nutrient medium determines the concentration of lead in the organism and this in turn determines the effects of lead on the organism.

The fundamental nutrient medium of a terrestrial ecosystem is the soil moisture film which surrounds organic and inorganic soil particles. This film of water is in equilibrium with other soil components and provides dissolved inorganic nutrients to plants. It is chemically different than ground water or rain water and there is little reliable information on the relationship between lead in soil and lead in soil moisture. Thus, it appears impossible to quantify all the steps by which atmospheric lead is transferred to plants. Until more information is available on lead in soil moisture, another approach may be more productive. This involves determining the degree of contamination of organisms by comparing the present known concentrations with calculated prehistoric concentrations.

Prehistoric concentrations of lead have been calculated for only a few types of organisms. However, the results are so low that any normal variation, even of an order of magnitude, would not seriously alter the degree of contamination. The link between lead in the prehistoric atmosphere and in prehistoric organisms may allow us to predict concentrations of lead in organisms based on present or future concentrations of atmospheric lead.

. It is now necessary to establish the relationship between degree of contamination and physiological effect. It seems appropriate to assume that natural levels of lead which were safe for organisms in prehistoric times would also be safe today. It is also reasonable that some additional atmospheric lead can be tolerated by all populations of organisms with no ill effects, that some populations are more tolerant than others, and that some individuals within populations are more tolerant of lead effects than others.

For nutrient elements, the concept of tolerance is not new. The Law of Tolerance (illustrated in Figure 8-2) states that any nutrient may be present at concentrations either too low or too high for a given population and that the ecological success of a population is greatest at some optimum concentration of the nutrient (Smith, 1980, p. 35). In a similar manner, the principle applies to non-nutrient elements. Although there is no minimum concentration below which the population cannot survive, there is a concentration above which the success of the population will decline (point of initial response) and a concentration at which the entire population will die (point of absolute toxicity). In this respect, both nutrients and non-nutrients behave in a similar manner at concentrations above some optimum.

Certain variables make the points of initial response and absolute toxicity somewhat imprecise. The point of initial response depends on the type of response investigated. This response may be at the molecular, tissue, or organismic level, with the molecular response occurring at the lowest concentration. Similarly, at the point of absolute toxicity, death may occur instantly at high concentrations or over a prolonged period of time at somewhat lower concentrations. Nevertheless, the gradient between these two points remains an appropriate basis on which to evaluate known environmental effects, and any information which correctly positions this part of the tolerance curve will be of great value.

The normal parameters of a tolerance curve, i.e., concentration and ecological success, can be replaced by degree of contamination and percent physiological dysfunction, respectively (Figure 8-3). Use of this method of expressing degree of contamination should not imply that natural levels are the only safe levels. It is likely that some degree of contamination can be tolerated with no physiological effect.

Data reported by the National Academy of Sciences (1980) are used to determine the typical natural lead concentrations shown in various compartments of ecosystems in Table 8-1. These data are from a variety of sources and are simplified to the most probable value within the range reported by NAS. The actual prehistoric air concentration was probably near the low end of

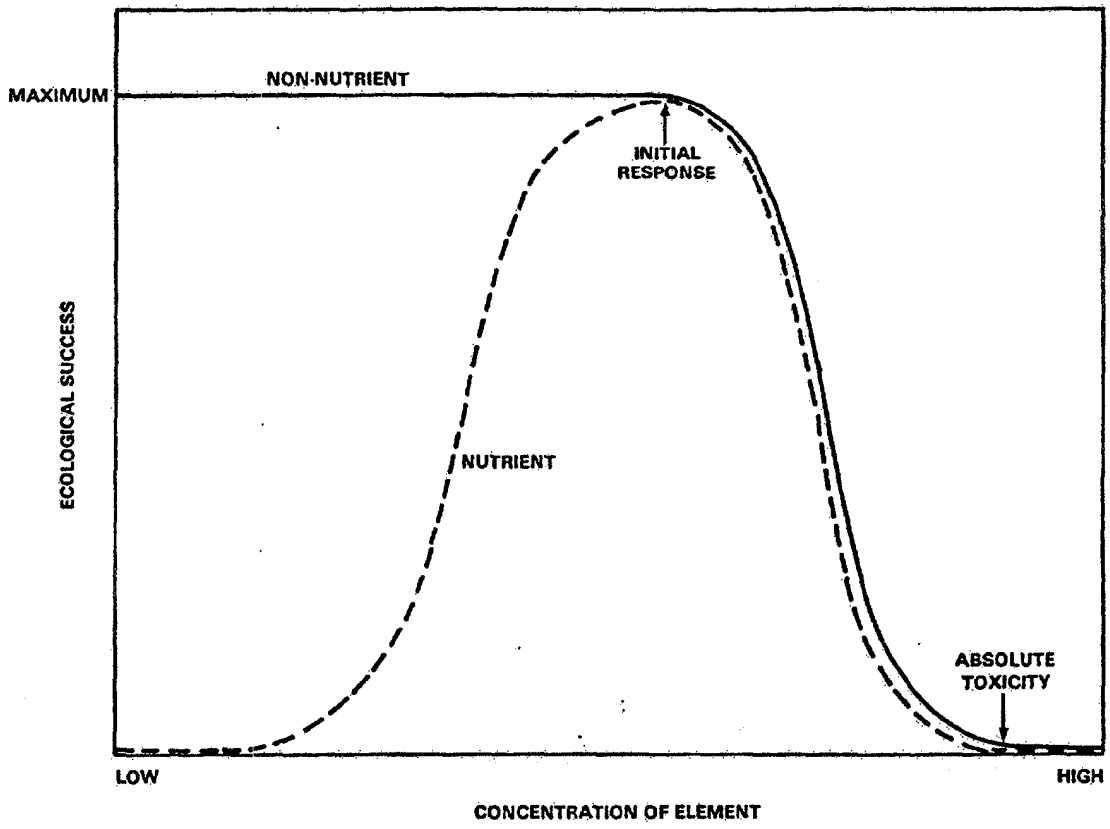

Figure 8-2. The ecological success of a population depends in part on the availability of all nutrients at some optimum concentration. The dashed line of this diagram depicts the rise and decline of ecological success (the ability of a population to grow, survive and reproduce) over a wide concentration range of a single element. The curve need not be symmetrically bell-shaped, but may be skewed to the right or left. Although the range in concentration that permits maximum success may be much wider than shown here, the important point is that at some high concentration, the nutrient element becomes toxic. The tolerance of populations for high concentrations of non-nutrients (solid line) is similar to that of nutrients, although there is not yet any scientific basis for describing the exact shape of this portion of the curve.

Source: Adapted from Smith (1980).

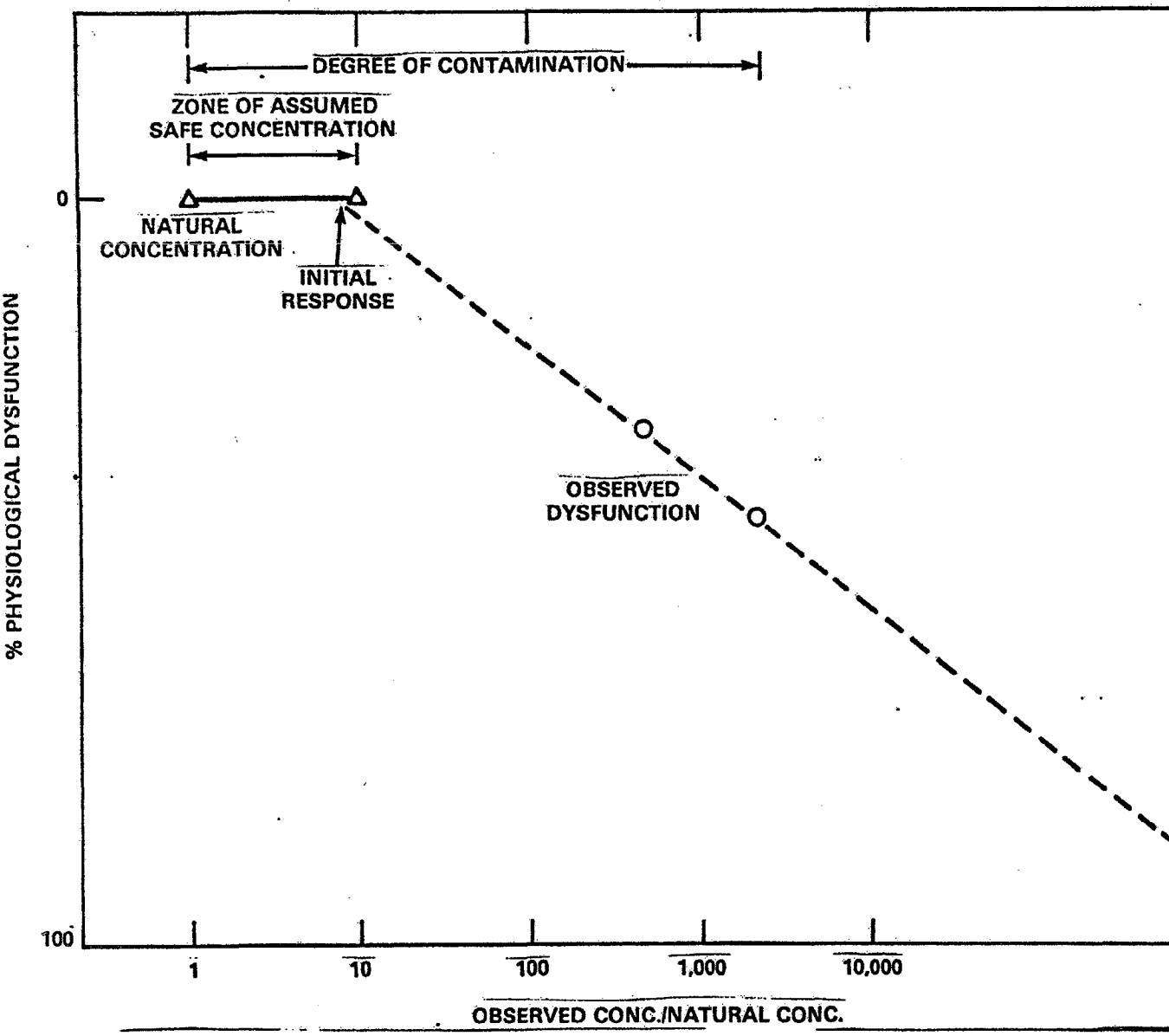

Figure 8-3. This figure attempts to reconstruct the right portion of a tolerance curve (Figure 8-2) for a po
using a limited amount of information. If the natural concentration is known for a population and if it is
assumed that 10x natural concentration is also safe, then the zone of assumed safe concentration defines t

TABLE 8-1. ESTIMATED NATURAL LEVELS OF LEAD IN KEY INDICATORS OF ECOSYSTEM CONTAMINATION

Component	Range	Best estimate
Air	0.01-1.0 ng/m^3	0.07
Soil		
Inorganic	5-25 µg/g	12.0
Organic	1 µg/g	1.0
Soil moisture	0.0002 µg/g	0.0002
Plant leaves	0.01-0.1 µg/g dw	0.05
Herbivore bones	0.04-0.12 µg/g dw	0.12
Carnivore bones	0.01-0.03 µg/g dw	0.03
Human bones	0.04 µg/g dw	0.04

Source: Ranges are from the National Academy of Sciences, 1980, best estimates are discussed in the text. Units for best estimates are the same as for ranges.

the range (0.02-1.0 ng/m^3), as present atmospheric concentrations of 0.3 ng/m^3 in the Southern Hemisphere and 0.07 ng/m^3 at the South Pole (Chapter 5), would seem to preclude natural lead values higher than this.

It may be reasoned that prehistoric soils contained only small amounts of lead in the organic fraction because plants contained very little lead. Therefore, the rate of entry of lead into the available pool was predominantly determined by the rate of weathering of inorganic minerals in fragments of parent rock material. Geochemical estimates of denudation and adsorption rates (Chapter 6) suggest a median value of 12 µg/g as the average natural lead content of total soil, with the concentration in the organic fraction at approximately 1 µg/g.

Studies have shown the lead content of leafy vegetation to be 90 percent anthropogenic, even in remote areas (Crump and Barlow, 1980; Elias et al., 1976, 1978). The natural lead content of nuts and fruits may be somewhat higher than leafy vegetation, based on internal lead concentrations of modern samples. The natural lead concentrations of herbivore and carnivore bones were reported by Elias et al. (Elias and Patterson, 1980, Elias et al., 1982). These estimates are based on predicted Pb/Ca ratios calculated from the observed biopurification of calcium reservoirs with respect to Sr, Ba, and Pb, on the systematic evaluation of anthropogenic lead inputs to the food chain (Section 8.5.3), and on measurements of prehistoric mammalian bones.

8.2 LEAD IN SOILS AND SEDIMENTS

8.2.1 Distribution of Lead in Soils

Because lead in soil is the source of most effects on plants, microorganisms, and ecosystems, it is important to understand the processes that control the accumulation of lead in soil. The major components of soil are: 1) fragments of inorganic parent rock material; 2) secondary inorganic minerals; 3) organic constituents, primarily humic substances, which are residues of decomposition or products of decomposer organisms; 4) Fe-Mn oxide films, which coat the surfaces of all soil particles and appear to have a high binding capacity for metals; 5) soil microorganisms, most commonly bacteria and fungi,

although protozoa and soil algae may also be found; and 6) soil moisture, the thin film of water surrounding soil particles which is the nutrient medium of plants. Some watershed studies consider that fragments of inorganic parent rock material lie outside the forest ecosystem, because transfer from this compartment is so slow that much of the material remains inert for centuries.

The concentration of lead ranges from 5 to 30 µg/g in the top 5 cm of most soils not adjacent to sources of industrial lead, although 5 percent of the soils contain as much as 800 µg/g (Chapter 5). Aside from surface deposition of atmospheric particles, plants in North America average about 0.5 to 1 µg/g dw (Peterson, 1978) and animals roughly 2 µg/g (Forbes and Sanderson, 1978). Thus, soils contain the greater part of total ecosystem lead. In soils, lead in parent rock fragments is tightly bound within the crystaline structures of the inorganic soil minerals. It is released to the ecosystem only by surface contact with soil moisture films.

Hutchinson (1980) has reviewed the effects of acid precipitation on the ability of soils to retain cations. Excess calcium and other metals are leached from the A horizon of soils by rain with a pH more acidic than 4.5. Most soils in the eastern United States are normally acidic (pH 3.5 to 5.2) and the leaching process is a part of the complex equilibrium maintained in the soil system. By increasing the leaching rate, acid rain can reduce the availability of nutrient metals to organisms dependent on the top layer of soil. Tyler (1978) reports the effect of acid rain on the leaching rate (reported as residence time) for lead and other metals. Simulated rain of pH 4.2 to 2.8 showed the leaching rate for lead increases with decreasing pH, but not nearly as much as other metals, especially Cu, Mn, and Zn. It appears from this limited information that acidification of soil may increase the rate of removal of lead from the soil, but not before several major nutrients are removed first. The effect of acid rain on the retention of lead by soil moisture is not known.

8.2.2 Origin and Availability of Lead in Aquatic Sediments

Atmospheric lead may enter aquatic ecosystems by wet or dry deposition (Dolske and Sievering, 1979) or by the erosional transport of soil particles (Baier and Healy, 1977). In waters not polluted by industrial, agricultural, or municipal effluents, the lead concentration is usually less than 1 µg/l. Of this amount, approximately 0.02 µg/l is natural lead and the rest is anthropogenic

lead, probably of atmospheric origin (Patterson, 1980). Surface waters mixed with urban effluents may frequently reach lead concentrations of 50 µg/l, and occasionally higher (Bradford, 1977).

In aqueous solution, virtually all lead is divalent, as tetravalent lead can exist only under extremely oxidizing conditions (reviewed by Rickard and Nriagu, 1978; Chapter 3). At pH higher than 5, divalent lead can form a number of hydroxyl complexes, most commonly $PbOH^+$, $Pb(OH)_2$, and $Pb(OH)_3^-$. At pH lower than 5, lead exists in solution as hydrated Pb. In still water, lead is removed from the water column by the settling of lead-containing particulate matter, by the formation of insoluble complexes, or by the adsorption of lead onto suspended organic particles. The rate of sedimentation is determined by temperature, pH, oxidation-reduction potential, ionic competition, the chemical form of lead in water, and certain biological activities (Jenne and Luoma, 1977). McNurney et al. (1977) found 14 µg Pb/g in stream sediments draining cultivated areas and 400 µg/g in sediments associated with urban ecosystems. Small sediment grain size and high organic content contributed to increased retention in sediments.

8.3 EFFECTS OF LEAD ON PLANTS

8.3.1 Effects on vascular plants

Some physiological and biochemical effects of lead on vascular plants have been detected under laboratory conditions at concentrations higher than normally found in the environment. The commonly reported effects are the inhibition of photosynthesis, respiration or cell elongation, all of which reduce the growth of the plant (Koeppe, 1981). Lead may also induce premature senescence, which may affect the long-term survival of the plant or the ecological success of the plant population. To provide a meaningful evaluation of these effects, it is necessary to examine the correlation between laboratory conditions and typical conditions in nature with respect to form, concentration, and availability of lead. First, the reader must understand what is known of the movement of lead from soil to the root to the stem and finally to the leaf or flower. Most notably, there are specific barriers to lead at the soil:soil moisture interface and at the root:shoot interface which retard the movement of lead and reduce the impact of lead on photosynthetic and meristematic (growth/reproduction) tissue.

8.3.1.1 Uptake by vascular plants--Most of the lead in or on a plant occurs on the surfaces of leaves and the trunk or stem. The surface concentration of lead in trees, shrubs, and grasses exceeds the internal concentration by a factor of at least five (Elias et al, 1978). There is little or no evidence of lead uptake through leaves or bark. Foliar uptake, if it does occur, cannot account for more than 1 percent of the uptake by roots, and passage of lead through bark tissue has not been detected (Arvik and Zimdahl, 1974; reviewed by Koeppe, 1981; Zimdahl, 1976). Krause and Kaiser (1977) were able to show foliar uptake and translocation of lead mixed with cadmium, copper, and manganese oxides when applied in large amounts (122 mg/m^2) directly to leaves. This would be comparable to 100,000 days accumulation at a remote site (0.12 $ng/cm^2 \cdot d$) (Elias et al., 1978). The uptake of lead was less than that of other metals and application of sulfur dioxide did not increase the foilar uptake of these metals. The major effect of surface lead at ambient concentrations seems to be on subsequent components of the grazing food chain (Section 8.4.1) and on the decomposer food chain following litterfall (Elias et al., 1982). (See also Section 8.2.2.)

Uptake by roots is the only major pathway for lead into plants. The amount of lead that enters plants by this route is determined by the availability of lead in soil, with apparent variations according to plant species. Soil cation exchange capacity, a major factor, is determined by the relative size of the clay and organic fractions, soil pH, and the amount of Fe-Mn oxide films present (Nriagu, 1978). Of these, organic humus and high soil pH are the dominant factors in immobilizing lead (Chapter 6). Under natural conditions, most of the total lead in soil would be tightly bound within the crystalline structure of inorganic soil fragments, unavailable to soil moisture. Available lead, bound on clays, organic colloids, and Fe-Mn films, would be controlled by the slow release of bound lead from inorganic rock sources. Since before 3000 B.C., atmospheric lead inputs through litter decomposition have increased the pool of available lead bound on organic matter within the soil reservoir (see Chapter 5).

Because lead is strongly immobilized by humic substances, only a small fraction (perhaps 0.01 percent in soils with 20 percent organic matter, pH 5.5) is released to soil moisture (see Chapter 6). In soil moisture, lead may pass along the pathway of water and nutrient uptake on either a cellular route

through the cell membranes of root hairs (symplastic route) or an extracellular route between epidermal cells into the intercellular spaces of the root cortex (apoplastic route) (Foy et al., 1978). Lead probably passes into the symplast by membrane transport mechanisms similar to the uptake of calcium or other bivalent cations. Lead may be immobilized in subcellular organelles or passed cell-to-cell through the cortex and endodermis into the vascular tissue of the root.

