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µg/dl	Microgram per deciliter (or per 100 ml)
µg/liter	Microgram per liter
µg/100 cm^3	Microgram per 100 cubic centimeters
µm	Micrometer
mg/kg	Milligram per kilogram
mg/liter	Milligram per liter
mg/m^2-mo	Milligram per square meter per month
ng	Nanogram
ng/cm^2	Nanogram per square centimeter
NAS	National Academy of Sciences
NASN	National Air Surveillance Network
NAQCAC	National Air Quality Criteria Advisory Committee
Pb	Lead
PbB	Concentration of lead in blood
ppm	Part per million
lb/hour	Pound per hour
RTP	Research Triangle Park, N. C.
scfm	Standard cubic feet per minute
SMSA	Standard Metropolitan Statistical Areas
TLM	Threshold Limit Median
wt percent	Weight percent
XRF	X-ray fluorescence

LIST OF ABBREVIATIONS

cm	Centimeter
ft^3/min	Cubic foot per minute
°C	Degree Celsius
ALAD	Delta aminolevulinic acid dehydrase
ALA-U	Delta aminolevulinic acid in urine
dscf	Dry standard cubic foot
EP	Erythrocyte protoporphyrin
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
FEP	Free erythrocyte protoporphyrin
gr	Grain
gr/scf	Grains per standard cubic foot
g	Gram
g/gal	Gram per gallon
HNO_3	Nitric acid
in.	Inch
kN/m^2	KiloNewtons per square meter
km	Kilometer
kph	Kilometers per hour
m	Meter
m^3/min	Cubic meters per minute
MMD	Mass median diameter
Mg	Megagram
mph	Miles per hour
MT	Metric ton
$\mu g/m^3$	Microgram per cubic meter

excess delta-aminolevulinic acid in the urine, appears at blood lead levels between 40 and 60 µg/100 g. Average lead levels in blood usually center around 20 µg/100 g.

ABSTRACT

The ubiquity of lead in the environment insures constant low-level exposures of all forms of life. Commercial consumption of lead in the United States is currently about 1.2 million metric tons per year; however, a large proportion of this lead is recycled. The greater portion of lead which is not recycled is that present in vehicle exhaust emissions.

The largest source of lead pollution to the environment is the combustion of lead-containing gasoline by motor vehicles. Lead emitted from motor vehicles is in particulate form. The particles emitted may be either coarse (>2 μm) or fine (<1 μm). The chief stationary sources of lead are the extraction and processing of metallic ores and the incineration of solid wastes. Lead emitted by stationary sources also may be in the form of both coarse and fine particulate. A small fraction of the lead emissions may be in the vapor phase, primarily emissions from gasoline production or from transfer at service stations.

The most important sources of lead exposure in humans and other animals are ingestion of foods and beverages, inhalation of airborne lead, and the eating of non-food substances. Undesirable effects of lead are seen only in humans and animals; plants and inanimate materials are not known to be injured by existing exposure levels. Clinical lead poisoning is accompanied by symptoms of intestinal cramps, peripheral nerve paralysis, anemia, and severe fatigue. Individuals with clinical cases of lead poisoning usually have blood lead levels above 80 μg/100 ml. Subtle effects of lead exposure, as indicated by the appearance of

the nation; however, except for smelters, they are concentrated primarily in urban areas. Lead product usage also is concentrated in high density population areas. Emissions are primarily to the atmosphere, although industrial discharges may result in a high degree of local contamination of soil and water. Emissions are primarily inorganic particulate; however, relatively small amounts of organic lead are emitted to the atmosphere primarily from gasoline storage or transfer facilities. Inorganic lead emissions from the combustion of leaded gasoline contribute over 90 percent of the total lead emitted to the atmosphere. Regulations have been established to reduce the lead content in gasoline. Other emission sources include mining and milling, coal and fuel oil combustion, smelting, and product manufacturing. Additional sources, which constitute only a small fraction of the total but are important from the standpoint of local human exposure, include weathering, abrasive cleaning, or burning of painted surfaces; reentrainment of dust containing lead (primarily by automobile traffic); and incineration of waste products containing lead.