Uptake of lead by plants may be enhanced by symbiotic associations with mycorrhizal fungi. The three primary factors that control the uptake of nutrients by plants are the surface area of the roots, the ability of the root to absorb particular ions, and the transfer of ions through the soil. The symbiotic relationship between mycorrhizal fungi and the roots of higher plants can increase the uptake of nutrients by enhancing all three of these factors (Voigt, 1969). The typical ectomycorrhiza consists of a mantle or sheath of mycelia that completely surrounds the root. The physical extension of the sheath may increase the volume of the root 2 to 3 times (Voigt, 1969). Mycorrhizal roots often show greater affinities for nutrients than do uninfected roots of the same species grown in the same conditions. In many soil systems, where the bulk of the nutrients are bound up in parent rock material, efficient uptake of these nutrients by plants depends on the ability of organisms in the rhizosphere (plant roots, soil fungi, and bacteria) to increase the rates of weathering. Mycorrhizal fungi are known to produce and secrete into their environment many different acidic compounds (e.g., malic and oxalic acids). In addition, mycorrhizal roots have been shown to release more carbon dioxide into the rhizosphere than do non-mycorrhizal roots as a result of their increased rates of respiration. Carbon dioxide readily combines with soil moisture to produce carbonic acid. All of these acids are capable of increasing the weathering rates of soil particles such as clays, and altering the binding capacity of organic material, thereby increasing the amount of nutrients in the soil solution. Mycorrhizae are known to enhance the uptake of zinc by pine roots (Bowen et al., 1974), and it is likely that lead uptake is similarly increased, by inference to the ability of mycorrhizae to enhance the uptake of calcium by pine roots (Melin and Nilsson, 1955; Melin et al., 1958).

The translocation of lead to aboveground portions of the plant is not clearly understood. Lead may follow the same pathway and be subject to the

same controls as a nutrient metal such as calcium. This assumption implies that the plant root has no means of discriminating against lead during the uptake process, and it is not known that any such mechanism exists. There may be several mechanisms, however, that excrete lead back out of the root or that prevent its translocation to other plant parts. The primary mechanisms may be storage in cell organelles or adsorption on cell walls. The apoplast contains an important supply of plant nutrients, including water. Lead in the apoplast remains external to the cells and cannot pass to vascular tissue without at least passing through the cell membranes of the endodermis. Because this extracellular region is bounded on all sides by cell walls, the surface of which is composed of layers of cellulose strands, the surface area of the apoplast is comparable to a sponge. It is likely that much of the lead in roots is adsorbed to the apoplast surface. Dictyosomes, cytoplasmic organelles which contain cell wall material, may carry lead from inside the cell through the membrane to become a part of the external cell wall (Malone et al., 1974), possibly replacing calcium in calcium pectate. Lead may also be stored and excreted as lead phosphate in dictyosome vesicles (Malone et al., 1974). Nevertheless, some lead does pass into the vascular tissue, along with water and dissolved nutrients, and is carried to physiologically active tissue of the plant.

8.3.1.2 Physiological Effects on Plants--Because most of the physiologically active tissue of plants is involved in growth, maintenance, and photosynthesis, it is expected that lead might interfere with one or more of these processes. Indeed, such interferences have been observed in laboratory experiments at lead concentrations greater than those normally found in the field, except near smelters or mines (Koeppe, 1981). It is likely that more is known of these effects because these are the physiological processes studied more vigorously than others. Studies of other plant processes, especially maintenance, flowering and hormone development, have not been conducted and no conclusion can be reached concerning possible lead effects on these processes.

Inhibition of photosynthesis by lead may be by direct interference with the light reaction or the indirect interference with carbohydrate synthesis. At 21 µg Pb/g reaction solution, Miles et al. (1972) demonstrated substantial inhibition of photosystem II near the site of water splitting, a biochemical process believed to require manganese. Homer et al. (1979) found a second

effect on photosystem II at slightly higher concentrations of lead. This effect was similar to that of DCMU [3-(3,4-dichlorophenyl)-1,1-dimethylurea], a reagent commonly used to uncouple the photosynthetic electron transport system. Bazzaz and Govindjee (1974) suggested that the mechanism of lead inhibition was a change in the conformation of the thylakoid membranes, separating and isolating pigment systems I and II. Wong and Govindjee (1976) found that lead also interferes with P700 photooxidation and re-reduction, a part of the photosystem I light reaction. Homer et al. (1981) found a lead tolerant population of the grass Phalaris arundinacea had lowered the ratio of chlorophyll a/chlorophyll b, believed to be a compensation for photosystem II inhibition. There was no change in the total amount of chlorophyll, but the mechanism of inhibition was considered different than that of Miles et al. (1972). Hampp and Lendzian (1974) found that lead inhibits the synthesis of chlorophyll b more than chlorophyll a at concentrations up to 500 µM lead chloride. Bazzaz et al. (1974, 1975) observed reduced net photosynthesis which may have been caused indirectly by inhibition of carbohydrate synthesis. Without carbohydrates, stomatal guard cells remain flaccid, transpiration ceases, carbon dioxide fixation decreases, and further carbohydrate synthesis is inhibited.

The stunting of plant growth may be by the inhibition of the growth hormone IAA (indole-3-ylacetic acid). Lane et al. (1978) found a 25 percent reduction in elongation at 10 µg/g lead as lead nitrate in the nutrient medium of wheat coleoptiles. This effect could be reversed with the addition of calcium at 18 µg/g. Lead may also interfere with plant growth by reducing respiration or inhibiting cell division. Miller and Koeppe (1979) and Miller et al. (1975) showed succinate oxidation inhibition in isolated mitochondria as well as stimulation of exogenous NADH oxidation with related mitochondrial swelling. Hassett et al. (1976), Koeppe (1977), and Malone et al. (1978) described significant inhibition of lateral root initiation in corn. Inhibition increased with the simultaneous addition of cadmium.

Sung and Yang (1979) found that lead at 1 µg/g can complex with and inactivate ATPase to reduce the production and utilization of ATP in kidney bean (Phaseolus vulgaris) and buckwheat leaves (Fagopyrum esculentum). The lead was added hydroponically at concentrations up to 1000 µg/g. Kidney bean ATPase showed a continued response from 1 to 1000 µg/g, but buckwheat leaves showed little further reduction after 10 µg/g. Neither extracted ATP nor

chemically added ATP could be used by the treated plants. Lee et al. (1976) found a 50 percent increase in the activity of several enzymes related to the onset of senescence in soybean leaves when lead was added hydroponically at 20 µg/g. These enzymes were acid phosphatase, peroxidase and alpha-amylase. A build-up of ammonia was observed along with a reduction in nitrate, calcium and phosphorus. Glutamine synthetase activity was also reduced by 65 percent. Continued increases in effects were observed up to 100 µg/g, including a build-up of soluble protein. Päivöke (1979) also observed a 60 percent increase in acid phosphatase activity during the first six days of pea seedling germination (Pisum sativum) at 2 µg/g, under low nutrient conditions. The accumulation of soluble protein was observed and the effect could be reversed with the addition of nutrients, including calcium.

The interaction of lead with calcium has been shown by several authors, most recently by Garland and Wilkins (1981), who demonstrated that barley seedlings (Hordeum vulgare), which were growth inhibited at 2 µg Pb/g sol. with no added calcium, grew at about half the control rate with 17 µg Ca/g sol. This relation persisted up to 25 µg Pb/g sol. and 500 µg Ca/g sol.

These studies of the physiological effects of lead on plants all show some effect at concentrations from 2 to 10 µg/g in the nutrient medium of hydroponically-grown agricultural plants. It is certain that no effects would have been observed at these concentrations had the lead solutions been added to normal soil. There is no firm relationship between soil lead and soil moisture lead, because each soil type has a unique capacity to retain lead and to release that lead to the soil moisture film surrounding the soil particle. Once in soil moisture, lead seems to pass freely to the plant root according to the capacity of the plant root to absorb water and dissolved substances (Koeppe, 1981).

It seems reasonable that there may be a direct correlation between lead in hydroponic media and lead in soil moisture. Hydroponic media typically have an excess of essential nutrients, including calcium and phosphorus, so that movement of lead from hydroponic media to plant root would be equal to or slower than movement from soil moisture to plant root.

Chapter 6 discusses the many parameters controlling the release of lead from soil to soil moisture, but so few data are available on observed lead concentrations in soil moisture that no model can be formed. Hughes (1981)

adopted the general conclusion that extractable soil lead is typically 10 percent of total soil lead. However, this lead was extracted chemically under laboratory conditions more rigorous than the natural equilibrium between soil and soil moisture. Ten percent should therefore be considered the upper limit, where the ability of soil to retain lead is at a minimum. A lower limit of 0.01 percent is based on the only known report of lead in both soil and soil moisture (16 μg/g soil, 1.4 μg/g soil moisture; Elias et al., 1982). This single value shows neither trends with different soil concentrations nor the soil component (organic or inorganic) that provides the lead to the soil moisture. But the number (0.01 percent) is a conservative estimate of the ability of soil to retain lead, since the conditions (pH, organic content) were optimum for retaining lead. A further complication is that atmospheric lead is retained at the surface (0-2 cm) of the soil profile (Martin and Coughtrey, 1981), whereas most reports of lead in soil pertain to samples from 0 to 10 cm as the "upper" layer of soil. Any plant that absorbs solely from the top few centimeters of soil obviously is exposed to more lead than one with roots penetrating to a depth of 25 cm or more. Agricultural practices that cultivate soil to a depth of 25 cm blend in the upper layers with lower to create a soil with average lead content somewhat above background.

These observations lead to the general conclusion that even under the best of conditions where soil has the highest capacity to retain lead, most plants would experience reduced growth rate (inhibition of photosynthesis, respiration, or cell elongation) in soils of 20,000 μg Pb/g or greater. Concentrations approaching this value typically occur around smelters (Martin and Coughtrey, 1981) and near major highways (Wheeler and Rolfe, 1979). These conclusions pertain to soil with the ideal composition and pH to retain the maximum amount of lead. Acid soils or soils lacking organic matter would inhibit plants at much lower lead concentrations.

The rate at which atmospheric lead accumulates in soil varies from 1.1 $mg/m^2 \cdot yr$ average global deposition (Table 6-4) to 3,000 $mg/m^2 \cdot yr$ near a smelter (Patterson et al., 1975). Assuming an average density of 1.5 g/cm^3, soil to a depth of 2 cm (20,000 cm^3/m^2) would incur an increase in lead concentration at a rate of 0.04 to 100 μg/g soil·yr. This means remote or rural area soils will never reach the 20,000 μg threshold but that soils closer to major sources may be within range in the next 50·years.

8.3.1.3 Lead Tolerance in Vascular Plants--Some plant species have developed populations tolerant to high lead soils (Antonovics et al., 1971). In addition to Homer et al. (1981) cited above, Jowett (1964) found populations of Agrostis tenuis in pure stands on acidic spoil banks near an abandoned mine. The exclusion of other species was attributed to root inhibition. Populations of A. tenuis from low-lead soils had no tolerance for the high lead soils. Several other studies suggest that similar responses may occur in populations growing in lead-rich soils (reviewed in Peterson, 1978). A few have suggested that crops may be cultivated for their resistance to high lead soils (Gerakis et al., 1980; John, 1977).

8.3.1.4 Effects of Lead on Forage Crops and Urban Gardens--In the 1977 Criteria Document (U.S. Environmental Protection Agency, 1977), there was a general awareness that most of the lead in plants was surface lead from the atmosphere. Most studies since then have addressed the problem of distinguishing between surface and internal plant lead. The general conclusion is that, even in farmlands remote from major highways or industrial sources, 90 to 99 percent of the total plant lead is of anthropogenic origin (National Academy of Sciences, 1980). Obviously, the critical agricultural problem concerns forage crops and leafy vegetables. There has been no observed decrease in lead in forage grasses. Estimates of the daily lead intake by foraging animals remain the same as in 1977.

Rolfe (1974) found 4-fold increases in both rural and urban trees using 10 year increments of annual rings for the period 1910-20 and comparing these to annual rings of the period 1963-73. Symeonides (1979) found a 2-fold increase from 1907-17 to 1967-77 in trees at a high-lead site, with no increase in trees from a low-lead site. Finally, Baes and Ragsdale (1981), using only ring porous species, found significant post-1930 increases in Quercus and Carya with high lead exposure, but only in Carya with low lead exposure. These chronological records confirm that lead can be translocated from roots to the upper portions of the plant and that the amounts translocated are in proportion to the concentrations of lead in soil.

8.3.1.5 Summary of Plant Effects. When soil conditions allow lead concentrations in soil moisture to exceed 2 to 10 µg/g, most plants will experience reduced growth due to the inhibition of one or more physiological processes. Excess calcium or phosphorus may reverse the effect. Plants that absorb

nutrients from deeper soil layers may receive less lead. Acid rain is not likely to release more lead until after major nutrients have been depleted from the soil. A few species of plants have the genetic capability to adapt to high lead soils.

8.3.2 Effects on Bacteria and Fungi

8.3.2.1 Effects on Decomposers--Tyler (1972) explained three ways in which lead might interfere with the normal decomposition processes in a terrestrial ecosystem. Lead may be toxic to specific groups of decomposers, it may deactivate enzymes excreted by decomposers to break down organic matter, or it may bind with the organic matter to render it resistant to the action of decomposers. Because lead in litter may selectively inhibit decomposition by soil bacteria at 2000 to 5000 µg/g (Smith, 1981, p. 160), forest floor nutrient cycling processes may be seriously disturbed near lead smelters (Bisessar, 1982; Watson et al., 1976). This is especially important because approximately 70 percent of plant biomass enters the decomposer food chain (Swift et al., 1979, p. 6). If decomposition of the biomass is inhibited, then much of the energy and nutrients remain unavailable to subsequent components of the food chain. There is also the possibility that the ability of soil to retain lead would be reduced, as humic substances are byproducts of bacterial decomposition.

During decomposition, plant tissues are reduced to resistant particulate matter, as soluble organic and inorganic compounds are removed by the chemical action of soil moisture and the biochemical action of microorganisms (Odum and Drifmeyer, 1978). Each group of microorganisms specializes in the breakdown of a particular type of organic molecule. Residual waste products of one group become the food for the next group. Swift et al. (1979, p. 101) explained this relationship as a cascade effect with the following generalized pattern (Figure 8-4). Organisms capable of penetrating hard or chemically resistant plant tissue are the primary decomposers. These saprotrophs, some of which are fungi and bacteria that reside on leaf surfaces at the initial stages of senescence, produce a wide range of extracellular enzymes. Others may reside in the intestinal tract of millipedes, beetle larvae, and termites capable of mashing plant tissue into small fragments. The feces and remains of this group and the residual plant tissue are consumed by secondary decomposers, i.e., the coprophilic fungi, bacteria, and invertebrates (including protozoa) specialized for consuming bacteria. These are followed by tertiary decomposers.

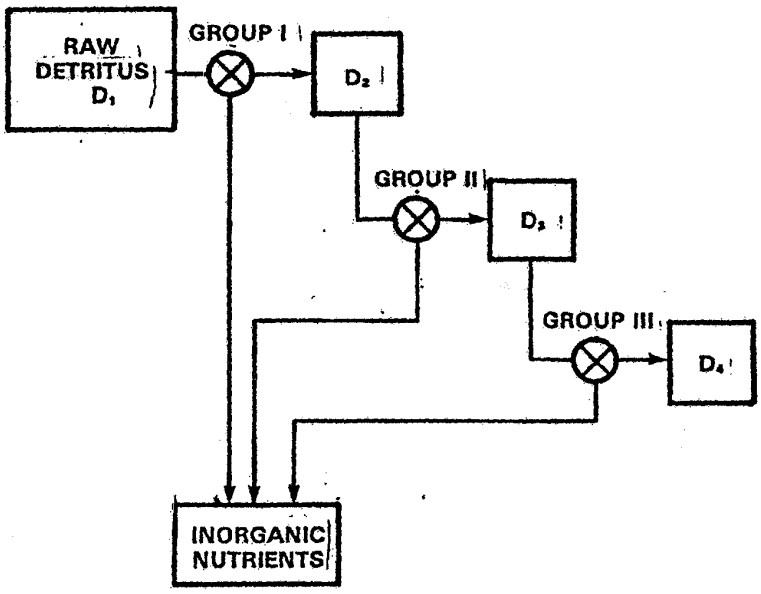

Figure 8-4. Within the decomposer food chain, detritus is progressively broken down in a sequence of steps regulated by specific groups of decomposers. Because of the cascade effect of this process, the elimination of any decomposer interrupts the supply of organic nutrients to subsequent groups and reduces the recycling of inorganic nutrients to plants. Undecomposed litter would accumulate at the stages preceding the affected decomposer.

Source: Adapted from Swift et al. (1979).

Microorganisms usually excrete enzymes that carry out this digestive process external to their cells. They are often protected by a thick cell coat, usually a polysaccharide. Because they are interdependent, the absence of one group in this sequence seriously affects the success of subsequent groups, as well as the rate at which plant tissue decomposes. Each group may be affected in a different way and at different lead concentrations. Lead concentrations toxic to decomposer microbes may be as low as 1 to 5 µg/g or as high as 5000 µg/g (Doelman, 1978).

Under conditions of mild contamination, the loss of one sensitive bacterial population may result in its replacement by a more lead-tolerant strain. Inman and Parker (1978) found that litter transplanted from a low-lead to a high-lead site decayed more slowly than high-lead litter, suggesting the presence of a lead sensitive microorganism at the low-lead site. When high-lead litter was transplanted to the low-lead site, decomposition proceeded at a rate faster than the low-lead litter at the low-lead site. In fact, the rate was faster than the high-lead litter at the high-lead site, suggesting even the lead tolerant strains were somewhat inhibited. The long term effect is a change in the species composition of the ecosystem, which will be considered in greater detail in section 8.5.2.

Delayed decomposition has been reported near smelters (Jackson and Watson, 1977), mine waste dumps (Williams et al., 1977), and roadsides (Inman and Parker, 1978). This delay is generally in the breakdown of litter from the first stage (O_1) to the second (O_2) with intact plant leaves and twigs accumulating at the soil surface. The substrate concentrations at which lead inhibits decomposition appear to be very low. Williams et al. (1977) found inhibition in 50 percent of the bacteria and fungal strains at 50 µg Pb/ml nutrient solution. The community response time for introducing lead tolerant populations seems very fast, however. Doelman and Haanstra (1979a; 1979b) found lead-tolerant strains had replaced non-tolerant bacteria within 3 years of lead exposure. These new bacteria were predominately thick-coated gram negative strains and their effectiveness in replacing lead-sensitive strains was not evaluated in terms of soil decomposition rates.

8.3.2.2 Effects on nitrifying bacteria. The conversion of ammonia to nitrate in soil is a two-step process mediated by two genera of bacteria, Nitrosomonas and Nitrobacter. Nitrate is required by all plants, although some maintain a

symbiotic relationship with nitrogen-fixing bacteria as an alternate source of nitrogen. Those which do not would be affected by a loss of free-living nitrifying bacteria, and it is known that many trace metals inhibit this nitrifying process (Liang and Tabatabai, 1977,1978). Lead is the least of these, inhibiting nitrification 14 percent at concentrations of 1000 µg/g soil. Many metals, even the nutrient metals, manganese and iron, show greater inhibition at comparable molar concentrations. Nevertheless, soils with environmental concentrations above 1000 µg Pb/g are common and even a 14 percent inhibition of nitrification can reduce the potential success of a plant population, as nitrate is usually the limiting nutrient in terrestrial ecosystems. In cultivated ecosystems, nitrification inhibition is not a problem if nitrate fertilizer is added to soil, but could reduce the effectiveness of ammonia fertilizer if the crops rely on nitrifying bacteria for conversion to nitrates.

8.3.2.3 Methylation by Aquatic Microorganisms--While methyllead is not a primary form of environmental lead, methylation greatly increases the toxicity of lead to aquatic organisms (Wong and Chau, 1979). There is some uncertainty about whether the mechanism of methylation is biotic or abiotic. Some reports (Wong and Chau, 1979, Thompson and Crerar, 1980) conclude that lead in sediments can be methylated by bacteria. Reisinger et al. (1981) report that biomethylation of lead under aerobic or anaerobic conditions does not occur and such reports are probably due to sulfide-induced chemical conversion of organic lead salts. These authors generally agree that tetramethyl lead can be formed under environmental conditions when another tetravalent organic lead compound is available, but methylation of divalent lead salts such as $Pb(NO_3)_2$ does not appear to be significant.

8.3.2.4 Summary of Effects on Microorganisms. It appears that microorganisms are more sensitive than plants to soil lead pollution and that changes in the composition of bacterial populations may be an early indication of lead effects. Delayed decomposition may occur at 750 µg/g soil and nitrification inhibition at 1000 µg/g. The environmental variables which can raise or lower these estimates are not known. In certain chemical environments, the highly toxic tetramethyllead can be formed, but this process does not appear to be mediated by aquatic microorganisms.

8.4 EFFECTS OF LEAD ON DOMESTIC AND WILD ANIMALS

8.4.1 Vertebrates

8.4.1.1 Terrestrial Vertebrates--Forbes and Sanderson (1978) have reviewed reports of lead toxicity in domestic and wild animals. Lethal toxicity can usually be traced to consumption of lead battery casings, lead-based paints, oil wastes, putty, linoleum, pesticides, lead shot, or forage near smelters. Except for lead shot ingestion, these problems can be solved by proper management of domestic animals. However, the 3000 tons of lead shot distributed annually along waterways and other hunting grounds continues to be a problem. Of the estimated 80 to 90 million waterfowl in North America, 3.5 million die of poisoning from lead shot annually (U.S. Fish and Wildlife Service, 1976).

Awareness of the routes of uptake is important in interpreting the exposure and accumulation in vertebrates. Inhalation rarely accounts for more than 10 to 15 percent of the daily intake of lead (National Academy of Sciences, 1980). Much of the inhaled lead is trapped on the walls of the bronchial tubes and passes to the stomach embedded in swallowed mucus. Because lead in lakes or running stream water is quite low, intake from drinking water may be insignificant unless the animal drinks from a stagnant or otherwise contaminated source.

Food is the largest contributor of lead to animals. The type of food an herbivore eats determines the rate of lead ingestion. More than 90 percent of the total lead in leaves and bark may be surface deposition, but relatively little surface deposition may be found on some fruits, berries, and seeds which have short exposure times. Roots intrinsically have no surface deposition. Similarly, ingestion of lead by a carnivore depends mostly on deposition on herbivore fur and somewhat less on lead in herbivore tissue.

The type of food eaten is a major determinant of lead body burdens in small mammals. Goldsmith and Scanlon (1977) and Scanlon (1979) measured higher lead concentrations in insectivorous species than in herbivorous, confirming the earlier work of Quarles et al. (1974) which showed body burdens of granivores<herbivores<insectivores, and Jeffries and French (1972) that granivores<herbivores. Animals in these studies were analyzed whole minus the digestive tract. It is likely that observed diet-related differences were somewhat diluted by including fur in the analysis, because fur-lead might be similar for small mammals from the same habitats with different feeding habits.

Since 1977, there has been a trend away from whole body analyses toward analysis of isolated tissues, especially bones and blood. Bone concentrations of lead are better than blood as indicators of long term exposure. Because natural levels of blood lead are not well known for animals and blood is not a good indicator of chronic exposure, blood lead is poorly suited for estimating total body burdens.

Chmiel and Harrison (1981) showed highest concentrations of lead in the bones of small mammals (Table 8-2), with kidneys and livers somewhat less. They also showed greater bone concentrations in insectivores than herbivores, both at the control and contaminated sites. Clark (1979) found lead concentrations in shrews, voles, and brown bats from roadside habitats near Washington, D.C., to be higher than any previously reported. His estimates of dosages (7.4 mg Pb/kg·day) exceed those that normally cause mortality or reproductive impairment in domestic mammals (1.5-9 mg Pb/g·day) (Hammond and Aronson, 1964; James et al., 1966; Kelliher et al., 1973). Traffic density was the same as reported by Chmiel and Harrison (1981), nearly twice that of Goldsmith and Scanlon (1977) (See Table 8-3). The body lead burden of shrews exceeded mice, which exceeded voles. Beresford et al. (1981) found higher lead in box turtles within 500 m of a lead smelter than in those from control sites. Bone lead exceeded kidney and liver lead as in small mammals. These bones may contain a chronological record of exposure, since the bones of these reptiles are formed by annual additions. Hutton (1980) found depression of hemoglobin synthesis and malformations of kidney tissue in feral pigeons of London.

There are few studies reporting lead in vertebrate tissues from remote sites. Elias et al. (1976, 1982) reported tissue concentrations in voles, shrews, chipmunks, tree squirrels, and pine martens from the remote High Sierra. Bone concentrations were generally only 2 percent of those reported from roadside studies and 10 percent of the controls of roadside studies (Table 8-2), indicating those controls were themselves contaminated to a large degree. Furthermore, biogeochemical calculations for these remote areas suggest that even these animals had bone lead concentrations 50 to 500 times natural background levels. The natural concentration of lead in the bones of herbivores is about 0.04 ng/g dry weight (Table 8-1). This value may vary regionally with geochemical anomalies in crustal rock, but provides a reasonable indicatpr of contamination. .Natural levels of lead in carnivore bone

TABLE 8-2. ESTIMATES OF THE DEGREE OF CONTAMINATION OF HERBIVORES, OMNIVORES, AND CARNIVORES

Organism	Bone Pb conc.	Ref.	Estimated degree of contamination bone
Herbivores			
vole-roadside	38	1	320
vole-roadside	17	2	140
-control	5	2	42
vole-orchard	73	5	610
-control	9	5	75
vole-remote	2	11	17
deer mouse-roadside	25	2	210
-control	5.7	2	48
deer mouse-roadside	29	3	240
-control	7.2	3	60
deer mouse-roadside	52	4	430
-control	5	4	42
mouse-roadside	19	2	160
-control	9.3	2	78
mouse-roadside	109	2	910
-control	18	2	150
Average Herbivore			
roadside (7)	41		340
control (7)	8.5		71
remote (2)	2		17
Omnivores/Frugivores			
woodmouse-roadside	67	1	840
-control	25	1	310
composite-roadside	22	7	280
-control	3	7	37
chipmunk-remote	2	11	25
tree squirrel-remote	1.3	11	16
ferral pigeon-urban	670	6	8400
-rural	5.7	6	71
starling-roadside	210	7	2600
-control	13	7	160
robin-roadside	130	7	1600
-control	41	7	510
sparrow-roadside	130	7	1600
-control	17	7	200
blackbird-roadside	90	7	1100
-control	7	7	88
grackle-roadside	63	7	790
-control	22	7	280

(continued)

TABLE 8-2. (continued)

Organism	Bone Pb conc.	Ref.	Estimated degree of contamination bone
rats-roadside	310[a]	9	10000
-control	15[a]	9	500
Average Omnivore			
roadside (7)	102		1260
urban (1)	670		8400
control (7)	18		230
remote (2)	1.7		21
Carnivores			
box turtle-smelter	91[a]	8	3000
-control	5.7[a]	8	190
egret-rural	12[a]	10	400
gull-rural	11[a]	10	370
shrew-roadside	67	2	2200
-control	12	2	400
shrew-roadside	193	1	6400
-control	41	1	1400
shrew-remote	4.6	11	150
pine marten-remote	1.4	11	47
Average Carnivore			
roadside (3)	190		6200
smelter (1)	91		3000
rural (2)	11		385
control (4)	18		620
remote (2)	3		99

aDry weight calculated from published fresh weights assuming 35 percent water.

Source: Data are based on published concentrations of lead in bone tissue (corrected to dry weight as indicated). Degree of contamination is calculated as observed/natural Pb. Natural lead concentrations are from Table 8-2. Concentrations are in µg/dw.

1. Chmiel and Harrison, 1981
2. Getz et al., 1977b
3. Welch and Dick, 1975
4. Mierau and Favara, 1975
5. Elfving et al., 1978
6. Hutton and Goodman, 1980
7. Getz et al., 1977a
8. Beresford et al., 1981
9. Mouw et al., 1975
10. Hulse et al., 1980
11. Elias et al., 1982

tissue should be somewhat lower, with omnivores generally in between (Elias and Patterson, 1980; Elias et al., 1982).

Table 8-2 shows the results of several studies of small animal bone tissue. To convert reported values to a common basis, assumptions were made of the average water content, calcium concentration, and average crustal concentration. Because ranges of natural concentrations of lead in bones, plants, soils and air are known with reasonable certainty (Table 8-1), it is possible to estimate the degree of contamination of vertebrates from a wide range of habitats. It is important to recognize that these are merely estimates that do not allow for possible errors in analysis or anomalies in regional crustal abundances of lead.

8.4.1.2 Effects on Aquatic Vertebrates--Two requirements limit the evaluation of literature reports of lead effects on aquatic organisms. First, any laboratory study should incorporate the entire life cycle of the organism studied. It is clear that certain stages of a life cycle are more vulnerable than others (Hodson, 1979, Hodson et al., 1979). For fish, the egg or fry is usually most sensitive. Secondly, the same index must be used to compare results. Christensen et al. (1977) proposed three indices useful for identifying the effects of lead on organisms. A molecular index reports the maximum concentration of lead causing no significant biochemical change; residue index is the maximum concentration showing no continuing increase of deposition in tissue; and a bioassay index is the maximum concentration causing no mortality, growth change or physical deformity. These indices are comparable to those of physiological dysfunction (molecular, tissue, and organismic) discussed in Section 8.1.4.

From the standpoint of environmental protection, the most useful index is the molecular index. This index is comparable to the point of initial response discussed previously and is equivalent to the "safe concentration" originally described by the U.S. Environmental Protection Agency (1971) as being the concentration that permits normal reproduction, growth, and all other life-processes of all organisms. It is unfortunate that very few of the toxicity studies in the aquatic literature report safe concentrations as defined above. Nearly all report levels at which some or all of the organisms die.

Hematological and neurological responses are the most commonly reported effects of extended lead exposures in aquatic vertebrates. Hematological

effects include the disabling and destruction of mature red blood cells and the inhibition of the enzyme ALA-D required for hemoglobin synthesis. At low exposures, fish compensate by forming additional red blood cells. These red blood cells often do not reach maturity. At higher exposures, the fish become anemic. Symptoms of neurological responses are difficult to detect at low exposure, but higher exposure can induce neuromuscular distortion, anorexia, and muscle tremors. Spinal curvature eventually occurs with time or increased concentration (Hodson 1979; Hodson et al., 1977).

The biochemical changes used by Christensen et al. (1977) to determine the molecular index for brook trout were 1) increases in plasma sodium and chloride and 2) decreases in glutamic oxalacetic transaminase activity and hemoglobin. They observed effects at 0.5 µg/l, which is 20-fold less than the lower range (10 µg/l) suggested by Wong et al. (1978) to cause significant detrimental effects. Hodson et al. (1978a) found tissue accumulation and blood parameter changes in rainbow trout at 13 µg/l. This was the lowest experimental level, and only slightly above the controls, which averaged 4 µg/l. They concluded, however, that because spinal curvature does not occur until exposures reach 120 µg/l, rainbow trout are adequately protected at 25 µg/l.

Aside from the biochemical responses discussed by Christensen et al. (1977), the lowest reported exposure concentration that causes hematological or neurological effects is 8 µg/l (Hodson, 1979). These results may be consistent, considering Christensen's group dealt with subcellular responses, whereas Hodson's group dealt primarily with responses at the cellular or higher level. Hodson et al. (1978a) also reported that lead in food is not available for assimilation by fish, that most of their lead comes from water, and that decreasing the pH of water (as in acid rain) increases the uptake of lead by fish (Hodson et al., 1978b). Patrick and Loutit (1978), however, reported that tissue lead in fish reflects the lead in food if the fish are exposed to the food for more than a few days. Hodson et al. (1980) also reported that, although the symptoms are similar (spinal deformation), lead toxicity and ascorbic acid deficiency are not metabolically related.

8.4.2 Invertebrates

Insects have lead concentrations that correspond to those found in their habitat and diet. Herbivorous invertebrates have lower concentrations than do

predatory types (Wade et al., 1980). Among the herbivorous groups, sucking insects have less lead than chewing insects, especially in regions near roadsides, where more lead is found on the surfaces of vegetation. Williamson and Evans (1972) found gradients away from roadsides are not the same as with vertebrates, in that invertebrate lead decreases more slowly than vertebrate lead relative to decreases in soil lead. They also found great differences between major groups of invertebrates. Wood lice in the same habitat, eating the same food, had eight times more lead than millipedes.

The distribution of lead among terrestrial gastropod tissues was reported by Ireland (1979). He found little difference among the foot, skin, mantle, digestive gland, gonad, and intestine. There are no reports of lead toxicity in soil invertebrates. In a feeding experiment, however, Coughtrey et al. (1980) found decreased tolerance for lead by microorganisms from the guts of insects at 800 μg Pb/g food. Many roadside soils fall in this range.

In Cepaea hortensis, a terrestrial snail, Williamson (1979) found most of the lead in the digestive gland and gonadal tissue. He also determined that these snails can lose 93 percent of their whole body lead burden in 20 days when fed a low-lead diet in the laboratory. Since no analyses of the shell were reported, elimination of lead from this tissue cannot be evaluated. A continuation of the study (Williamson, 1980) showed that body weight, age, and daylength influenced the lead concentrations in soft tissues.

Gish and Christensen (1973) found lead in whole earthworms to be correlated with soil lead, with little rejection of lead by earthworms. Consequently, animals feeding on earthworms from high lead soils might receive toxic amounts of lead in their diets, although there was no evidence of toxic effects on the earthworms (Ireland, 1977). Ash and Lee (1980) cleared the digestive tracts of earthworms and still found direct correlation of lead in earthworms with soil lead; in this case, soil lead was inferred from fecal analyses. These authors found differences among species of earthworms. Ireland and Richards (1977) also found species differences in earthworms, as well as some localization of lead in subcellular organelles of chloragogue and intestinal tissue. In view of the fact that chloragocytes are believed to be involved with waste storage and glycogen synthesis, the authors concluded that this tissue is used to sequester lead in the manner of vertebrate livers. Species differences in whole body lead concentrations could not be attributed

to selective feeding or differential absorption, unless the differential absorption occurs only at elevated lead concentrations. The authors suggested that the two species have different maximum tolerances for body lead but gave no indication of physiological dysfunction when the maximum tolerance was reached. In soils with a total lead concentration of 1810 µg/g dry weight (Ireland, 1975), Lumbricus rubellus had a whole body concentration of 3600 µg/g, while Dendrobaene rubida accumulated 7600 µg/g in the same location (Ireland and Richards, 1977). Because this difference was not observed at the control site (15 µg/g soil), it can be assumed that at some soil concentration between 15 and 1800 µg/g, different species of earthworms begin to accumulate different amounts of lead. The authors concluded that D. rubida can simply tolerate higher tissue lead concentrations, implying that soil concentrations of 1800 µg/g are toxic to L. rubellus. This concentration would be considerably lower than soil lead concentrations that cause effects in plants, and similar to that which can affect soil microorganisms.

Aquatic insects appear to be resistant to high levels of lead in water. To be conclusive, toxicity studies must observe invertebrates through an entire life cycle, although this is infrequently done. Anderson et al. (1980) found LC_{50}'s for eggs and larvae of Tanytarsus dissimilis, a chironomid, to be 260 µg/l. This value is 13 to 250 times lower than previously reported by Warnick and Bell (1969), Rehwoldt et al. (1973), and Nehring (1976). However, Spehar et al. (1978) found that mature amphipods (Gammarus pseudolimnaeus) responded negatively to lead at 32 µg/l. Fraser et al. (1978) found that adult populations of a freshwater isopod (Asellus aquaticus) have apparently developed a genetic tolerance for lead in river sediments.

Borgmann et al. (1978) found increased mortality in a freshwater snail, Lymnaea palutris, associated with stream water with a lead content as low as 19 µg/l. Full life cycles were studied to estimate population productivity. Although individual growth rates were not affected, increased mortality, especially at the egg hatching stage, effectively reduced total biomass production at the population level. Production was 50 percent at 36 µg/l and 0 percent at 48 µg Pb/l.

The relationship between LC_{50} and initial physiological response is not immediately obvious. It is certain that some individuals of a population experience physiological dysfunction well before half of them die. For example,

Biesinger and Christensen (1972) observed minimum reproductive impairment in Daphnia at 6 percent of the LC_{50} (450 µg/l) for this species.

8.4.3 Summary of Effects on Animals. While it is impossible to establish a safe limit of daily lead consumption, it is reasonable to generalize that a regular diet of 2 to 8 mg Pb/kg·day body weight over an extended period of time (Botts, 1972) will cause death in most animals. Animals of the grazing food chain are affected most directly by the accumulation of aerosol particles on vegetation surfaces, and somewhat indirectly by the uptake of lead through plant roots. Many of these animals consume more than 1 mg Pb/kg·day in habitats near smelters and roadsides, but no toxic effects have been documented. Animals of the decomposer food chain are affected indirectly by lead in soil which can eliminate populations of microorganisms preceeding animals in the food chain or occupying the digestive tract of animals and aiding in the breakdown of organic matter. Invertebrates may also accumultate lead at levels toxic to their predators.

Aquatic animals are affected by lead at concentrations of lead lower than previously considered safe (50 µg/l) for wildlife. These concentrations occur commonly, but the contribution of atmospheric lead to specific sites of high aquatic lead is not clear.

8.5 EFFECTS OF LEAD ON ECOSYSTEMS

There is wide variation in the mass transfer of lead from the atmosphere to terrestrial ecosystems. Even within the somewhat artificial classification of undisturbed, cultivated and urban ecosystems, reported fluxes in undisturbed ecosystems vary by nearly 20-fold. Smith and Siccama (1981) report 266 g/ha·yr in the Hubbard Brook forest of New Hampshire, Lindberg and Harriss (1981) found 50 g/ha·yr in the Walker Branch watershed of Tennessee; and Elias et al. (1976) found 15 g/ha·yr in a remote subalpine ecosystem of California. Jackson and Watson (1977) found 1,000,000 g/ha·yr near a smelter in southeastern Missouri. Getz et al. (1979) estimated 240 g/ha·yr by wet precipitation alone in a rural ecosystem largely cultivated, and 770 g/ha·yr in an urban ecosystem.

One factor causing great variation is remoteness from source, which translates to lower air concentrations, smaller particles, and greater dependence on wind as a mechanism of deposition (Elias and Davidson, 1980). Another factor is type of vegetation cover. Deciduous leaves may, by the nature of

their surface and orientation in the wind stream, be more suitable deposition surfaces than conifer needles. Davidson et al. (1982) discussed the influence of leaf surface on deposition rates to grasses.

The history of lead contamination in roadside ecosystems has been reviewed by Smith (1976). Recent studies have shown three areas of concern where the effects of lead on ecosystems may be extremely sensitive (Martin and Coughtrey, 1981; Smith, 1981). These problems arise because lead in ecosystems accumulates in the soil reservoir and is not removed with the surface and ground water passing out of the ecosystem. First, decomposition is delayed by lead, as some decomposer microorganisms and invertebrates are inhibited by soil lead. Secondly, the natural processes of calcium biopurification are being circumvented by the accumulation of lead on the surfaces of vegetation and in the soil reservoir. Thirdly, some ecosystems may be experiencing subtle shifts toward lead tolerant plant populations. Other potential effects are discussed that may occur because of the longterm build-up of lead in soil.

8.5.1 Delayed Decomposition

The flow of energy through an ecosystem is regulated largely by the ability of organisms to trap energy in the form of sunlight and to convert this energy from one chemical form to another (photosynthesis). Through photosynthesis, plants convert light to stored chemical energy. Starch is only a minor product of this energy conversion. The most abundant substance produced by net primary production is cellulose, a structural carbohydrate of plants. Terrestrial ecosystems, especially forests, accumulate a tremendous amount of cellulose as woody tissue of trees. Few animals can digest cellulose and most of them require symbiotic associations with specialized bacteria. It is no surprise then, that most of this cellulose must eventually pass through the decomposer food chain. Litterfall is the major route for this pathway. Because 80 percent or more of net primary production passes through the decomposing food chain (Swift et al., 1979), the energy of this litter is vital to the rest of the plant community and the inorganic nutrients are vital to plants.

The amount of lead that causes litter to be resistant to decomposition is not known. Although laboratory studies show that 50 µg Pb/ml nutrient medium definitely inhibits soil bacterial populations, field studies indicate little or no effect at 600 µg/g litter (Doelman and Haanstra, 1979b). One explanation is that the lead in the laboratory nutrient medium was readily available,

protection from temperature extremes, are obliterated by the succession of lead-tolerant plant populations. Smith and Bradshaw (1972) concluded that lead-tolerant plant populations of Festuca rubra and Agrostis tenuis can be used to stabilize toxic mine wastes with lead concentrations as high as 80,000 µg/g.