Fugitive dust particles emitted from stationary sources are generally >2 μm, and hence contribute to a primarily local pollutant problem. Lead particles in stack effluents from stationary sources are <2 μm and so contribute to ambient air levels over a broader geographical area. Both large (>2 μm) and small (<1 μm) particles are emitted from the exhaust of mobile sources using leaded gasoline. On the average, over the lifetime of the vehicle, approximately 35 percent of the lead contained in gasoline is emitted as small particles and approximately 40 percent is emitted as large particles. The remainder is stored as deposits in the engine and exhaust system. Engine deposits are gradually transferred to the lubricating oil and eventually removed in waste oil. A portion

1. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

1.1 SUMMARY

Lead is one of the oldest metals known to man. Its metallic form rarely occurs in nature. The most abundant natural ores containing lead are in the form of sulfide, carbonate, sulfate, and chlorophosphate. Lead is produced commercially by roasting galena (lead sulfide) in an oxidizing atmosphere. Most inorganic forms of lead have a very low solubility. The physical characteristics (high density, softness, ductility, malleability, and relatively low melting point) account for the numerous uses of lead. The equilibrium model for the chemistry of lead indicates that at low pH elemental lead can be readily dissolved. This may have health implications where soft water and lead piping are used for potable supplies.

Lead occurs naturally in water and air as a result of erosion, dust formation from soil, and diffusion of gases from the earth's crust. Since lead has been mined and used for centuries, natural background levels are difficult to determine. Based upon geochemical data, the natural background concentration in the atmosphere has been estimated to be about 0.0006 $\mu g/m^3$, resulting mainly from airborne dust containing 10 to 15 µg/g of lead. Natural concentrations in fresh water have been estimated to be about 0.5 µg/liter and in ocean water about 0.05 µg/liter.

The mining, smelting, and use of lead in human activities has significantly altered the distribution of lead in the environment. Mobile and stationary emission sources of lead are located throughout

precipitation or street cleaning, and deposited in storm sewers. Ultimately the material reaches a local water system and is deposited as sediment. Lead particles flaking or powdering from painted surfaces are of large size and therefore behave in a similar manner, so that they are deposited on soil surfaces immediately adjacent to the painted structure. Because this material generally is not collected in the normal atmospheric sample, few quantitative data are available. It is clear, however, that high concentrations, with wide variations in space and time, might be expected on a microscale in the air near the ground surface, the soil, and sediments in local water systems. The atmosphere serves as a transport medium for both large and small particles, but with significantly different distribution and deposition patterns. This has important implications relative to biological exposure patterns, and consequently to regulatory and control strategies.

The majority of environmental studies on lead have been carried out using methods that measure the element but do not determine the associated anions. Several lead compounds emitted from the exhausts of automobiles using leaded gasoline have been identified. The chief lead emission products are lead bromochloride (particles 2 to 10 μm mass mean diameter), the alpha and beta forms of ammonium chloride and lead bromochloride (particles <1 μm), lead sulfate, and the mixed oxide and halide. Limited laboratory studies on the aging of automobile exhaust have shown significant chemical transformations. Information on the chemical behavior in the atmosphere is not available. Lead alkyl vapors are readily broken down by light and heat, so that their presence in the atmosphere should be

of the lead deposited in the exhaust gradually flakes off as very large particles, and rapidly falls to the surface on or near the road bed.

Emissions or waste products resulting from mining, smelting, and product manufacturing and use, if not controlled, may cause high occupational, or local, exposure conditions.

The atmosphere is the primary transport medium for the widespread redistribution of man-made lead waste in the environment. Submicron particles suspended in the atmosphere may have residence times of a week or of months, depending upon particle size, and be transported for thousands of kilometers. The tendency toward uniform distribution, i.e., mixing with concomitant dilution, of material injected in the atmosphere increases with an increase in residence time (decrease in particle size). Therefore, the concentration and distribution of fine-particle lead, as normally measured, is generally a reflection of the total emissions from combustion processes, primarily the combustion of leaded gasoline. The principal atmospheric removal mechanisms for these small particles are precipitation and dry deposition, resulting in the widespread deposit of lead in small amounts on the surface layers of the soil, where it accumulates and remains for long periods of time. However, the lead concentration in individual rain water samples is usually below the detectable level.