8.5.4 Mass Balance Distribution of Lead in Ecosystems

Inputs of natural lead to ecosystems, approximately 90 percent from rock weathering and 10 percent from atmospheric sources, account for slightly more than the hydrologic lead outputs in most watersheds (Patterson, 1980). The difference is small and accumulation in the ecosystem is significant only over a period of several thousand years. In modern ecosystems, with atmospheric inputs exceeding weathering by factors of 10 to 1000, greater accumulation occurs in soils and this reservoir must be treated as lacking a steady state condition (Heinrichs and Mayer, 1977; Siccama and Smith, 1978). Odum and Drifmeyer (1978) describe the role of detrital particles in retaining a wide variety of pollutant substances, and this role may be extended to include non-nutrient substances. It appears that plant communities have a built-in mechanism for purifying their own nutrient medium. As a plant community matures through successional stages, the soil profile develops a stratified arrangement which retains a layer of organic material near the surface. This organic layer becomes a natural site for the accumulation of lead and other non-nutrient metals which might otherwise interfere with the uptake and utilization of nutrient metals.

Lead in the detrital reservoir is determined by the continued input of atmospheric lead from the litter layer, the passage of detritus through the decomposer food chain, and the rate of leaching into soil moisture. There is strong evidence that soil has a finite capacity to retain lead (Zimdahl and Skogerboe, 1977). Harrison et al. (1981) observed that most of the lead in roadside soils above 200 µg/g is found on Fe-Mn oxide films or as soluble lead carbonate. Elias et al. (1982) have shown that soil moisture lead is derived from the leachable/organic fraction of soil, not the inorganic fraction. Lead is removed from the detrital reservoir by the digestion of organic particles in the detrital food chain and by the release of lead to soil moisture. Both mechanisms result in a redistribution of lead among all of the reservoirs of the ecosystem at a very slow rate. A closer look at the mechanisms whereby

lead is bound to humic and fulvic acids leads to the following conclusions: 1) because lead has a higher binding strength than other metals lead can displace other metals on the organic molecule (Schnitzer and Khan, 1978); 2) if calcium is displaced, it would be leached to a lower soil horizon (B), where it may accumulate as it normally does during the development of the soil profile; and 3) if other nutrient metals, such as iron or manganese, are displaced, they may be unavailable to roots if they pass out of the system.

Fulvic acid plays an important role in the development of the soil profile. This organic acid has the ability to remove iron from the lattice structures of inorganic minerals, resulting in the decomposition of these minerals as a part of the weathering process. This breakdown releases nutrients for uptake by plant roots. If all binding sites on fulvic acid are occupied by lead, the role of fulvic acid in providing nutrients to plants will be circumvented. While it is reasonably certain that such a process is possible, there is no information about the soil lead concentrations that would cause such an effect.

Ecosystem inputs of lead by the atmospheric route have established new pathways and widened old ones. Insignificant amounts of lead are removed by surface runoff or ground water seepage. It is likely that the ultimate fate of atmospheric lead will be a gradual elevation in lead concentration of all reservoirs in the system, with most of the lead accumulating in the detrital reservoir.

8.6 SUMMARY

There is no protection from industrial lead once it enters the atmosphere. Of the 450,000 tons emitted annually on a global basis, 115,000 tons of lead fall on terrestrial ecosystems. Evenly distributed, this would amount to 0.1 g/ha·yr, which is much lower than the range of 15 to 1,000,000 g/ha·yr reported in ecosystem studies in the United States. Lead has permeated these ecosystems and accumulated in the soil reservoir where it will remain for decades (Chapter 6). Within 20 meters of every major highway, up to 10,000 µg Pb have been added to each gram of surface soil since 1930 (Getz et al., 1979). Near smelters, mines, and in urban areas, as much as 130,000 µg/g have been observed in the upper 2.5 cm of soil (Jennett et al., 1979). At increasing distances up to 5 kilometers away from sources, the gradient of lead added since 1930 drops to less than 10 µg/g (Page and Ganje, 1970), and 1 to 5 µg/g have been added in regions more distant than 5 kilometers (Nriagu, 1978). In undisturbed

ecosystems, atmospheric lead is retained by soil organic matter in the upper layer of soil surface. In cultivated soils, this lead is mixed with soil to a depth of 25 cm.

Because of the special nature of the soil reservoir, it must not be regarded as an infinite sink for lead. On the contrary, atmospheric lead which is already bound to soil will continue to pass into the grazing and detrital food chains until equilibrium is reached, whereupon the lead in all reservoirs will be elevated proportionately higher than natural background levels. This conclusion applies also to cultivated soils, where lead bound within the upper 25 cm is still within the root zone.

Few plants can survive at soil concentrations in excess of 20,000 μg/g, even under optimum conditions. Some key populations of soil microorganisms and invertebrates die off at 1000 μg/g. Herbivores, in addition to a normal diet from plant tissues, receive lead from the surfaces of vegetation in amounts that may be 10 times greater than from internal plant tissue. A diet of 2 to 8 mg/day·kg body weight seems to initiate physiological dysfunction in many vertebrates.

Whereas previous reports have focused on possible toxic effects of lead on plants, animals, and humans, it is essential to consider the degree of contamination as one measure of safe concentration. Observed toxic effects occur at environmental concentrations well above levels that cause no physiological dysfunction. Small animals in undisturbed ecosystems are contaminated by factors of 20 to 600 over natural background levels, and in roadside and urban ecosystems by 300 to 6200. Extrapolations based on sublethal effects may become reliable when these measurements can be made with controls free of contamination. The greatest impact may be on carnivorous animals, which generally have the lowest concentrations of natural lead, and may thus have the greatest percent increase when the final equilibrium is reached.

Perhaps the most subtle effect of lead is on ecosystems. The normal flow of energy through the decomposer food chain may be interrupted, the composition of communities may shift toward more lead-tolerant populations, and new biogeochemical pathways may be opened, as lead flows into and throughout the ecosystem. The ability of an ecosystem to compensate for atmospheric lead inputs, especially in the presence of other pollutants such as acid precipitation, depends not so much on factors of ecosystem recovery, but on undiscovered

factors of ecosystem stability. Recovery implies that inputs of the perturbing pollutant have ceased and that the pollutant is being removed from the ecosystem. In the case of lead, the pollutant is not being eliminated from the system nor are the inputs ceasing. Terrestrial ecosystems will never return to their original, pristine levels of lead concentrations.

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TABLE OF CONTENTS

Chapter 6
TRANSPORT AND TRANSFORMATION

LIST OF TABLES

LIST OF FIGURES

6. TRANSPORT AND TRANSFORMATION

6.1 INTRODUCTION

This chapter describes the transition from the emission of lead particles into the atmosphere to their ultimate deposition on environmental surfaces, i.e., vegetation, soil or water. At the source, lead emissions are typically around 10,000 $\mu g/m^3$ (see Chapter 5), while in city air, lead values are usually between 0.1 and 10 $\mu g/m^3$ (Dzubay et al., 1979; Reiter et al., 1981; also see Chapter 7). These reduced concentrations are the result of dilution of effluent gas with of clean air, and the removal of particles by wet or dry deposition. Characteristically, lead concentrations are highest in confined areas close to sources and are progressively reduced by dilution or deposition in districts more removed from sources.

At any particular location and time, the concentration of lead found in the atmosphere depends on the amount of lead emitted from sources, especially nearby ones, and the degree of mixing provided by the motion of the atmosphere. It is possible to quantitatively describe the physics of atmospheric mixing in a variety of ways and, within some limiting assumptions, to develop simulation models that predict atmospheric lead concentrations. These models are not sensitive to short-term variations in air motion over a period of weeks or months; many of the short-term variations in air motion are damped by integration.

In highly confined areas, such as parking garages or tunnels, atmospheric lead concentrations can be about ten times greater than values measured near roadways or in urban areas. In turn, atmospheric lead concentrations are usually about two and one-half times greater in the central city than in residential suburbs. Rural areas have even lower concentrations.

Because lead emissions in the United States have declined dramatically in the past few years, lead concentrations on which dispersion studies are based may no longer exist in the United States. The reader is cautioned that the intent here is to illustrate principles of atmospheric dispersion and its consequences, and not to report presently existing levels of lead, which are described in Chapter 7.

Transformations which may occur during dispersion are changes in particle size distribution, changes from the organic to the inorganic phase, and

chemical changes in the inorganic phase of lead particles. Particle size distribution stabilize within a few hundred kilometers of the source, although atmospheric concentration continues to decrease with distance. Concentrations of organolead compounds are relatively small (1 to 6 percent of total lead) except in special situations where gasoline is handled or where engines are started cold within confined areas. Ambient organolead concentrations decrease more rapidly than inorganic, suggesting conversion from the organic to the inorganic phase during transport. Inorganic lead appears to convert from lead halides and oxides to lead sulfates.

Lead is removed from the atmosphere by wet or dry deposition. The mechanisms of dry deposition have been incorporated into models which estimate the flux of atmospheric lead to the earth's surface. Of particular interest is deposition on vegetation surfaces, since this lead may be incorporated into food chains. Between wet and dry deposition, it is possible to calculate a budget for atmospheric lead which balances the emission inputs from Chapter 5 with deposition outputs.

6.2 TRANSPORT OF LEAD IN AIR BY DISPERSION

6.2.1 Fluid Mechanics of Dispersal

Particles in air streams are subject to the same principles of fluid mechanics as particles in flowing water (Friedlander, 1977). On this basis, the authors of several texts have described the mathematical arguments for the mixing of polluted air with clean air (Benarie, 1980; Dobbins, 1979; Pasquill, 1974). The first principle is that of diffusion along a concentration gradient. If the airflow is steady and free of turbulence, the rate of mixing is determined by the diffusivity of the pollutant. In the case of gases, this diffusivity is an inherent property of the molecular forces between gases. For particles, diffusivity is a property of Brownian movement, hence a function of particles size and concentration. For both cases, the diffusivity for dilute media is a constant (Dobbins, 1980).

If the steady flow of air is interrupted by obstacles near the ground, tubulent eddies or vortices may be formed. Diffusivity is no longer constant, but may be influenced by factors independent of concentration, such as windspeed, atmospheric stability and the nature of the obstacle. By making generalizations of windspeed stability and surface roughness, it is possible to construct models using a variable transport factor called eddy diffusivity

(K), in which K varies in each direction, including vertically. There is a family of K-theory models which describe the dispersion of particulate pollutants.

The simplest K-theory model assumes that the surface is uniform and the wind is steady; thus, turbulence is predictable for various conditions of atmospheric stability (Pasquill, 1974). This model produces a Gaussian plume, called such because the concentration of the pollutant decreases according to a normal or Gaussian distribution in both the vertical and horizontal directions. These models have some utility and are the basis for most of the air quality simulations accomplished to date (Benarie, 1980). However, the assumptions of steady windspeed and smooth surface place constraints on their utility.

Several approaches have been used to circumvent the constraints of the Gaussian models. Some have been adapted for studying long range transport (more than 100 km) of pollutants. Johnson (1981) discusses 35 LRT models developed during the 1970's to describe the dispersion of atmospheric sulfur compounds. A few models that address specific problems of local and regional transport merit further discussion because they emphasize the scope of the modeling problem.

One family of models is based on the conservative volume element approach, where volumes of air are seen as discrete parcels having conservative meteorological properties such as water vapor mixing ratio, potential temperature, and absolute vorticity (Benarie, 1980). The effect of pollutants on these parcels is expressed as a mixing ratio. These parcels of air may be considered to move along a trajectory which follows the advective wind direction. These models are particularly good for dealing with surface roughness, but they tend to introduce artifact diffusion or pseudodiffusion, which must be suppressed by calculation (Egan and Mahoney, 1972; Liu and Seinfeld, 1975; Long and Pepper, 1976).

An approach useful for estimating dispersion from a roadway derives from the similarity approach of Prandtl. A mixing length parameter is related to the distance traveled by turbulent eddies during which violent exchange of material occurs. This mixing length is mathematically related to the square root of the shear stress between the atmosphere and the surface. Richardson (1925) formulated these concepts in a law of atmospheric diffusion which was

further extended to boundary layer concepts by Obukhou (1941). At the boundary layer, the turbulent eddy grows and its energy decreases proportionately with time and distance away from the source.

Although physical descriptions of turbulent diffusion exist for idealized circumstances such as isolated roadways and flat terrain, the complex flow and turbulence patterns of cities has defied theoretical description. The permeability of street patterns and turbulent eddy development in street canyons are two major problem areas that make modeling urban atmospheres difficult. Kotake and Sano (1981) have developed a simulation model for describing air flow and pollutant dispersion in various combinations of streets and buildings on two scales. A small scale, 2 to 20 m, is used to define the boundary conditions for 2 to 4 buildings and associated roadways. These subprograms are combined on a large scale of 50 to 500 meters. Simulations for nitrous oxides show nonlinear turbulent diffusion, as would be expected. The primary utility of this program is to establish the limits of uncertainty, the first step toward making firm predictions. It is likely that the development of more complete models of dispersion in complex terrains will become a reality in the near future.

An important point in this discussion is that none of the models described above have been tested for lead. The reason for this is simple. All of the models require sampling periods of two hours or less in order for the sample to conform to a well-defined set of meteorological conditions. In most cases, such a sample would be below the detection limits for lead. The common pollutant used to test models is SO_x which can be measured over very short, nearly instantaneous, time periods. The relationship between particles bearing lead and particles or gases of SO_4 and SO_2 remains to be established.

6.2.2 Influence of Dispersion on Ambient Lead Concentrations

Dispersion within confined situations, such as parking garages, residential garages and tunnels, and away from expressways and other roadways not influenced by complex terrain features depends on emission rates and the volume of clean air available for mixing. These factors are relatively easy to estimate and some effort has been made to describe ambient lead concentrations which can result under selected conditions. On an urban scale, the routes of transport are not defined clearly but can be inferred from an isopleth, i.e., a plot connecting points of identical ambient concentrations.

These plots usually show that lead concentrations are maximum where traffic density is highest.

Dispersion beyond cities to regional and remote locations is complicated by the fact that there are no monitoring networks from which to construct isopleths, that removal by deposition plays a more important role with time and distance, and that emissions from many different sources converge. Some techniques of source reconciliation are described, but these become less precise with increasing distance from major sources of lead. Dispersion from point sources such as smelters and refineries is described with isopleths in the manner of urban dispersion, although the available data are notably less abundant.

6.2.2.1 Confined and Roadway Situations--Obviously, the more source emissions are diluted by clean air, the lower ambient air concentrations of lead will be. Ingalls and Garbe (1982) used a variety of box and Gaussian plume models to calculate typical levels of automotive air pollutants that might be present in microscale situations having limited ventilation. Table 6-1 shows a comparison of six exposure situations, recomputed for a flat-average lead emissions factor of 1.0 mg/mile for roadway situations and 10 mg/min for garage situations. The roadway emission factor chosen roughly corresponds to values chosen by Dzubay et al. (1979) and Pierson (1978) scaled to 1979 lead use statistics. The parking garage factor was estimated from roadway factors by correction for fuel consumption (Ingalls and Garbe, 1982).

Confined situations, with low air volumes and little ventilation, allow automotive pollutant concentrations to build up to one to two orders of magnitude higher than are found in open air. Thus, parking garages and tunnels are likely to have considerably higher ambient lead concentrations than are found in crowded, high traffic density expressways or in city streets. Purdue et al. (1973) found total lead levels of 1.4 to 2.3 $\mu g/m^3$ in five of six U.S. cities in 1972. In similar samples from an underground parking garage, total lead was 10.8 to 12.2 $\mu g/m^3$.

Table 6-1 also shows that the high concentration of automotive lead near roadways declines significantly at distances greater than about 100 meters. Dzubay et al. (1979) found lead concentrations of 4 to 20 $\mu g/m^3$ in air over Los Angeles freeways in 1976; at nearby sites off the freeways, concentrations of 0.3 to 4.7 $\mu g/m^3$ were measured.

TABLE 6-1. SUMMARY OF MICROSCALE CONCENTRATIONS[a]

Situation			Concentration, $\mu g/m^3$
1. Residential garage (1 mg/min emission rate)			
Typical[b] (30 second idle time)			80
Severe[c] (5 min idle time)			670
2. Parking garage (1 mg/min emission rate)			
Typical			40
Severe			560
3. Roadway tunnel (10 mg/mile emission rate)			
Typical			11
Severe			29
4. Street canyon (sidewalk receptor) (10 mg/mile emission rate)			
Typical	a) 800 vehicles/hr		0.4
	b) 1,600 vehicles/hr		0.9
Severe	a) 800 vehicles/hr		1.4
	b) 1,600 vehicles/hr		2.8
5. On expressway (wind: 315 deg. rel., 1 m/sec) (10 mg/mile emission rate)			
Typical			2.4
Severe			10
6. Beside expressway (10 mg/mile emission rate)		30 min	Annual average
Severe	1 meter	8	1.2
	10 meters	6	1.0
	100 meters	2	0.3
	1,000 meters	0.25	0.03

[a]Recalculated from Ingalls and Garbe (1982) using 1979 Pb emission factors.

[b]"Typical" conditions refer to neutral atmospheric stability and average daily traffic volumes.

[c]"Severe" conditions refer to Class D stability, i.e., inversion conditions, and maximum hourly traffic volumes.

Tiao and Hillmer (1978) and Ledolter and Tiao (1979) have analyzed three years (1974-1977) of ambient air lead data from one site on the San Diego Freeway in Los Angeles, California. Particulate lead concentrations were measured at five locations: in the median strip and at distances of 8 and 30 to 35 meters from road edge on both sides of the road. Average lead concentrations at the 35 meter point were two- to four-fold lower than at the 8 meter location (Tiao and Hillmer, 1978). An empirical model involving traffic count and traffic speed, which are related to road emissions, used only wind speed as a predictor of dispersion conditions.

Witz et al. (1982) found that meteorological parameters besides windspeed, such as inversion frequency and duration and ambient temperature, correlate well with ambient levels of lead. At a different site about 100 m from the San Diego freeway in Los Angeles, California, monthly ambient particulate lead and meteorological variables were measured through 1980. Multiple linear regression analysis techniques showed that monthly average surface-based inversion factor, ambient temperature at 6 AM, and wind speed and direction, which were used to develop an empirical model, quite accurately predicted monthly average lead concentrations. In this data set, lead values for December were about five-fold higher than those measured in the May-September summer season, suggesting that seasonal variations in wind directions and the occurrence of surface-based inversions favor high winter lead values. Unusually high early morning temperatures and wind speed during the winter increased dispersion and reduced lead concentrations. The success of this empirical model depends on the interplay of windspeed and atmospheric stability (Witz et al., 1982).

6.2.2.2 Dispersion of Lead on an Urban Scale--In cities, air pollutants including lead that are emitted from automobiles tend to be highest in concentration in high traffic areas. Most U.S. cities have a well-defined central business district (CBD) where lead concentrations are highest. To illustrate the dispersion of lead experienced in cities, two cases are presented below.