Larger particles (>2 μm to 100's μm), which also may be injected into the atmosphere, are confined to a small geographical area, are less uniformly distributed vertically in the atmosphere near the surface, have much shorter residence times, and are removed primarily by gravitational settling. Once removed, however, they may be reentrained by the wind or mechanical forces such as automobile traffic. The material is eventually washed from paved streets, and to some degree other soil surfaces, by

Measurements are marginally adequate for establishing the general distribution of suspended inorganic lead in the environment. Few reliable measurements are available for organic lead. Rural airborne suspended particulate lead levels are commonly below 0.5 $\mu g/m^3$. Urban levels are mainly 1 to 2 $\mu g/m^3$, but in a few dense population areas the daily averages may be 3 to 5 $\mu g/m^3$. During periods of maximum traffic density levels up to 20 $\mu g/m^3$ may exist for several hours. In the vicinity of large stationary sources levels of 300 $\mu g/m^3$ may occur for short periods during unfavorable meteorological conditions. Only limited information is available regarding the large lead particles which flake off from automobile exhaust systems and remain very near the surface; therefore, concentrations and distribution are unknown. It is important to note that current ambient air measurements of lead do not include dust very near the ground surface.

Lead concentrations in U. S. surface waters are usually well under the 50 µg/liter drinking water standard; however, exceptionally high values have been reported. A U. S. Geological Survey study reported values which ranged from 1 to 890 µg/liter, with the median values from 1 to 6 µg/liter. The highest values were reported in New England and the northwest. The ratio of soluble lead to the lead in suspended solids generally ranged from 1 to 5 for rural areas, and 2 to 29 for urban areas. The larger amount in urban areas is thought to be due to particulate deposited on city paved streets and later washed into storm sewers.

Lead concentrations in soil generally range from 10 to 15 µg/g. Levels are higher in surface than in deep layers. Levels may be 5 to 10 times higher near well-traveled roadways. Even higher levels are found near mines or older smelters (several thousand µg/g). Soil concentrations

transient; however, short-lived peaks have been found. Though little information is available regarding biotransformation, recent evidence indicates that microorganisms in lake sediments can convert some inorganic and organic lead compounds into a volatile tetraalkyl lead.

An extensive effort has been devoted to the development of sampling and measurement techniques for lead in air, water, soil, and biological samples. Analytical methods include: (1) atomic absorption spectroscopy, (2) x-ray fluorescence, (3) dithizone (colorimetric spectrophotometry), (4) spark source mass spectrometry, (5) photon activation, (6) optical emission spectroscopy, and (7) proton induced x-ray emission. The capability is generally adequate for inorganic lead measurements (less so for organic); however, extreme care must be taken in the sampling, preparation, and analytical procedures, particularly for biological samples. Many of the available biological data are of questionable accuracy. The difficulty lies in preparing an analytical sample suitable for presentation to the instrument.

Transfer of air lead to the biomass may be direct or indirect. The deposition contribution may be direct on the above-ground portions of plants, or it may be secondary by way of the soil. Definitive transfer rates have not been determined. Evidence indicates that transfer from the air to plant leaves and other exposed surfaces can be detected when air lead concentrations are about 1.5 $\mu g/m^3$, a level considerably above that normally found in nonurban areas. Trace amounts of lead are absorbed by plants from soil; however, the range is variable and is probably dependent upon the chemical characteristics of both lead and soils, the pH of the soil, and the species of plants. Transfer of lead from plants to animals is not well defined; however, there is no evidence of biomagnification.

exposure conditions which are not applicable to the general population. The most serious exposure problem for children is thought to be the ingestion of lead paint on exposed surfaces of houses or other products. High concentrations of lead in dirt without ground cover and in dust may be the second most serious exposure problem for children. In this case the route of exposure may be either ingestion or inhalation; however, since the dust particles are very large, the principal route is probably ingestion. The large dust particles would be deposited in the upper airways, coughed up, and swallowed. Overexposure in adults, other than occupational, is primarily from contaminated food and beverages, including illegal whiskey. Except in special cases exposure via inhalation of ambient air in the general population is insignificant compared to exposure via ingestion.

Overexposure in lower animals is due to consumption of: surface-contaminated pasture herbage or harvested feed grown near large stationary sources of lead; lead-contaminated rubbish (waste oil, paint, batteries, etc.); and spent shotgun pellets (by wild birds).

The absorption, excretion, and storage of lead in the body are interdependent. Once absorbed, the lead is generally distributed throughout the body. Approximately 90 percent of the total body burden is stored in the bones and the remainder in soft tissue including the blood. When the rate of absorption exceeds the rate of excretion and storage, the concentration of lead in the soft tissues rises. Lead concentration in the bones changes very slowly, while that in soft tissue may change more rapidly. The rate of absorption is dependent upon the route of administration, chemical and physical properties of the lead, the chemical nature of the diet, nutritional status, and age. Absorption rates vary widely, both

around older houses where lead paint was used on exterior surfaces may be higher than those found in the vicinity of motor freeways. Soil concentrations in the vicinity of plants and trees sprayed with lead arsenate may be three to four times that (50 to 65 µg/g) normally found in soil.

Lead levels in vegetation tissues normally range from 0.1 to 2.0 µg/g. Lead deposited on the leaves and stems may be much higher in areas of high lead dust-fall; for example, in the vicinity of roadways and smelters. The lead content in foodstuffs varies widely. Concentrations may reach several hundred µg/g, although the average values are much lower. Intake from a normal diet has been estimated at about 200 µg/day.

Lead levels in the tissues of domestic and wild animals have not been studied extensively. Most information comes from high-exposure sites near stationary sources, where the tissue levels are usually elevated.

Information on the effects of lead on microorganisms is sparse.

Extensive data are available on lead concentrations in humans, particularly on blood and urine levels. Human exposure to environmental lead may be from inhalation, ingestion, or cutaneous absorption. Under normal conditions, the concentrations of organic lead present in the environment are so low that cutaneous absorption of organic lead can be ignored, except in accidental or occupational exposure cases. Ingestion of inorganic lead is the most important route of exposure for the general population. Inhalation is usually the more important route of occupational exposure, and may be an equally or more important route of exposure for persons living in the immediate vicinity of major stationary sources (smelters), or large automobile freeways. However, these are special

It appears at blood lead levels of 40 to 60 µg/100 g and above. Although illness is not directly attributable to it, an increase in ALA-U reflects a change in the body's metabolism. Recent evidence suggests that when blood lead levels and FEP levels disagree, the FEP level more reliably reflects a child's true clinical status. The FEP provides a better estimate of soft tissue lead, adverse metabolic response, and therefore risk. It should be noted, however, that elevated FEP levels (60-189 µg/dl) may be due to iron deficiency anemia, but extremely elevated levels ($\geq$ 190 µg/dl) are due amost exclusively to lead toxication. Data are not yet adequate to firmly establish the blood lead level at which evidence of metabolic impairment is first indicated by FEP tests. The level is within the range of 30 to 50 µg/dl PbB. Metabolic impairment probably precedes functional impairment of the nervous system.

Many data have been published on the above described biological indicators. However, the results are not always comparable because of sampling and analytical problems, and a lack of complete understanding of all factors controlling individual variability. Taken together, the data provide a reasonable basis for establishing the distribution of blood lead levels in normal healthy populations. The data also provide the information necessary to identify segments of the population which have special exposure problems. The following distribution of blood lead levels constitutes an acceptable biological guideline (see section 8 for details):

for inhalation and ingestion, from one individual to another. On the average, absorption of ingested lead is about 8 to 12 percent of intake, and about 30 to 50 percent of inhaled lead in adults. Absorption may be higher in children. Diets deficient in calcium or iron may result in a significant increase in the absorption of lead -- this is particularly important in children. The principal routes of excretion of lead are the feces and the urine.

A number of biological indicators may be used to estimate exposure, and/or responses or effects. These include levels of lead in blood (Pb-B) and urine (Pb-U), increased urinary delta-aminolevulinic acid (ALA-U) increased "free" erythrocyte protoporphyrin (FEP), increased urinary coproporphyrin (CP-U), decreased delta-aminolevulinic acid dehydrase (ALA-D) in peripheral blood, and anemia. These biochemical derangements are taken as general toxicity indicators reflecting the effects of lead on the synthesis of all heme proteins - both those in red blood cells and those in mitochondria throughout the body. The blood lead level is the most widely used biological indicator of recent human exposure to lead. It indirectly reflects external exposure and also indicates the internal biologically active lead, except in cases of previous prolonged overexposure which has resulted in high blood lead levels. ALA-D has been found to be an extremely sensitive biological indicator of recent exposure to lead, except, again, in those cases where prolonged overexposure has been experienced. ALA-D activity begins to decrease at blood lead levels of 5 to 15 µg/100 g, with 60 to 70 percent inhibition at levels of 40 µg/100 g. A 20 to 30 percent decrease in ALAD activity does not appear to be accompanied by any detectable changes in the biological functions of a healthy individual. ALA-U has been shown to be closely related to elevated lead levels in soft tissue and reflects biochemical changes.