Trijonis (1979) reported lead concentrations for 7 sites in St. Louis, Missouri; annual averages for 1977 are shown in Figure 6-1. Values around the CBD are typically 2-3 times greater than those found in the outlying suburbs in St. Louis County to the west of the city. Bradow (1980) presented results from the RAM gaussian plume model (Novak and Turner, 1979) for St. Louis

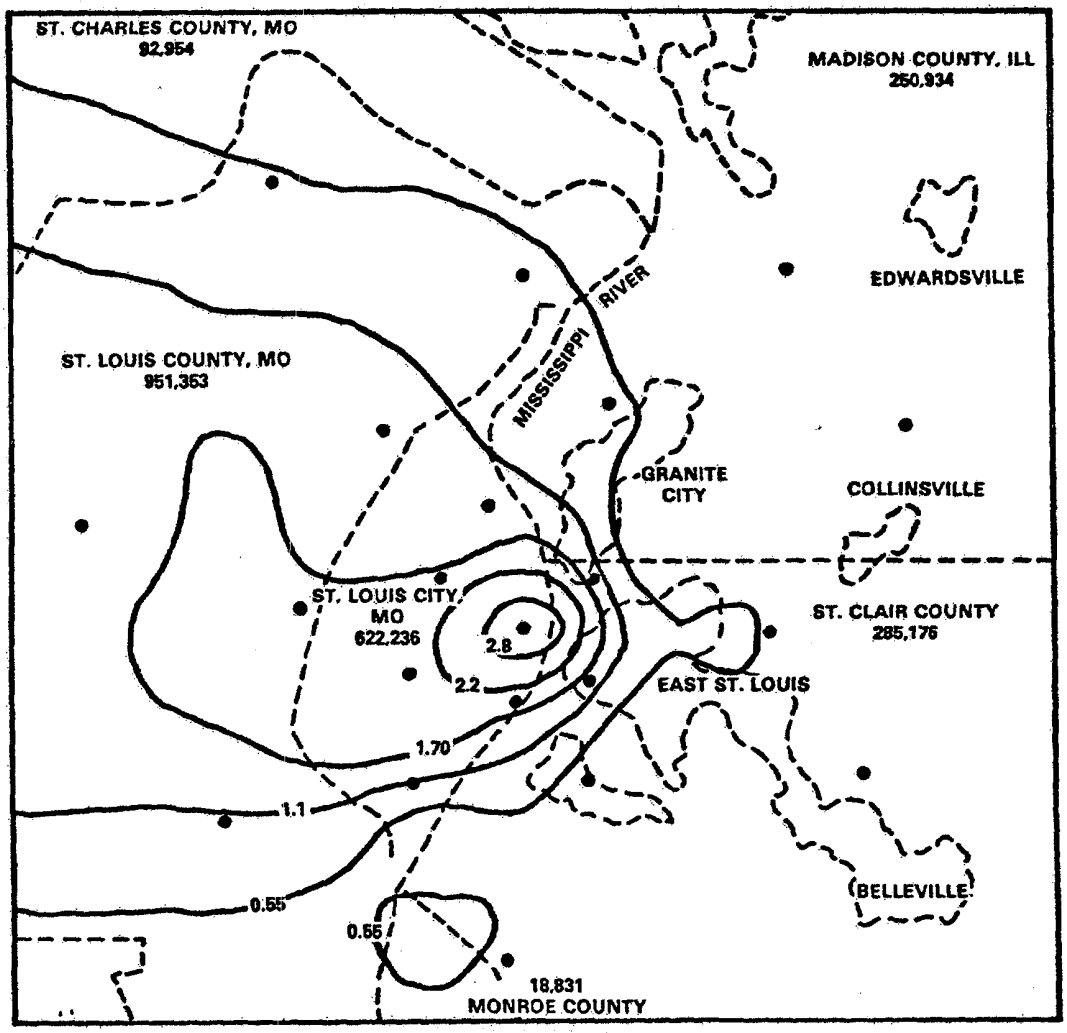

Figure 6-1. Isopleths are shown for annual average particulate lead in $\mu g/m^3$. RAM Model calculations predict lead concentrations in St. Louis for 1977. Numerical values below place names are 1970 population counts for these areas.

Source: Calculated from Bradow (1980) on the basis of a fleet average lead emissions factor of 54 mg/mile for 1977.

for the 1977 calendar year. Figure 6-1 also presents isopleths for lead concentration calculated from that model. The general picture is one of peak concentrations within congested commercial districts which gradually decline in outlying areas. However, concentration gradients are not steep and the whole urban area has levels of lead above 0.5 $\mu g/m^3$.

For the South Coast Basin of Southern California, the area of high traffic density is more widespread than is characteristic of many cities. Ambient concentrations of lead tend to be more uniform. For example, Figures 6-2 and 6-3 show the average daily traffic by grid square and the contour plots of annual average lead concentration, respectively, for 1969 (Kawecki, 1978). In addition, Figure 6-3 shows annual average lead measured at eight sites in the Basin for that year. It is clear that the central portion had atmospheric particulate lead concentrations in the range of 3 $\mu g/m^3$; the outer areas were about 1 to 2 $\mu g/m^3$.

Reiter et al. (1981) have shown similar results for the town of Fort Collins, Colorado for a 5½ hour period in May of 1973. In that study, modeling results showed maximum lead concentrations around 0.25 $\mu g/m^3$ in the center of town which decreased to 0.1 $\mu g/m^3$ in the outermost region. Presumably, still lower values were predicted at more remote locations.

Apparently, then, lead in the air decreases 2½-fold from maximum values in center city areas to well populated suburbs, with a further factor of 2 decrease in the outlying areas. These modeling estimates are generally confirmed by measurement in the cases cited above and in the data presented in Chapter 7.

6.2.2.3 Dispersion from Smelter and Refinery Locations. The 15 mines and 7 primary smelters and refineries shown on Figure 5-3 are not located in urban areas. Most of the 56 secondary smelters and refineries are likewise non-urban. Consequently, dispersion from these point sources should be considered separately, but in a manner similar to the treatment of urban regions. In addition to lead concentrations in air, concentrations in soil and on vegetation surfaces are often used to determine the extent of dispersion away from smelters and refineries.

6.2.2.4 Dispersion to Regional and Remote Locations. Beyond the immediate vicinity of urban areas and smelter sites, lead in air declines rapidly to concentrations of 0.1 to 0.5 $\mu g/m^3$. Two mechanims responsible for this change

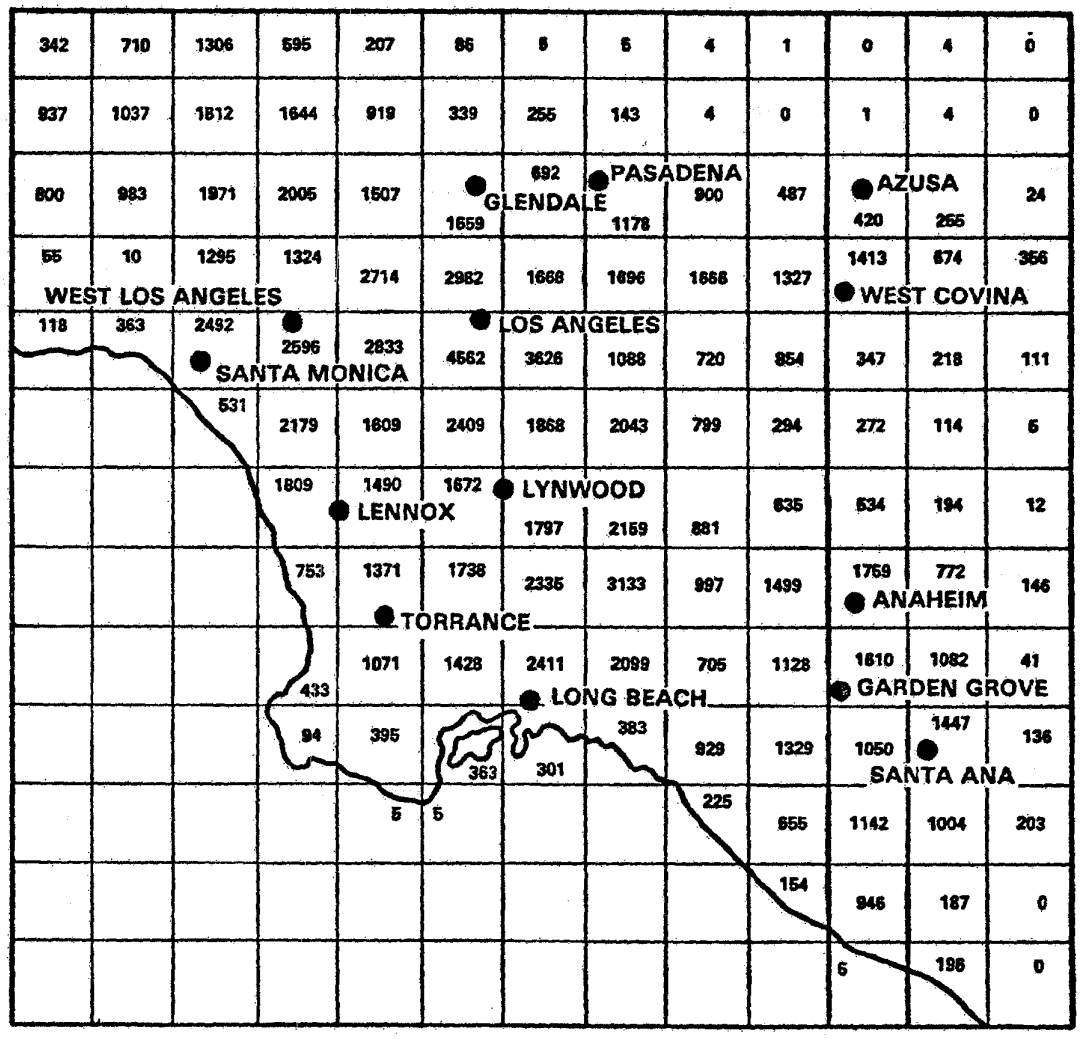

Figure 6-2. Spatial distribution of surface street and freeway traffic in the Los Angeles Basin (10^3 VMT/day) for 1979.

Source: Kawecki (1978).

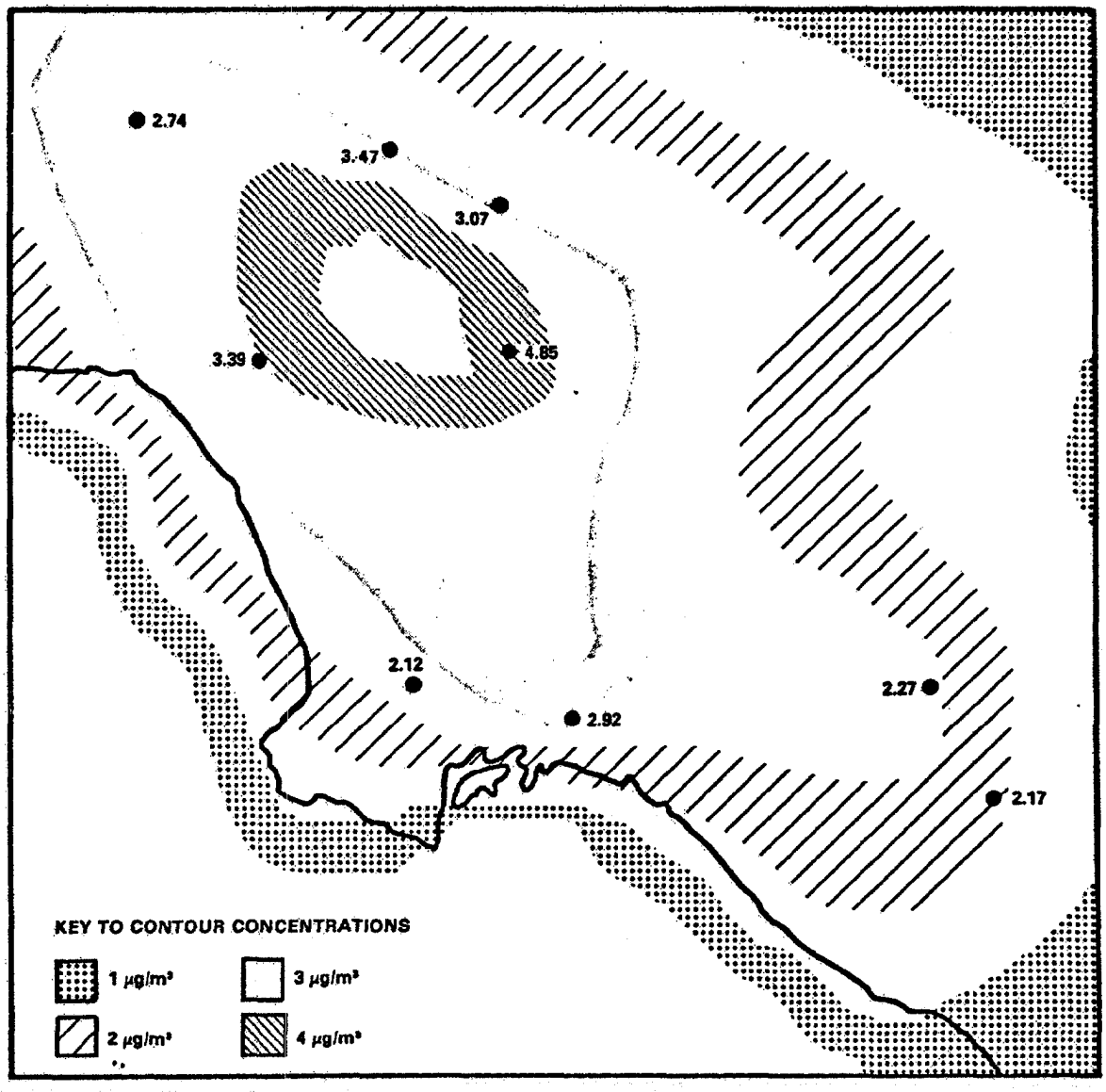

Figure 6-3. Annual average suspended lead concentrations for 1969 in the Los Angeles Basin, calculated from the model of Cass (1975).

Source: Kawecki (1978).

are dilution with clean air and removal by deposition (Section 6.4). In the absence of monitoring networks which might identify the source of lead in remote areas, two techniques of source identification have been attempted. Vector gradient analysis was attempted by Everett et al. (1979) and source reconciliation has been reported by Sievering et al. (1980). A third technique, isotopic composition, has been used to identify anthropogenic lead in air, sediments, soils, plants and animals in urban, rural and remote locations (Chow et al. 1975), but this technique is not discussed here because it provides no information on the mechanism of transport.

During vector gradient analysis, the sampler is oriented in the direction of the incoming wind vector and samples are taken only during the time the wind is within a 30° arc of that vector. Other meteorological data are taken continuously. As the wind vector changes, a different sampler is turned on. A 360° plot of concentration vs. wind direction gives the direction from which the pollutant is arriving at that location. Only one report of this technique occurs in the literature (Everett et al., 1978) and analysis of this experiment was complicated by the fact that in more than half the samples, the lead concentrations were below the detection limit. The study was conducted at Argonne National Laboratory and the results reflected the influence of automobile traffic east and northeast of this location.

Source reconciliation is based on the concept that each type of natural or anthropogenic emission has a unique combination of elemental concentrations. Measurements of ambient air, properly weighted during multivariate regression analysis, should reflect the relative amount of pollutant derived from each of several sources (Stolzenberg et al., 1982). Sievering et al. (1982) used the method of Stolzenberg et al. (1982) to analyze the transport of urban air from Chicago over Lake Michigan. They found that 95 percent of the lead in Lake Michigan air could be attributed to various anthropogenic sources, namely coal fly ash, cement manufacture, iron and steel manufacture, agricultural soil dust, construction soil dust, and incineration emissions. This information alone does not describe transport processes, but the study was repeated for several locations to show the changing influence of each source.

A type of source reconciliation, chemical mass balance, has been used for many years by geochemists in determining the anthropogenic influence on the

global distribution of elements. Two studies which have applied this technique to the transport of lead to remote areas are Murozumi et al. (1969) and Shirahata et al. (1980). In these studies, the influence of natural or crustal lead was determined by mass balance, and the relative influence of anthropogenic lead was determined. In the Shirahata et al. (1980) study, the influence of anthropogenic lead was confirmed quantitatively by analysis of isotopic compositions in the manner of Chow et al. (1975).

Knowledge of lead concentrations in the oceans and glaciers provides some insight into the degrees of atmospheric mixing and long-range transport. Tatsumoto and Patterson (1963a,b), Chow and Patterson (1966) and Schaule and Patterson (1980) measured dissolved lead concentrations in sea water off the coast of California , in the Central North Atlantic (near Bermuda), and in the Mediterranean, respectively. The profiles obtained by Schaule and Patterson (1980) are shown in Figure 6-4. Surface concentrations in the Pacific were found to be higher than those of the Mediterranean or the Atlantic, and decreased abruptly to a relatively constant level of 1 to 2 ng/kg with depth. The vertical gradient was found to be much less in the Atlantic. Based upon the Pacific data, Tatsumoto and Patterson (1963a) estimated an average surface lead concentration of 0.2 µg/kg in the northern hemispheric oceans. Chow and Patterson (1966) revised this estimate downward to 0.07 µg/kg. There appears to be no difference between lead concentrations in deep water in the Atlantic and Pacific. These investigators calculated that industrial lead currently is 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 wet and dry deposition directly into the ocean. Their data suggest considerable contamination of surface waters near shore, diminishing toward the open ocean (Chow and Patterson, 1966).

Duce et al. (1975), Taylor (1964), and Zoller et al. (1974) 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, while the manmade source is particulate air pollution. Enrichment factors for concentrations relative to standard values for the oceans and the crust were calculated (Table 6-2); the mean crustal enrichment factors for the North Atlantic and the South Pole are shown in Figures 6-5 and 6-6. The

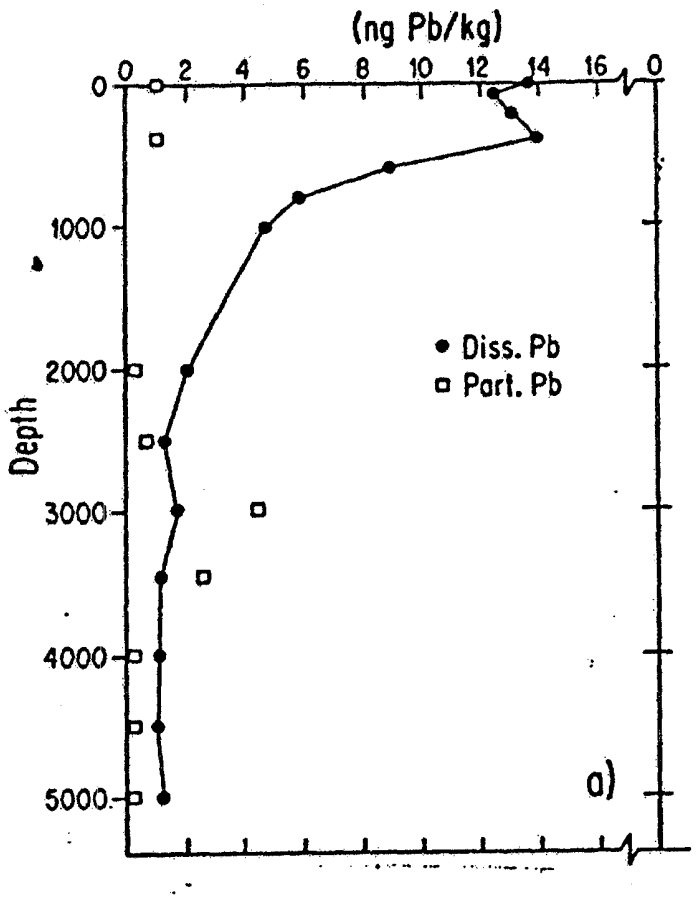

Figure 6-4. Profile of lead concentrations in the central northeast pacific. Values below 1000 m are an order of magnitude lower than reported by Tatsumoto and Patterson (1963) and Chow and Patterson (1966).

Source: Schaule and Patterson (1980).

TABLE 6-2. CONCENTRATION RANGE AND MEAN EF_{crust} VALUES FOR ATMOSPHERIC TRACE METALS COLLECTED OVER THE ATLANTIC NORTH OF 30°N (DUCE ET AL., 1975)

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

[a]Calculated on the basis of the mean crustal abundances of Taylor (1964).

significance of the comparison in Figure 6-6 is that 90 percent of the particulate pollutants in the global troposphere are injected in the northern hemisphere (Robinson and Robbins, 1971). Since the residence times for particles in the troposphere (Poet et al., 1972) are much less than the interhemispheric mixing time, it is unlikely that significant amounts of particulate pollutants can migrate from the northern to the southern hemisphere via the troposphere; however, this does not rule out stratospheric transfer.

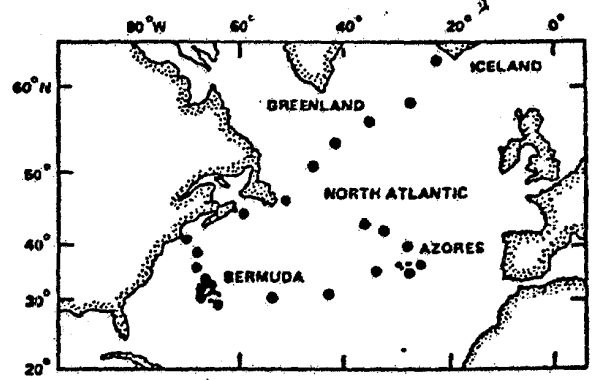

Figure 6-5. Midpoint collection location for atmospheric samples collected from R.V. Trident north of 30 N, 1970—1972.

Source: Duce et al. (1975); Zoller et al. (1974).