In order to assess the impact of exposure to airborne lead upon PbB levels, the blood lead distributions in Okeana, Ohio and Honolulu, Hawaii are assumed to be representative of relatively clean environments for adults and children, respectively (Figures 8-4 and 8-9, Section 8). The maximum (100th percentile) blood lead value reported for Okeana was 32 µg/100 ml. Assuming that the relationship of 1 $\mu g/m^3$ air exposure will result in an increase of 1 µg/100 ml PbB, an airborne lead concentration of 8 $\mu g/m^3$ would shift the upper end of the population distribution in Okeana to 40 µg/100 ml PbB, which is the biological guideline for adults. By similar reasoning an increase in airborne lead levels of 4.6 $\mu g/m^3$ to a total of 8 $\mu g/m^3$ (3.4 $\mu g/m^3$ observed plus 4.6 $\mu g/m^3$) in Pasadena would result in a 100th percentile level of 40.1 µg/100 ml PbB. The maximum blood lead level for children in Honolulu was not reported; however, 11 percent were in the PbB level interval of 21 to 30 µg/100 ml. Assuming a 100th percentile level of 30 µg/100 ml, an increase in air lead of 3.8 $\mu g/m^3$ to a total of 5 $\mu g/m^3$ (1.2 $\mu g/m^3$ observed plus 3.8 $\mu g/m^3$) would shift the upper end of the PGB distribution to 33.8 µg/100 ml, which is slightly below the biological guideline for children. The above rationale of course assumes that total exposure is limited to intake via normal diet and inhalation. Therefore, based upon the premise that children represent the most susceptible segment of the population in terms of risk, an average of 5 $\mu g/m^3$ represents an air lead level, with an inherent margin of safety, at or below which no adverse health effects should be observed in any segment of a normally healthy population.

Percentage of population	Blood lead levels, µg Pb/100 ml	OR	ALAD activity, blood units/liter
50	<20		>35
90	<30		>25
98	<35		>20

Based upon present knowledge there is no evidence that health, in a broad sense, in individual adult males is affected if the blood lead level never exceeds 40 µg/100 ml. A comparable level for females and children is slightly lower (about 35 µg/100 ml). For clinical screening purposes in children a PbB level of 30 µg/100 ml is suggested. The distribution stated above reflects exposure both via inhalation and ingestion. Estimates of the contribution to total blood lead from atmospheric exposure is about 10 to 50 percent in adults, and 2 to 20 percent in children (3 years old), assuming air lead levels of 0.5 to 5 $\mu g/m^3$. Blood lead levels increase about 1 µg/100 ml for every 1 $\mu g/m^3$ of lead present in the atmosphere. Blood lead levels in urban populations usually do not exceed the above guideline. In those cases where the entire population distribution is above the guideline, excessive macroenvironmental exposure problems are indicated. In those cases where only the upper portion of the cumulative frequency distribution (~90 to 100 percent) exceeds the guideline distribution, macroenvironmental exposure problems, or possibly other factors, such as nutritional status, which require special consideration are indicated.

intake from ambient air is relatively small. Residential proximity to high-density traffic may contribute to increased blood lead levels in children, although data are not available to quantify the change with certainty.

Approximately 25 to 30 percent of the children who survive an attack of acute encephalopathy due to lead poisoning sustain severe permanent neurologic injury. Mental retardation found in asymptomatic children is difficult to evaluate. The true incidence of lead poisoning in young children is not known; therefore, the incidence of significant permanent injury to the central nervous system is also not known. The limited evidence available indicates not only that children absorb a greater portion of lead from ingested materials than do adults, but also that they excrete more. The influence of nutritional deficiencies upon lead absorption in children may be extremely important. Calcium and iron deficiencies may materially increase the rate of lead absorption. With young children it is not exclusively a matter of lead intake via inhalation and ingestion of food and beverages, since they indescriminately mouth and actually eat non-food materials of all sorts. All available sources of lead have an additive effect upon total intake. Except in cases of residence and play in the immediate vicinity of large stationary sources, or high traffic density, the contribution via inhalation of the small-particle airborne lead to total intake in children would likely be relatively small compared to intake from paint, dust and dirt, and food.

Severe or fatal lead poisoning of domestic animals grazing near major lead sources continues to be reported. Horses are more susceptible than ruminants to fatal lead poisoning, because of the early onset of critical nerve paralysis. There is no evidence that ambient airborne

Undesirable effects of lead are seen only in humans and animals. Plants are not injured by existing atmospheric lead levels, and there are no major effects on materials. Poisoning in humans is accompanied by symptoms of intestinal cramps, peripheral nerve paralysis, anemia, and severe fatigue. Very severe exposure results in encephalitis and is frequently fatal. In cases of clinically defined lead poisoning, blood lead levels are usually above 80 µg/100 ml. There are no known cases of lead poisoning in the general population as a result of ambient air exposure. Persons living in the vicinity of large stationary sources have elevated blood lead levels; however, overt clinical signs of lead toxicity have rarely been observed. Segments of the population exposed to high concentrations of lead in their work environment (garage workers, traffic policemen, etc.) may have blood lead levels greater than 40 µg/100 ml, but, again, clinical symptoms of lead toxicity have rarely been observed.