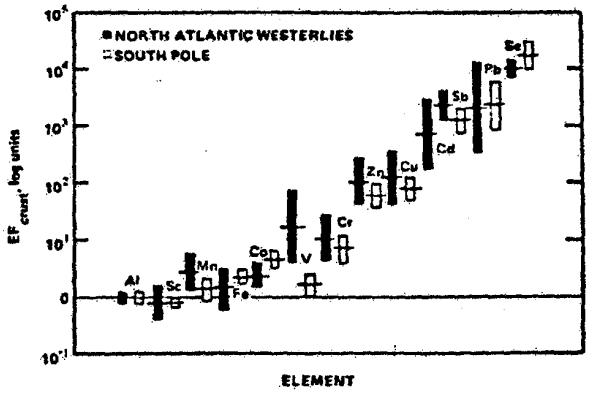

Figure 6-6. The EF_{crust} values for atmospheric trace metals collected in the North Atlantic westerlies and at the South Pole. The horizontal bars represent the geometric mean enrichment factors, and the vertical bars represent the geometric standard deviation of the mean enrichment factors. The EF_{crust}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

Source: Duce et al. (1975); Zoller et al. (1974).

Murozumi et al. (1969) have shown that long-range transport of lead aerosols emitted from automobiles has significantly polluted the polar glaciers. They collected samples of snow and ice from Greenland and the Antarctic. As shown in Figure 6-7, 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 µg/kg) and have risen to 0.2 µg/kg in recent snow.

Jaworowski (1967) found that lead concentrations in two glaciers have increased by a factor of 10 during the last century. The concentrations in the most recent ice layers were extremely high (148 µg/kg). Jaworowski et al. (1975) also studied stable and radioactive pollutants from ice samples from Storbreen glaciers in Norway. The mean stable lead concentration in Storbreen

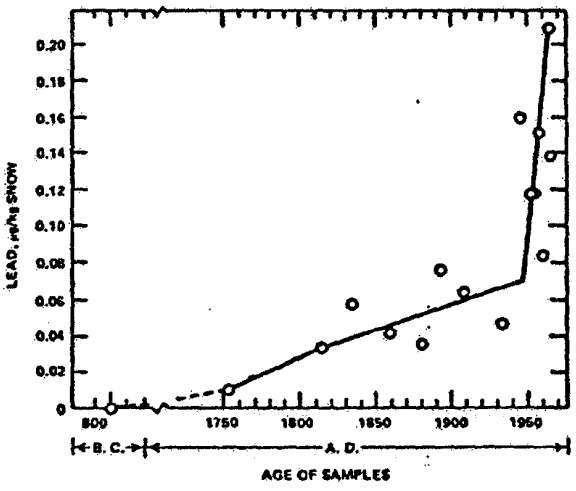

Figure 6-7. Lead concentration profile in snow strata of Northern Greenland.

Source: Murozumi et al. (1969).

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, while the mean concentration in the Polish glacier reached 148 µg/kg. Jaworowski et al. (1975) attributed the large increase of lead concentrations in the Polish glacier to local sources.

Evidence from remote areas of the world suggests that lead and other fine particle components are transported substantial distances, up to thousands of kilometers, by synoptic weather systems. The degree of surface contamination of remote areas with lead probably depends both on weather influences and on the degree of air contamination.

However, even in remote areas, man's primitive activities can play an important role in atmospheric lead levels. Davidson et al. (1982) have shown that there are significant levels of fine particle lead, up to 0.5 µg/m^3, in remote villages in Nepal. Apparently, the source is combustion of dried yak dung, which contains small amounts of naturally occurring lead derived from plant life in those remote valleys. Therefore, it is presently difficult to sort out the importance of anthropogenically generated lead in remote environments.

6.3 TRANSFORMATION OF LEAD IN AIR

6.3.1 Particle Size Distribution

Whitby (1975) placed atmospheric particles into three different size regimes: the nuclei mode (<0.1 µm), the accumulation mode (0.1 to 2 µm) and the large particle mode (>2 µm). Lead particle emissions are generally in the nuclei and large particle modes. Large particles are removed by deposition close to the source and particles in the nuclei mode diffuse to surfaces or agglomerate while airborne to form larger particles of the accumulation mode. Thus it is in the accumulation mode that particles are dispersed great distances.

In Figure 6-8, size distributions for lead particles in automobile exhaust are compared with those found in air samples at a receptor site in Pasadena, California, "not in the immediate influence of traffic" (Huntzicker et al., 1975). The authors conclude that the large particle mode found in

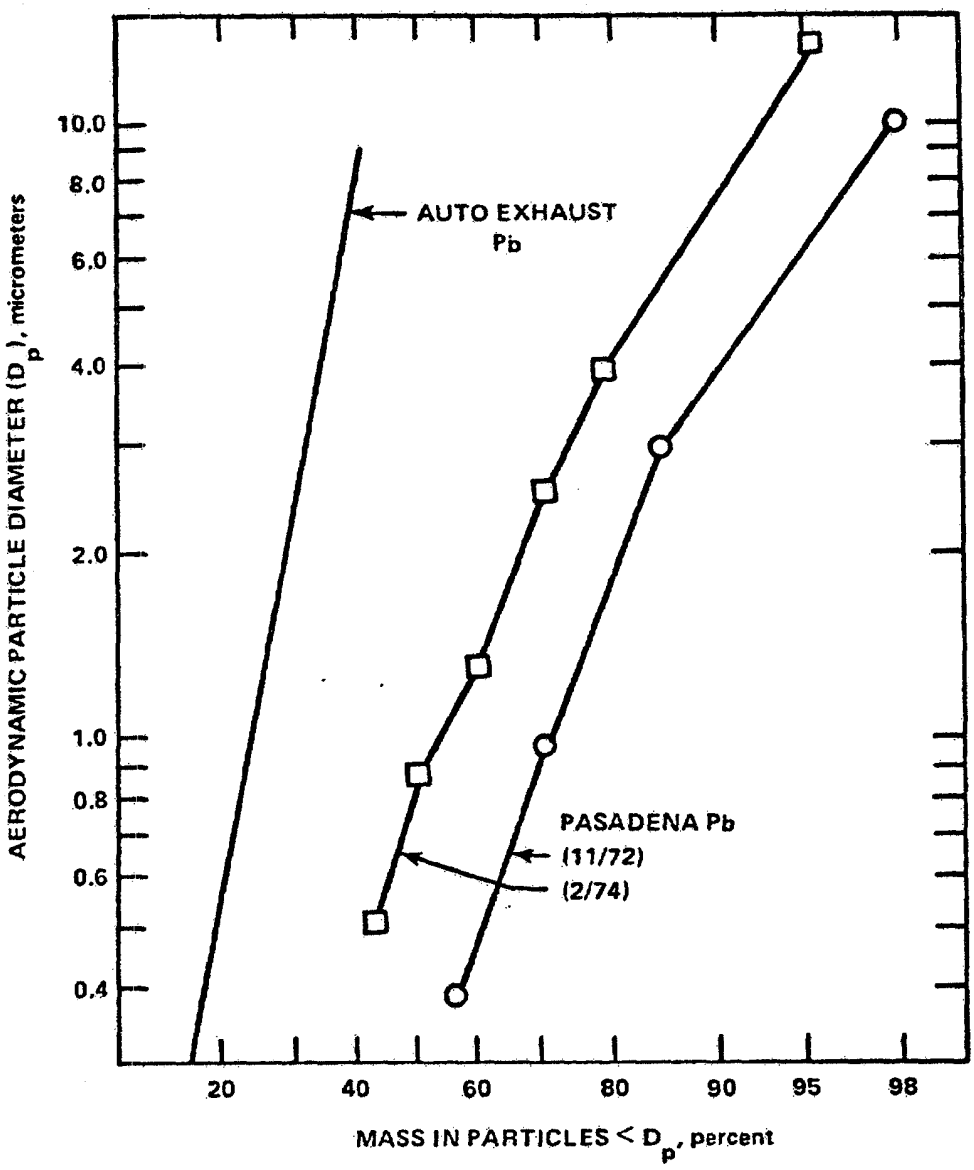

Figure 6-8. Cumulative mass distribution for lead particles in auto exhaust and at an urban site in Pasadena, Calif. some distance from high traffic density roadways.

Source: Huntzicker et al. (1975).

exhaust (> 9 μm) is severely attenuated in ambient air samples. Therefore, large particle lead must be deposited near roadways. Similar data and conclusions had been reported earlier by Daines et al. (1970).

Pierson and Brachaczek (1976) reported particle size distributions that were larger in ambient air than in a roadway tunnel, where vehicle exhaust must be dominant (see Figure 6-9). The large particles may have deposited in the roadway itself and small particles may have agglomerated during transport from the roadway to the immediate roadside. Since 40 to 1,000 μm particles are found in gutter debris (Figure 6-10), deposition of large particles appears confirmed.

Little and Wiffen (1976) reported a mass median equivalent diameter (MMED) for lead of 0.1 μm in the roadway but 0.3 μm 1 m from the road edge in an intercity expressway in England. Further, particle size distributions reported by Huntzicker et al. (1975) show bimodal distributions for on-roadway samples, with peak mass values at about 0.1 and 10 μm. For off-roadway Pasadena samples, there is no evidence of bimodality and only a broad maximum in lead mass between 0.1 and 1 μm.

In cities or in rural areas, there is a remarkable consistency in lead particle size range. For example, Robinson and Ludwig (1964) report cascade impactor MMED values for lead ranging from 0.23 to 0.3 μm in six U.S. cities and three rural areas as shown in Table 6-3. Stephens et al. (1978) have reported dichotomous sampler data for six U.S. cities, as shown in Table 6-4, and Stephens et al. (1980, 1982) have made similar measurements in remote locations. Virtually every other study reported in the literature for Europe, South America, and Asia has come to the conclusion that ambient urban and rural air contains predominantly fine particles (Cholak et al., 1968; DeJonghe and Adaro, 1980; Dwardo and Aragon, 1982; Lee et al., 1968; Nay Htun and Ramachandra, 1977).

It appears that lead particle size distributions are stabilized close to roadways and remain constant with transport into remote environments (Gillette and Winchester, 1972).

6.3.2 Organic and Vapor Phase Lead in the Air

Although lead additives used in gasoline are less volatile than gasoline itself (see Chapter 3), small amounts may escape to the atmosphere by evaporation from fuel systems or storage facilities. Tetraethyllead (TEL) and

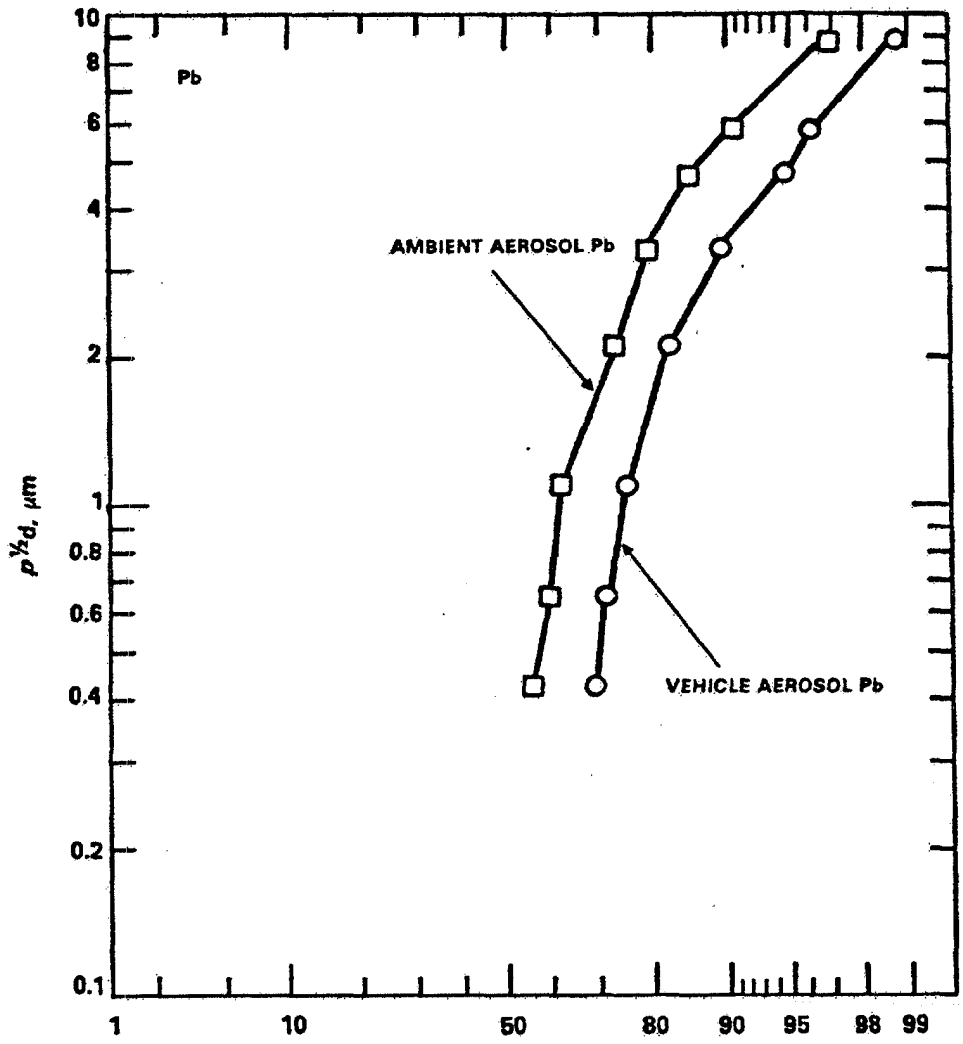

Figure 6-9. Particulate lead size distribution measured at the Allegheny Mountain Tunnel, Pennsylvania Turnpike, 1975.

Source: Pierson and Brachaczek (1976).

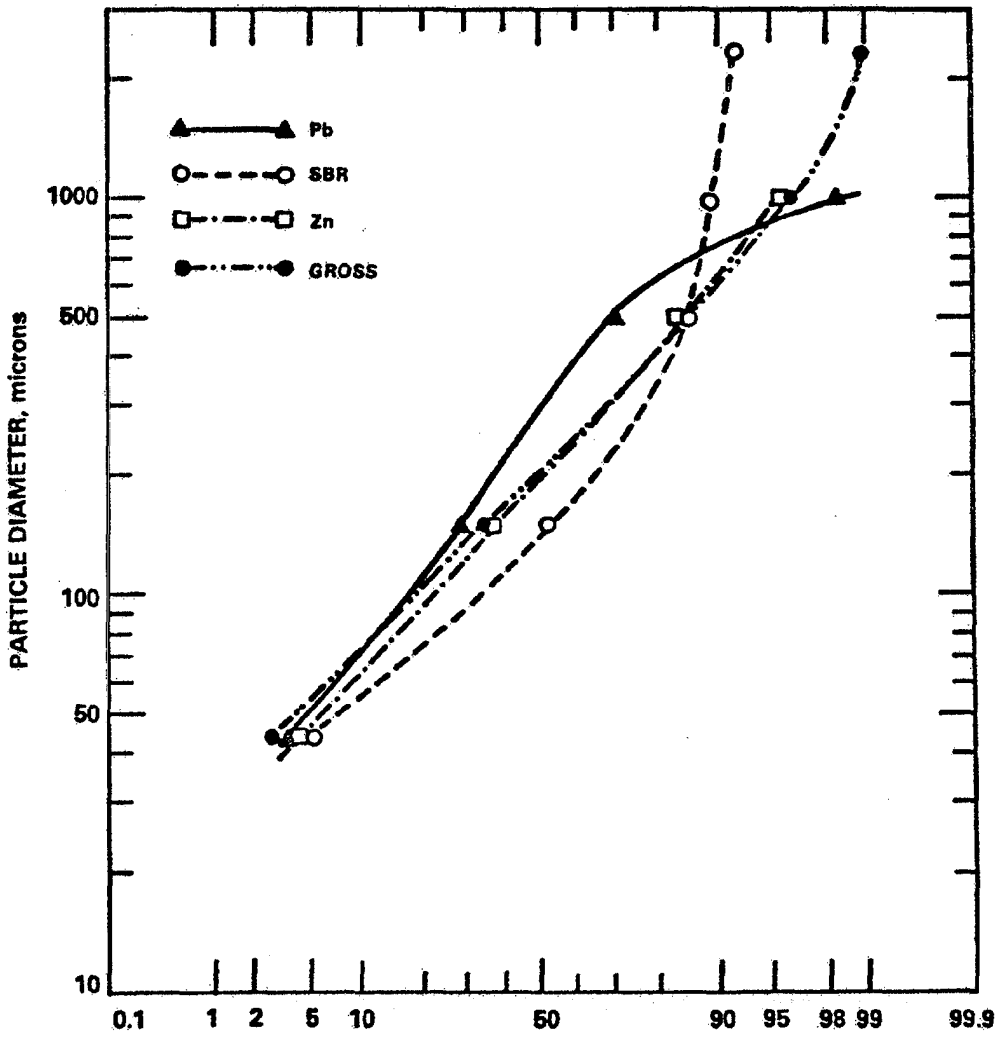

Figure 6-10 Particle size distributions of substances in gutter debris, Rotunda Drive, Dearborn, Michigan.

Source: Pierson and Brachaczek (1976).

TABLE 6-3. COMPARISON OF SIZE DISTRIBUTIONS OF LEAD-CONTAINING PARTICLES IN MAJOR SAMPLING AREAS (ROBINSON AND LUDWIG, 1964)

Sample area	No. of samples	Distribution by particle size, μm					
		25%[c]		MMED[a]		75%[c]	
		Avg.	Range	Avg.	Range	Avg.	Range
Chicago	12	0.19(7)[b]	0.10-0.29	0.30	0.16-0.64	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	

[a]MMED = mass median equivalent diameter.

[b]Numbers in parentheses indicate number of samples available for a specific value when different from total number of samples.

[c]% refers to the percentile of the mass distribution. Thus in the column labeled 25% are the particle sizes at which 25% of the particle mass is in smaller sizes. Similarly, the 75% column contains values of particle sizes at which 75% of the mass is in smaller sizes.

TABLE 6-4. DISTRIBUTION OF LEAD IN TWO SIZE FRACTIONS AT SEVERAL SITES IN THE UNITED STATES (nanograms/m^3)

Location		Fine	Coarse	F/C Ratio
New York, NY	2/1977	1057	177	6.0
Philadelphia, PA	23/1977	945	170	5.6
Charlestown, W. WA	4-8/1976	623	134	4.6
St. Louis, MO	12/1975	833	243	3.4
Portland, OR	12/1977	866	174	5.0
Glendora, CA	3/1977	614	92	6.7
Average				5.2

Source: Stevens et al. (1978)

tetramethyllead (TML) are light-sensitive and undergo photochemical decomposition when they reach the atmosphere (Huntzicker et al., 1975; National Air Pollution Control Administration, 1965). The lifetime of TML is 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 (Edwards, 1974). Laveskog (1971) found that transient peak concentrations of lead alkyls up to 5000 $\mu g/m^3$ 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 $\mu g/m^3$ of air, a peak of about 0.5 $\mu g/m^3$ 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. Harrison et al. (1975) found levels as high as 0.59 $\mu g/m^3$ (9.7 percent of total lead) at a busy gasoline service station in England. Nielsen et al. (1979) using GC-MS techniques, found elevated levels (0.1 $\mu g/m^3$) of TML in city streets in Denmark and Norway. These authors attributed the finding to the volatility of TML compared with TEL.

A number of studies have used gas absorbers behind filters to trap vapor-phase lead compounds. Because it is not clear that all the lead captured in the backup traps is, in fact, in the vapor phase in the atmosphere, "organic" or "vapor-phase" lead is an operational definition in these studies. Purdue (1973) measured both particulate and organic lead in atmospheric samples. He found that the particulate lead fraction was about 20 times larger than vapor-phase (presumably organic) lead in most samples. The results are consistent with the studies of Huntzicker et al. (1975) who reported an organic component of 6 percent of the total airborne lead in Pasadena for a 3-day period in June 1974, and of Skogerboe (1975), who measured fractions in the range of 4 to 12 percent at a site in Fort Collins, Colorado. It is noteworthy, however, that in an underground garage total lead concentrations are approximately five times those in the urban areas, and the percentage of organic lead increases to approximately 17.

Harrison et al. (1979) report typical organolead/total lead ratios in ambient urban air of 1 to 6 percent. Rohbock et al. (1980) reported higher ratios, up to 20 percent, but the data and interpretations have been questioned by Harrison et al. (1980). Rohboch et al. (1980) and DeJonghe and Adams (1980) report one to two orders of magnitude decrease in organolead concentrations from the central urban areas to residential areas.

6.3.3 Chemical Transformations of Lead in Air

Lead is emitted into the air from automobiles as lead halides and as double salts with ammonium halides. From mines and smelters, $PbSO_4$, $PbO \cdot PbSO_4$, and PbS appear to be the dominant species. In the atmosphere, lead is present mainly as the sulfate with minor amounts of halide. It is not completely clear just how the chemical composition changes in transport.

Biggins and Harrison (1978, 1979) have studied the chemical composition of lead particles in exhaust and in city air in England by X-ray diffractometry. These authors reported predominant exhaust forms including PbBrCl, $PbBrCl \cdot 2NH_4Cl$, and $\alpha\text{-}2PbBrCl \cdot NH_4Cl$, in substantial agreement with the earlier studies of Hirschler and Gilbert (1964) and Ter Haar and Bayard (1972).

At sampling sites in Lancaster, England, Biggins and Harrison (1978, 1979) found $PbSO_4 \cdot (NH_4)_2SO_4$, and $PbSO_4 \cdot (NH_4)_2BrCl$ together with minor amounts of the lead halides and double salts found in auto exhaust. These authors

suggested that emitted lead halides react with acidic gases or aerosol components (SO_2 or H_2SO_4) on filters to form substantial levels of sulfate salts. It is not clear whether these processes occur to a greater extent in the atmosphere or on filters.

Several authors have reported loss of halide, preferentially bromine, from lead salts in atmospheric transport (Dzubay and Stevens, 1973; Pierrard, 1969; Ter Haar and Bayard, 1971). Both photochemical decomposition (Lee et al., 1971; Ter Haar and Bayard, 1971) and acidic gas displacement (Robbins and Snitz, 1970) have been postulated as mechanisms. Chang et al. (1972) have reported only very slow decomposition of lead bromochloride in natural sunlight; currently the acid displacement of halide seems to be the most likely mechanism. O'Connor et al. (1980) have reported no loss in bromine in comparison of roadside and suburban-rural aerosol samples from western Australia; low levels of SO_2 and sulfate aerosol could account for that result.

Habibi et al. (1970) studied the composition of auto exhaust particles as a function of particle size. Their main conclusions follow:

1. Chemical composition of emitted exhaust particles is related to particle size.

    a. 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 aerosolized 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 (15 to 17 percent) lead oxide (PbO) occurring as the $2PbO \cdot PbBrCl$ 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.)

    b. PbBrCl is the major lead salt in particles of 2 to 10 μm equivalent diameter, with $2PbBrCl \cdot NH_4Cl$ present as a minor constituent.

    c. Submicrometer-sized lead salts are primarily $2PbBrCl \cdot NH_4Cl$.

2. Lead-halogen molar ratios in particles of less than 10 μm MMED indicate that much more halogen is associated with these solids than the amount expected from the presence of $2PbBrCl \cdot NH_4Cl$, as identified by X-ray diffraction. This is particularly true for particles in the 2 to 0.5 μm size range.

3. There is considerably more soot and carbonaceous material associated with fine-mode particles than with coarse mode 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.

4. Particulate matter emitted under typical driving conditions is rich in carbonaceous-type material. There is substantially less such material emitted under continuous hot operation.

5. Only small quantities of $2PbBrCl \cdot NH_4Cl$ were found in samples collected at the tailpipe from the hot exhaust gas. Its formation therefore takes place primarily during cooling and mixing of exhaust with ambient air.

Foster and Lott (1980) have studied the composition of lead compounds associated with ore handling, sintering, and blast furnace operations around a lead smelter in Missouri by X-ray diffractometry . PbS was the main constituent of those samples associated with ore handling and fugitive dust from open mounds of ore concentrate. The major constituents from sintering and blast furnace operations appeared to be $PbSO_4$ and $PbO \cdot PbSO_4$, respectively.

6.4 REMOVAL OF ATMOSPHERIC LEAD

6.4.1 Dry Deposition

Before atmospheric lead can have any effect on organisms or ecosystems, it must be transferred from the air to a surface. For natural ground surfaces and vegetation, this process may be either dry or wet deposition.

6.4.1.1 Mechanisms of dry deposition. Transfer by dry deposition requires that the particle move from the main air stream through the boundary layer to a surface. The boundary layer is defined as the region of minimal air flow immediately adjacent to that surface. The thickness of the boundary layer depends mostly on the windspeed and rooughness of the surface.

Airborne particles do not follow a smooth, straight path in the air stream. On the contrary, the path of a particle may be affected by micro-turbulent air currents, gravitation, or its own inertia. There are several mechanisms which alter the particle path sufficient to cause transfer to a surface. These mechanisms are a function of particle size, windspeed and surface characteristics.

Particles larger than a few micrometers in diameter are influenced primarily by sedimentation, where the particle accelerates downward until aerodynamic drag is exactly balanced by gravitational force. The particle

continues at this velocity until it reaches a surface. Sedimentation is not influenced by windspeed or surface characteristics. Particles moving in an airstream may be removed by impaction whenever they are unable to follow the air stream around roughness elements of the surface, such as leaves, branches or tree trunks. In this case, the particle moves parallel to the air stream and strikes a surface perpendicular to the air stream. A related mechanism, turbulent inertial deposition, occurs when a particle encounters turbulence within the airstream causing the particle to move perpendicular to the air stream. It may be then strike a surface parallel to the air stream. In two mechanisms, wind eddy diffusion and interception, the particle remains in the air stream until it is transferred to a surface. With wind eddy diffusion, the particle is transported downward by turbulent eddies. Interception occurs when the particle in the air stream passes within one particle radius of a surface. This mechanism is more a function of particle size than windspeed. The final mechanism, Brownian diffusion, is important for very small particles at very low windspeeds. Brownian diffusion is motion, caused by random collision with molecules, in the direction of a decreasing concentration gradient.

Transfer from the main air stream to the boundary layer is usually by sedimentation or wind eddy diffusion. From the boundary layer to the surface, transfer may be by any of the six mechanisms, although those which are independent of windspeed (sedimentation, interception, Brownian diffusion) are more likely.

6.4.1.2 Dry deposition models. A particle influenced only by sedimentation may be considered to be moving downward at a specific velocity usually expressed in cm/sec. Similarly, particles transported to a surface by any mechanism are said to have an effective deposition velocity (V_d) which is measured not by rate of particle movement but by accumulation on a surface as a function of air concentration. This relationship is expressed in the equation:

$$V_d = J/C$$

where J is the flux or accumulation expressed in $ng/cm^2 \cdot s$ and C is the air concentration in ng/cm^3. The units of V_d become cm/sec.

Several recent models of dry deposition have evolved from the theoretical discussion of Fuchs (1964) and the wind tunnel experiments of Chamberlain

(1967). From those early works, it was obvious that the transfer of particles from the atmosphere to the earth's surface involved more than rain or snow. The models of Slinn (1982) and Davidson et al. (1982) are particularly useful for lead deposition and were strongly influenced by the theoretical considerations of Friedlander (1977). Slinn's model considers a multitude of vegetation parameters to find several approximate solutions for particles in the size range of 0.1 to 1.0 μm. In the absence of appropriate field studies, Slinn (1982) estimates deposition velocities of 0.01 to 0.1 cm/sec.

The model of Davidson et al. (1982) is based on detailed vegetation measurements and wind data to predict a V_d of 0.05 to 1.0 cm/sec. Deposition velocities are specific for each vegetation type. This approach has the advantage of using vegetation parameters of the type made for vegetation analysis in ecological studies (density, leaf area index, height, diameter) and thus may be applicable to a broad range of vegetation types for which data are already available in the ecological literature.

Both models show a decrease in deposition velocity with decreasing particle size down to about 0.1 to 0.2 μm, followed by an increase in V_d deposition velocity with decreasing diameter from 0.1 to 0.001 cm/sec. On a log plot of diameter vs. V_d, this curve is v-shaped, and the plots of several vegetation types show large changes (10 X) in minimum V_d, although the minima commonly occur at about the same particle diameter (Figure 6-11).

In summary, it is not correct to assume that air concentration and particle size alone determine the flux of lead from the atmosphere to terrestrial surfaces. The type of vegetation canopy and the influence of the canopy on windspeed are important predictors of dry deposition. Both of these models predict deposition velocities more than one order of magnitude lower than reported in several earlier studies (e.g., Schmel and Hodgson, 1976).

6.4.1.3 Calculation of dry deposition. The data required for calculating the flux of lead from the atmosphere by dry deposition are leaf area index (LAI), windspeed and air concentration by particle size. The LAI should be total surface rather than upfacing surface, as used in photosynthetic productivity measurements. Leaf area indices should also be expressed for the entire community rather than by individual plant, in order to incorporate variations in density.

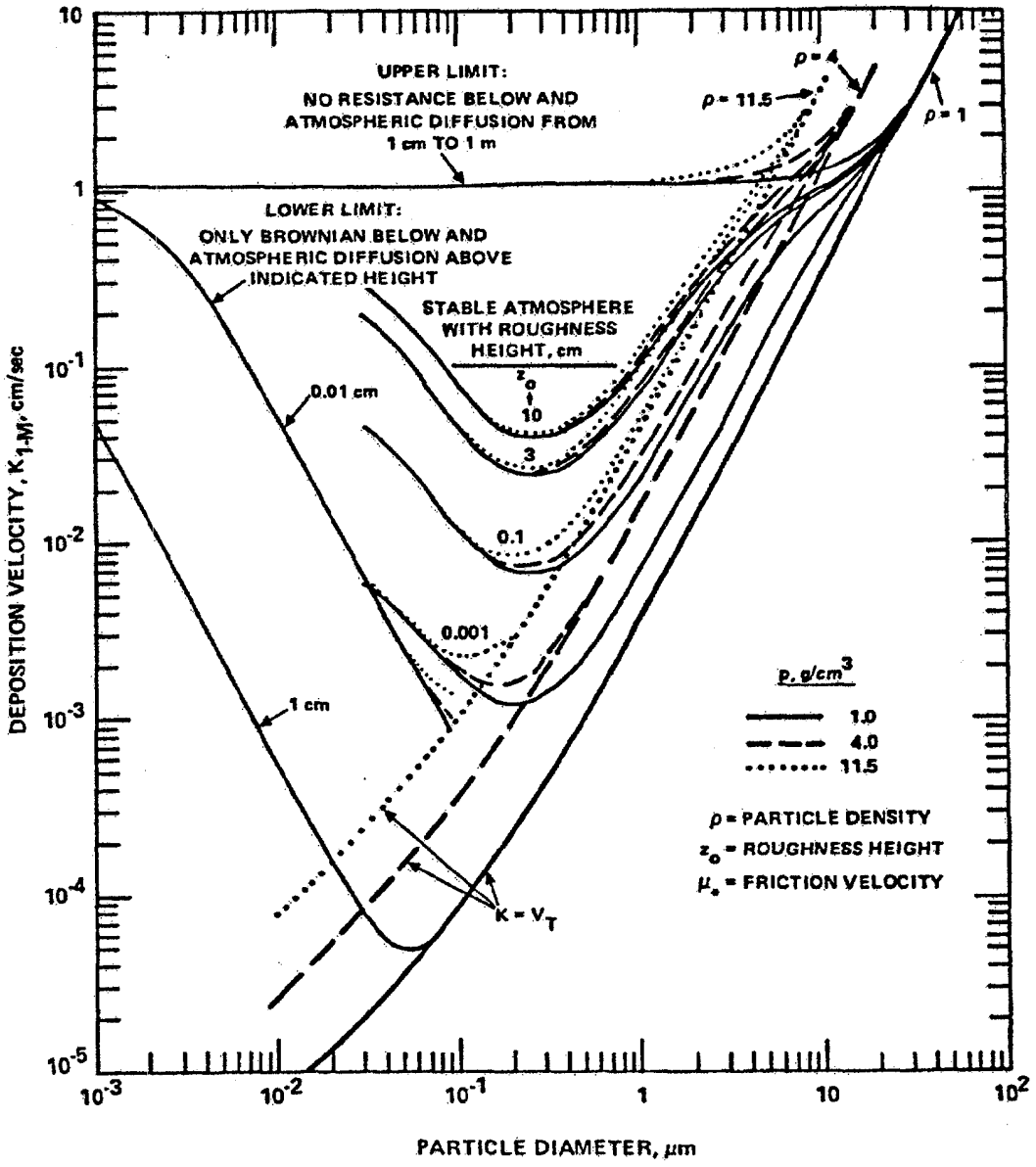

Figure 6-11. Predicted deposition velocities at 1 m for $\mu* = 30$ cm s^{-1} and particle densities of 1, 4, and 11.5 g cm^{-3}.

Source: Sehmel (1980).

6.4.1.4 Field measurements of dry deposition on surrogate and natural surfaces.

Several investigators have used surrogate surface devices similar to those described in Chapter 4. These data are summarized in Table 6-5. The few studies available on deposition on vegetation surfaces show deposition rates comparable to those of surrogate surfaces and deposition velocities in the range predicted by the models discussed above. In Section 6.4.3, these data are used to make a crude estimate in an effort to show that global emissions are in balance with global deposition. It is reasonable that future refinements of field measurements and model calculations will permit more accurate estimates of dry deposition in specific regions or under specific environmental conditions.

6.4.2. Wet Deposition: Removal of Lead Particles from Air by Precipitation

Precipitation, or wet deposition, removal processes include rainout and washout. Rainout occurs when particulate matter is present in the supersaturated environment of a growing cloud. The small particles (0.1 to 0.2 μm) act as nuclei for the formation of small droplets, which grow into raindrops (Junge, 1963). Droplets also collect particles under 0.1 μm 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. Washout, on the other hand, 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. As with dry deposition, wet deposition influences both the transfer of lead to a surface and lead concentration in the atmosphere.

Results on scavenging of lead by falling rain are conflicting. In a laboratory study employing simulated rainfall, Edwards (1975) found that less than 1 percent of auto exhaust lead particles could be removed by washout. However, Ter Haar et al. (1967) found that intense rainfall removed most of the atmospheric lead. As a result, the lead content of rain water is smaller for intense rainfall than in steady showers, presumably because the air contains progressively less lead. It is not clear which of the two phenomena, nucleation or washout, is responsible.

TABLE 6-5. SUMMARY OF SURROGATE AND VEGETATION SURFACE DEPOSITION MEASUREMENTS

Depositional Surface	Flux ng Pb/cm^2·day	Air Conc ng/m^3	Deposition Velocity cm/sec	Reference
tree leaves (Paris)	0.38		0.086	1
tree leaves (Tennessee)	0.29-1.2			2
plastic disk (remote California)	0.02-0.08	13-31	0.05-0.4	3
plastic plates (Tennessee)	0.29-1.5	110	0.05-0.06	4
tree leaves (Tennessee)		110	0.005	4
snow (Greenland)	0.004	0.1-0.2	0.1	5
grass (Pennsylvania)		590	0.2-1.1	6

1. Servant, 1975
2. Lindbert et al., 1982
3. Elias and Davidson, 1980
4. Lindberg and Harriss, 1981
5. Davidson et al., 1981
6. Davidson et al., 1982

Lazrus et al. (1970) 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, implying the existence of a process by which lead is depleted after precipitation reaches the ground. Russian studies (Konalov et al., 1966) point to the insolubility of lead compounds in surface waters and acknowledge this removal by natural sedimentation and filtration.

Atkins and Kruger (1968) conducted a field sampling program in Palo Alto, California, to determine the effectiveness of sedimentation, impaction, rainout, and washout in removing lead 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 $\mu g/m^3$ to a maximum of 19 $\mu g/m^3$ in the fall and winter seasons, and were a maximum of 9.3 $\mu g/m^3$ in the spring. During periods of light rainfall in the spring, the maximum concentration observed was 7.4 $\mu g/m^3$. More than 90 percent of the lead pollutants reaching the surface during the one-year sampling period were collected in dry fallout. Wet deposition (approximately 33 cm of rain per year) accounted for 5 to 10 percent of the lead removal at the sampling sites.

Andren et al. (1975) evaluated the contribution of wet and dry deposition of lead in a study of the Walker Branch Watershed in Oak Ridge, Tennessee, during the period June 1973 to July 1974. The mean precipitation in the area is approximately 130 cm/yr. Results reported for the period January through June 1974 are presented in Table 6-6. Rainfall, or wet deposition, contributed approximately 67 percent of the total deposition for the period.

TABLE 6-6. DEPOSITION OF LEAD AT THE WALKER BRANCH WATERSHED, 1974 (ANDREN ET AL., 1975)

Period	Lead deposition (g/ha)	
	Wet	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

[a]Total deposition ~172 g/ha. Wet deposition ~67 percent of total.

6.4.3 Global Budget of Atmospheric Lead

The geochemcial mass balance of lead in the atmosphere may be determined from quantitative estimates of inputs and outputs. Inputs are from natural and anthropogenic emissions described in Chapter 5. They amount to 450,000 to 475,000 metric tons annually (Nriagu, 1979). There are no published estimates of global deposition from the atmosphere, but the data provided in sections 6.4.1 and 6.4.2 can provide a reasonable basis on which to make an estimate. Table 6-7 shows an average concentration of 0.4 μg Pb/kg precipitation. The total mass of rain and snowfall is 5.2×10^7kg, so the amount of lead removed by wet deposition is approximately 208,000 MT/yr. For dry deposition, a crude estimate may be derived by dividing the surface of the earth into three types based on surface roughness or leaf area index. Oceans, polar regions and deserts have a very low surface roughness and can be assigned a deposition velocity 0.01 cm/sec, which gives a flux of 0.2 $\mu g/m^2 \cdot yr$ assuming 75 ng Pb/m^3 air concentration. Grasslands, tundra and other areas of low-lying vegetation might have a somewhat higher deposition velocity, forests would have the highest. Values of 0.3 and 0.65 can be assigned to these two vegetation types, based on the data of Davidson et al. (1982). Whittaker (1975) gives the global surface area of each of the three types to be 405, 46, and 59 x $10^{12}km^2$, respectively. In the absence of data on global distributions of air concentrations of lead, an average of 0.075 $\mu g/m^3$ is assumed. Multiplying air concentrations by deposition velocity gives the deposition flux for each vegetation type shown on Table 6-7. The combined wet and dry deposition is 410,000 MT, which compares favorably with the estimated 450,000 to 475,000 MT emissions.

Mass balance calculations of this type serve to accentuate possible errors in the data which are not otherwise obvious. The data used above are not held to be absolutely firm. Certainly, more refined estimates of air concentrations and deposition velocities can be made in the near future. On the other hand, the calculations above show some published calculations to be unreasonable. In particular, values of 36 μg/kg rain reported by Lazrus (1970) would account for more than 50 times the total global emissions. Likewise, deposition fluxes of 0.95 $\mu g/cm^2 \cdot$ reported by Jaworowski (1981) would account for 10 times global emissions. Chemical budgets are an effective means of establishing reasonable limits to environmental lead data.

TABLE 6-7. ESTIMATED GLOBAL DEPOSITION OF ATMOSPHERIC LEAD

	Deposition from Atmosphere		
	Mass 10^{17} kg/yr	Concentration 10^{-6} g/kg	Deposition 10^{6} kg/yr
Wet			
To oceans	4.1	0.4	164
To continents	1.1	0.4	44
Dry	Area 10^{12} km^2	Deposition rate 10^{-3} g/m^2·yr	Deposition 10^{6} kg/yr
To oceans, ice caps, deserts	405	0.2	89
Grassland, agricultural areas, and tundra	46	0.71	33
Forests	59	1.5	80
		Total dry:	202
		Total wet:	208
		Global:	410

6.5 TRANSFORMATION AND TRANSPORT IN OTHER ENVIRONMENTAL MEDIA

6.5.1 Soil

Lead occurs in the mineral structure of inorganic parent rock fragments, in complexes of iron and manganese hydrous oxides and humic substances, in solution with soil moisture, or as an insoluble precipitate, generally of the carbonate, phosphate, or sulfate form. Of these categories, the most mobile form is in soil moisture, where lead can move freely into plant roots or soil microorganisms with dissolved nutrients. The least mobile is parent rock material, where lead may be bound within crystalline structures over geologic periods of time. Intermediate are the lead complexes and precipitates. Transformation from one form to another depends on the chemical environment of the soil. For example at pH 6 to 8, insoluble organic-Pb complexes are favored if sufficient organic matter is available; otherwise hydrous oxide complexes may form or the lead may precipitate with the carbonate or phosphate ion. In the pH range of 4 to 6, the ionic form of lead in solution is favored, along with voluble organic-Pb complexes. Soils outside the pH range of 4 to 8 are rare and are not considered in this report.