Age, pica, diet, nutritional status, and multiple sources of exposure serve to increase the risk of lead poisoning in children. The prevalence of lead poisoning in children is greatest in the inner cities where old deteriorated housing prevails, and is due primarily to the ingestion of lead paint. Blood lead levels in the case of lead poisoning are usually in excess of 80 µg/100 g. Many children in large cities have blood lead levels of 40 to 60 µg/100 g, without clinical signs of lead toxicity; however, significant numbers of these children have evidence of metabolic impairment as detected by FEP tests. These high blood lead levels may be due in part to a combined exposure from ingestion of small amounts of paint, dust, and dirt containing high concentrations of lead; and inhalation of lead in ambient air. However,

or dry deposition. The physical and chemical properties of lead result in long residence times in the deposits in the upper layers of soils and sediments.

2. Because of the dilution and dispersive characteristics of the atmosphere, airborne concentrations of lead high enough to make inhalation the primary intake route for human exposure occur only in areas of occupational exposure; in areas immediately adjacent to uncontrolled large stationary sources, under meteorological conditions which minimize dispersion; or in areas immediately adjacent to very high-density automobile traffic.

3. The total body burden of lead is a function of total exposure via ingestion, inhalation, and percutaneous absorption of organic lead. From the standpoint of the general population, cutaneous absorption does not constitute a significant route of intake. Intake is primarily via ingestion. Except in special cases, the contribution to the total body burden of lead via inhalation of airborne lead in urban areas is usually less than 30 percent. In nonurban areas it is usually less than 5 percent. The fraction of intake absorbed into the body is greater from inhalation than from ingestion.

4. Except for occupational cases, overexposure to lead in the United States is primarily a problem in children. In adults low levels of intake (<500 μg/day) and normal absorption of lead are not known to cause harm. Lead is distributed throughout the body, with about 90 percent stored in the bones and the remainder in soft tissues. Excretion is primarily via the feces and urine. Undesirable biological effects may result from overexposure (>500 μg/day). The effects range from

lead has contributed significantly to lead poisoning in domestic animals from inhalation.

Lead emissions from most stationary sources are in the form of solid particles, with particle sizes ranging from 0.3 μm to 1.6 μm MMD. Lead mist may be formed from sprayed lead arsenate insecticide, and vapor may be emitted from volatile lead alkyl compounds. Techniques of varying degrees of efficiency are available for the control of particulate emissions. The techniques employed depend upon the chemical and physical characteristics of the emissions. Certain products containing lead may be controlled by recycling. The lead content used in interior house paints and paints for toys is now controlled. Control of lead emissions from mobile sources may be accomplished by removal of lead from gasoline additives or possibly by on-vehicle control measures. Regulations have already been promulgated requiring a gradual reduction in the average amount of lead, in the form of additives, employed in the production of gasoline. Emission standards for particulates also reduce lead emissions from certain stationary sources.

1.2 CONCLUSIONS

1. The mining, processing, and use of lead in human activities have significantly altered the distribution of lead in the environment. The combustion of leaded gasoline currently accounts for over 90 percent of the emissions. Lead emissions from large stationary sources and lead in waste products not recycled can cause significant local pollution problems. The atmosphere is the principal transport medium for lead emissions. Lead particles are removed from the atmosphere by precipitation

with children. A significant number of children (primarily in large cities) have elevated PbB levels, indicating excessive exposure. Ingestion of lead-pigment paints is thought to be the principal source of exposure in children. Ingestion, or inhalation with subsequent swallowing, of dust containing high concentrations of lead probably contributes to overexposure; however, this has not been shown conclusively. Inhalation of airborne particulate lead contributes to exposure (1 $\mu g/100$ ml PbB per 1 $\mu g/m^3$ air), but is not a principal source. Evidence regarding neurologic and behavioral effects as a result of low-level exposure is incomplete.

7. Exposure of populations living in the immediate vicinity of large stationary lead sources (smelters) has resulted in elevated PbB levels, indicating excessive exposure, but has rarely produced observable clinical toxicity.