Soil transformation processes affect the mobility of lead by converting it from a soluble to an insoluble form, or vice versa. Because transformation toward insoluble forms is far more common, these processes are generally considered immobilization processes. It must be recognized, however, that these are equilibrium processes, even though the equilibrium is shifted toward the insoluble form so strongly that 99.9 percent of the lead may be immobilized. It will be shown in Chapter 8 that 0.01 percent of the 10,000 µg/g total soil lead is still of significance to plant and microorganisms when mobilized in soil moisture.

Atmospheric lead may enter the soil system as wet or dry deposition by mechanisms described earlier. There is good evidence that this lead enters as $PbSO_4$ or is rapidly converted to $PbSO_4$ at the soil surface (Olson and Skogerboe, 1975). Lead sulfate is relatively soluble and thus could remain mobile if not transformed. Lead could be immobilized by precipitation as less soluble compounds [$PbCO_3$, $Pb(PO_4)_2$], by ion exchange with hydrous oxides or clays, or by chelation wtih humic and fulvic acids. Santillan-Medrano and Jurinak (1975) discussed the possibility that the mobility of lead is regulated by the formation of $Pb(OH)_2$, $Pb_3(PO_4)_2$, $Pb_5(PO_4)_3OH$, and $PbCO_3$.

This model, however, did not consider the possible influence of organic matter on lead immobilization. Zimdahl and Skogerboe (1977), on the other hand, found lead varied linearly with cation exchange capacity (CEC) of soil at a given pH, and linearly with pH at a given CEC (Figure 6-12).

Some of the possible mechanisms mentioned above can be eliminated by experimental evidence. If surface adsorption on clays plays a major role in lead immobilization, then the capacity to immobilize should vary directly with the surface-to-volume ratio. Two separate experiments by Zimdahl and Skogerboe (1977) using the nitrogen BET method and size fractionation techniques demonstrated that this was not the case. They also showed that precipitation as lead phosphate or lead sulfate is not significant, although carbonate precipitation can be important in soils that are are carbonaceous in nature or to which lime ($CaCO_3$) has been added.

Of the two remaining processes, lead immobilization is more strongly correlated with organic chelation than with hydrous oxide formation (Zimdahl and Skogerboe, 1977). It is possible, however, that chelation with fulvic and humic acids is catalyzed by the presence of iron and manganese oxides (Saar and Weber, 1982). This would explain the positive correlation for both mechanisms observed by Zimdahl and Skogerboe (1977).

If organic chelation is the correct model of lead immobilization in soil, then several features of this model merit further discussion. First, the total capacity of soil to immobilize lead can be predicted from the linear relationship developed by Zimdahl and Skogerboe (1977) (Figure 6-12) based on the equation:

$$N = 2.8 \times 10^{-6} (A) + 1.1 \times 10^{-5} (B) - 4.9 \times 10^{-5}$$

where N is the saturation capacity of the soil expressed in moles/g soil, A is the cation exchange capacity (CEC) of the soil in meq/100 g soil and B is the pH in normal pH units. Because the CEC of soil is more difficult to determine than total organic carbon, it is useful to define the relationship between CEC and organic content. Pratt (1957) and Klemmedson (1959) found a linear correlation between CEC and organic carbon for soils of similar sand, silt, and clay content. The data of Zimdahl and Skogerboe (1977) also show this relationship when grouped by soil type. They show that sandy clay loam with

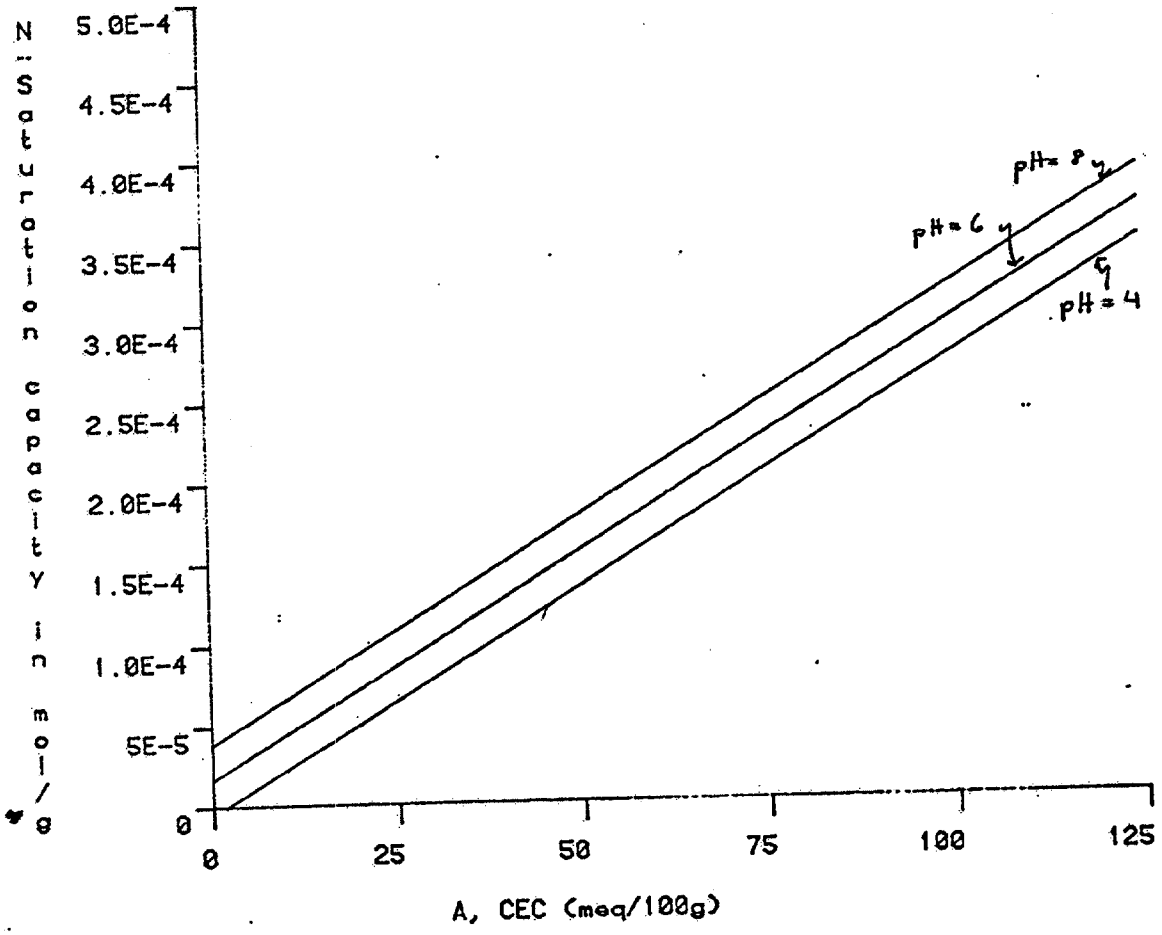

Figure 6-12. Variation of lead saturation capacity with cation exchange capacity in soil at selected pH values.

Source: Data from Zimdahl and Skogerboe (1977)

an organic content of 1.5 percent might be expected to have a CEC of 12 meq/100 g. From the equation, the saturation capacity for lead in soil of pH 5.5 would be 45 μmoles/g soil or 9300 μg/g. The same soil at pH 4.0 would have a total capacity of 5900 μg/g.

The soil humus model also facilitates the calculation of lead in soil moisture using values available in the literature for conditional stability constants with fulvic acid. The term conditional is used to specify that the stability constants are specific for the conditions of the reaction. Conditional stability constants for humic acid (HA) and fulvic acid (FA) are comparable. The values reported for log K are linear in the pH range of 3 to 6 (Buffle and Greter, 1979; Buffle et al., 1976; Greter et al., 1979), so that interpolations in the critical range of pH 4 to 5.5 are possible (Figure 6-12). Thus, at pH 4.5, the ratio of complexed lead to ionic lead is expected to be 3.8×10^3. For soils of 100 μg/g, the ionic lead in soil moisture solution would be 0.03 μg/g. The significance of this ratio is discussed in Chapter 8.

It is also important to consider the stability constant of the Pb-FA complex relative to other metals. Schnitzer and Hansen (1970) showed that at pH 3, Fe^{3+} is the most stable in the sequence $Fe^{3+} > Al^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Pb^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$. At pH 5, this sequence becomes $Ni^{2+} = Co^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+} = Mn^{2+} > Ca^{2+} > Mg^{2+}$. This means that at normal soil pH's of 4.5 to 8, Pb is bound to FA + HA in preference to many other metals that are known plant nutrients. Furthermore, if lead displaces iron in this scheme, an important function of FA may be inhibited at near saturation capacity. Fulvic acid is believed to play a role in the weathering of parent rock material by the removal of iron from the crystalline structure of the minerals, causing the rock to weather more rapidly. In the absence of this process, the weathering of parent rock material and the subsequent release of nutrients to soil would proceed more slowly.

6.5.2 Water

6.5.2.1 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 (1973) have reviewed the chemistry of lead in water in detail; 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 (Lovering, 1976). 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 µg/l and about 500 µg/l in soft water (pH >5.4) (Davies and Everhar, 1973). Lead sulfate ($PbSO_4$) is present in soft water and limits the lead concentration in solution. Above pH 5.4, $PbCO_3$ and $Pb_2(OH)_2CO_3$ limit the concentration. The carbonate concentration is in turn dependent on the partial pressure of CO_2 as well as the pH. Calculations by Hem and Durum (1973) 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. (1970) 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 µg/l to remove the lead at the rate of 138 g/ha·mo. Concentrations as high as 330 µg/l could be stable in water with pH near 6.5 and an alkalinity of about 25 ng bicarbonate ion/l 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 concentration of lead less than 1 µg/l could be retained in solutions at equilibrium (Lovering, 1976).

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; it may occur either as sorbed ions or surface coatings on sediment mineral particles or be carried as a part of suspended

living or nonliving organic matter (Lovering, 1976). A laboratory study by Hem (1976) 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 6-13 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 (1975). 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.

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 is 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 form (Lovering, 1976) 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.

6.5.2.2 Organic--The organic components of a 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 (Lovering, 1976). 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.

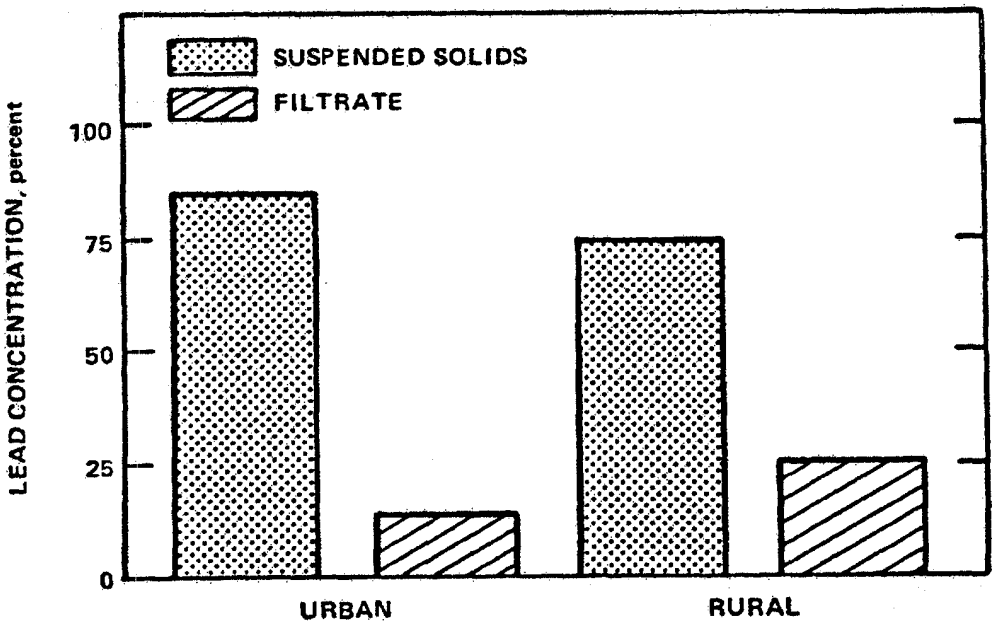

Figure 6-13. Lead distribution between filtrate and suspended solids in stream water from urban and rural compartments.

Source: Hem (1976); Rolfe and Jennett (1975).

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 (Bondarenko, 1968; Lovering, 1976). At pH values near 7, soluble lead-fulvic acid complexes are present in solution. At initial pH values between 7.4 and about 9, the lead-fulvic acid complexes are partially decomposed, and lead hydroxide and carbonate are precipitated. At initial pH values of about 10, the lead-fulvic acid complexes again increase. This increase is attributed to dissociation of phenolic groups at high pH values, which increases the complexing capacity of the fulvic acid. But it also may be due to the formation of soluble lead-hydroxyl complexes.

The transformation of inorganic lead, especially in sediment, to tetramethyllead (TML) has been observed and biotransformation has been postulated (Schmidt and Huber, 1975; Wong et al., 1975). However, Reisinger et al. (1981) have reported extensive studies of the methylation of lead in the presence of numerous bacterial species known to alkylate mercury and other heavy metals. In these experiments no biological methylation was found under any condition. Chemical alkylation from methylcobalamine was found to occur in the presence of sulfide or of aluminum ion; this process was independent of the presence of bacteria.

Jarvie et al. (1977, 1981) have recently shown that tetraalkyllead compounds are unstable in water. Small amounts of Ca^{+2} and Fe^{+2} ions and sunlight have been shown to cause decomposition of tetraethyllead (TEL) over time periods of 5-50 days. The only product detected was Et_3Pb^+ which appears to be considerably more stable than the tetraalkyl compound. Tetramethyllead is decomposed much more rapidly than TEL in water, to form the trimethyl lead ion. Initial concentrations of 10^{-4} molar were reduced by one order of magnitude either in the dark or light in one day, and were virtually undetectable after 21 days. Apparently, chemical methylation of lead to the trialkyllead $^+$ cation does occur in some water systems, but evolution of tetramethyllead appears unimportant.

There is considerable evidence of deposits of lead in riverine and estuarial waters and alluvial deposits. For example, Laxen and Harrison (1977) have found quite large concentrations of lead (~/mg/dm^3) in rainwater runoff from a roadway; but only 5 to 10 percent of this is soluble in water.

Concentrations of lead in ground water appear to decrease exponentially with distance from a roadway. Rainwater runoff has been found to be an important transport mechanism in the removal of lead from a roadway surface in a number of studies (Bryan, 1974; Hedley and Lockley, 1975; Laxen and Harrison, 1977). Apparently, only a light rainfall, 2 to 3 mm, is sufficient to remove 90 percent of the lead from the road surface, mainly to surrounding soil and to waterways (Laxen and Harrison, 1977).

Webb (1978) has reported elevated lead concentrations (40 ppm and above) in about 30 percent of stream bed sediment samples from England and Wales in a study of 50,000 such samples. Abdullah and Royle (1973) have reported lead levels in coastal areas of the Irish sea of 400 ppm and higher. Therefore, there is no doubt that coastal sediments and stream beds in England contain quite large amounts of lead.

6.5.3 Vegetation Surfaces

The deposition of lead on the leaf surfaces of plants where the particles are often retained for long time periods must also be considered (Dedolph et al., 1970; Gange and Joshi, 1971; Schuck and Locke, 1970). 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 (Schuck and Locke, 1970). 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 (Arvik and Zimdahl, 1974b; Gange and Joshi, 1971; Lagerwerff et al., 1973). 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 (Arvik and Zimdahl, 1974b). 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 chemically inert. Arvik and Zimdahl (1974b) have shown that entry of ionic lead through plant leaves is of minimal importance. Using the leaf cuticles of several types of plants essentially as dialysing membranes, they found that even high concentrations of lead ions would not pass through the cuticles into distilled water on the opposite side.

The uptake of soluble lead by aquatic plants can be an important mechanism for depleting lead concentrations in downstream waterways. Gale and Wixon (1978, 1979) have studied the influence of algae, cattails, and other aquatic plants on lead and zinc levels in wastewater in the New Lead Belt of Missouri. These authors report that heavy mineral particles become trapped by roots, stems, and filaments of aquatic plants. Numerous anionic sites on and within cell walls participate in cation exchange, replacing heavy metals such as lead with Na^+, K^+, and H^+ ions. Elevated lead levels were found in most stream vegetation, but there was no evidence for biomagnification in fish or other aquatic animals. Apparently, once found in plant material, the lead passes through digestive systems to form plant litter-sediment.

Mineralization of lead in these Missouri waters may also be promoted by water alkalinity. However, construction of stream meanders and settling ponds have greatly reduced downstream water concentrations of lead, mainly because of absorption in aquatic plants (Gale and Wixson, 1979).

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

1. The uptake of lead from soil by plants 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.

6.6 SUMMARY

From the source of emission to the site of deposition, lead particles are dispersed by the flow of the airstream, transformed by physical and chemical processes, and removed from the atmosphere by wet or dry deposition. Under the simplest of conditions (smooth, flat terrain), the dispersal of lead particles has been modeled and can be predicted (Banarie, 1980). Dispersion modeling in complex terrains is still under development and these models have not been evaluated (Kotake and Sano, 1981).

Air lead concentrations decrease logarithmically away from roadways (Edwards, 1975) and smelters (Roberts, 1974). Within urban regions, air concentrations decrease from the central business district to the outlying residential areas by a factor of 2 to 3. In moving from urban to rural areas, air concentrations decrease from 1 to 2 $\mu g/m^3$ down to 0.1 to 0.5 $\mu g/m^3$ (Chapter 7). This decrease is caused by dilution with clean air and removal by deposition. During dispersal to remote areas, concentrations decrease to 0.01 $\mu g/m^3$ in the United States (Elias and Davidson, 1980), to 0.001 $\mu g/m^3$ in the Atlantic Ocean (Duce et al., 1975) and 0.0001 $\mu g/m^3$ in Antarctica (Zoller et al., 1974).

Physical transformations of lead particles cause a shift in the particle size distribution. The bimodal distribution of large and small particles normally found on the roadway changes to a single mode of intermediate-sized particles with time and distance (Huntzicker, 1975). This is probably because large particles deposit near roadways and small particles agglomerate to medium-sized particles with an MMED of about 0.2 to 0.3 μm.

Particles transform chemically from the lead halides to lead sulfates and oxides. Organolead compounds usually comprise 1 to 6 percent of the total airborne lead in ambient urban air (Harrison et al., 1979).

Wet deposition accounts for about half of the removal of lead particles from the atmosphere. The mechanisms may be rainout, where the lead may be from another region, or washout, where the source may be local. The other half of the atmosphere lead is removed by dry deposition. Mechanisms may be gravitational for large particles or a combination of gravitational and wind-related mechanisms for small particles (Elias and Davidson, 1980). Models of dry deposition predict deposition velocities as a function of particle size, windspeed and surface roughness. Because of their large

surface area to ground area ratio, vegetation surfaces receive the bulk of dry deposited particles over continental areas. Between wet and dry deposition, removal of over 400,000 MT/year of the estimated 450,000 MT/yr emissions (Nriaga, 1971) can be accounted for.

Lead enters soil as a moderately-insoluble lead sulfate and is immobilized by complexation with humic and fulvic acids. This immobilization is a function of pH and the concentration of humic substances. At low pH (4.0) or low organic content (< 5 percent), immobilization of lead in soil may be limited to a few hundred µg/g (Zimdahl and Skogerboe, 1976), but at 20 percent organic content and pH 6.0, 10,000 µg Pb/g soil may be bound.

In natural waters, lead may precipitate as lead sulfate or carbonate or it may form a complex with ferric hydroxide (Lovering, 1976). The solubility of lead in water is a function of pH and hardness (a combination of Ca and Mg content). Below pH 5.4, concentrations of dissolved lead may vary from 30 µg/l in hard water to 500 µg/l in soft water at saturation (Lovering, 1976).

Particles deposited by dry deposition on vegetation surfaces (leaves and bark) are retained for the lifetime of the plant part. The particles are not easily washed off by rain nor are they taken up by the leaf (Arvik and Zimdahl, 1974b).

6.7 REFERENCES FOR CHAPTER 6

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