8. There are no known cases of lead toxicity or overexposure in the general urban population (excluding residents in the vicinity of large stationary sources) which could be eliminated by control of ambient airborne lead (as measured) alone; however, the reduction of lead emissions from mobile sources would significantly reduce exposure levels in high-density-traffic areas. Overexposure in children can best be identified through biological screening programs.

9. There is no evidence that exposure to short-term (hourly) peak lead levels in the ambient air have caused adverse health effects in any segment of the general population, although these conditions have not been studied specifically.

10. Lead toxicity in domestic animals is a result of contamination of pasture by lead emissions from point sources or from mobile sources; and from consumption of rubbish containing lead. Plants are not adversely

reversible clinical or metabolic symptoms, which disappear after cessation of exposure, to permanent damage or death from a single extreme dose or prolonged overexposure. Observed effects indirectly reflect the internal load or body burden.

5. Lead in blood indirectly reflects recent individual external exposure and is indicative of the internal biologically active lead. Lead in urine or other biochemical indicators serve as similar indices. The relationship between blood lead and external exposure is altered, however, in individuals who have experienced biologically significant overexposure. The distribution of blood lead levels (PbB), when properly interpreted, serves as a biological guideline for the protection of public health. Levels of exposure and/or of biological response to exposure will vary among individuals within the population due to differences in diets, nutritional status, activity patterns, rates of absorption and metabolism, and microenvironmental exposure patterns. The distribution of blood lead levels therefore reflects variability in exposure and response to lead in a population. A cumulative frequency distribution in which 98 percent of the population has PbB levels <35 µg/100 ml, 90 percent <30 µg/100 ml, and 50 percent <20 µg/100 ml indicates that no lead overexposure has occurred in the population. Blood lead levels which have never exceeded 40 µg/100 ml and 35 µg/100 ml represent a no-adverse-effect level for adults and children, respectively. When the PbB level distribution among the population exceeds the above guideline, unusual exposure conditions or abnormal absorption is indicated.

6. There is no definitive evidence of adverse biological effects in the general adult population in the U. S. due to exposure to lead, except in limited areas around smelters. The problem is primarily one

need to be studied. The levels, forms, and particle sizes of the various chemical species need to be established.

5. The contribution via inhalation of ambient airborne lead to the total blood lead level should not exceed 5 μg/100 ml, which corresponds to an atmospheric level of approximately 5 $\mu g/m^3$ averaged over at least 3 months. (Note that this does not include dirt to which children may be exposed). As indicated in the above summary, maintenance of the inhalation contribution at this recommended level will not eliminate the lead toxicity problem, particularly in children, but should help to ensure that blood lead in segments of the general population not subject to abnormal exposure patterns via ingestion will not exceed the stated biological guidelines. Removal of lead from paint and gasoline will greatly reduce further contamination of the environment; however, the long residence time of lead in soils and dusts will require continuing surveillance of children with evidence of early lead toxicity.

6. A comprehensive study of potential stationary sources of airborne lead emissions is needed to completely characterize the gas stream produced. The effectiveness of control technology on lead emissions will depend largely upon knowledge of the particle size, physical properties, and concentration of the lead particles in the gas stream, and the subsequent optimization of applied control technology as dictated by these properties.

affected at the present mean concentration of lead in the atmosphere and soil. Effects upon microorganisms are not well known.

11. Lead emissions to the air from stationary sources are generally in the form of particles of varying sizes. Present particulate control technology is incapable of chemically selecting particle species for removal from waste gas streams; thus, the effective control of such emissions and resultant compliance with an ambient air quality standard is uncertain and inexact.

1.3 RECOMMENDATIONS

1. An extensive biological screening program should be established, particularly for children, for early identification of overexposure. This should be coupled with a monitoring program to assess the specific sources of environmental exposure. This screening program should include children living in nonurban as well as urban areas.

2. Further studies of lead metabolism, especially in children, are needed, particularly to supply information on the mechanisms and rates of absorption from the respiratory and digestive tracts, and the behavior of the mobile fraction of the total body burden, in relation to variations in health status, age, diet, and nutritional balance.

3. Studies should be conducted to resolve the question regarding neurologic and behavioral toxicity of lead in children at comparatively low-level, chronic exposures as well as during critical periods of development.

4. The chemistry of lead in the environment should be studied. The chemical forms of lead, particularly the complex chemistry of biotransformation, relative to the movement of lead through the environment

This document focuses primarily upon lead as found in the ambient atmosphere; however, in order to assess its effects, the distribution and biological availability of lead in other environmental media must be considered. Discussions in this report are oriented toward the physical and chemical properties of lead; emissions from various sources; environmental transformation and transport; sampling and measurement methodology; and observed environmental concentrations which represent potential sources of external exposure for man and other animals. Mechanisms of response and normal metabolism are discussed, and, finally, undesirable effects are considered in relation to exposure levels.

The scientific literature has been reviewed through October 1976. This document is not intended as a complete, detailed literature review, and it does not cite every published article relating to lead in the environment and its effects. The literature has been reviewed thoroughly for information relative to criteria. An attempt has been made to identify the major deficiencies in our current scientific knowledge, again relative to criteria, and to make recommendations for further research.

Control technology for lead is discussed briefly. More detailed discussions can be found in (list OAQPS documents).

2. INTRODUCTION

Pursuant to the authority delegated to the Administrator of the Environmental Protection Agency, Air Quality Criteria for Atmospheric Lead is issued in accordance with Section 108 of the Clean Air Act, as amended.

Air quality criteria are expressions of the scientific knowledge of the relationships between various concentrations, averaged over a suitable time period, of pollutants in the atmosphere and their adverse effects upon public health and the environment. Criteria are issued to assist in the formulation of decisions regarding the need for control of a pollutant, and the development of air quality standards governing the pollutant. Air quality criteria are descriptive; that is, they describe the effects that have been observed to occur as a result of external exposure at specific levels of a pollutant. In the development of criteria, many factors must be considered. Natural background levels serve as a point of departure from which redistribution within the environment resulting from human activities can be assessed. The number and distribution of sources and the extent to which the specific pollutant is emitted to the environment, impact directly upon receptor exposure levels and must be assessed. The chemical and physical characteristics must be considered. The criteria must also include consideration of the contribution of all known variables relative to exposure versus effects upon human health, other environmental biological systems, agriculture, materials, visibility, and climate. Further, the individual characteristics of the receptor must be taken into account.

controlled circumstances. Lead oxides are amphoteric, forming salts with strong acids and plumbites and plumbates with strong bases. Stable isotopes of lead are numbered 204, 206, 207, and 208; radioactive isotopes are 209, 210, 211, and 214.

Lead readily alloys with antimony, arsenic, bismuth, cadmium, copper, and silver, either alone or in various combinations. Antimony alloys are widely used, e.g., in battery plates, because the alloy is harder and stronger than the pure metal.. Tin alloys of lead vary in the opposite direction and are widely employed as solders.

Some stable organometallic compounds of lead can be synthesized under appropriate conditions. In these compounds lead has a valence of +4. Two of these compounds--tetramethyl and tetraethyl lead--are widely employed as additives in gasoline used in motor vehicles.

3.2 CHEMICAL FORMS OF LEAD IN THE ENVIRONMENT

3.2.1 Chemical Forms of Lead in Air

From the known chemical properties of lead it would be expected that lead compounds produced by combustion processes from materials not rich in halogens would consist in the main of the oxides, hydroxides, or oxycarbonates; depending in detail, of course, on the parameters of the exhaust stream, e.g., the temperature and the amount of carbon dioxide, water, and other chemical species. In the case of automobile exhausts where they are expected to be present in significant concentrations, chlorine and bromine would be expected to react with lead to form lead halogens, inter-halogens, and their hydrolysis products, which include hydroxyhalides and oxyhalides. These might possibly be converted to carbonates. If sulfur were present in an oxidizing atmosphere, sulfate

3. CHEMICAL AND PHYSICAL PROPERTIES

3.1 GENERAL PROPERTIES

Lead (Pb) is a soft, dull gray, odorless, and tasteless heavy metal. The metallic form of lead rarely occurs in nature. The most abundant natural ores containing lead are galena (the sulfide form), cerusite (the carbonate form), angelsite (the sulfate form), and pyromorphite (the chlorophosphate form)--all of which have very low solubility in water. The relative abundance of ore deposits and the advantage of a low melting point contributed to the discovery, extraction, and use of lead early in human history. Its malleability and resistance to corrosion make it a very useful metal.

The metallic form of lead is reactive, but the reactions are usually self-limiting. In the presence of damp air or aerated water, it usually forms coatings of carbonates or sulfates, which protect it from further corrosion. Many lead salts show little ionization in water solution.

The specific gravity of lead varies from 10.42 to 11.37, depending on temperature and form. Its melting point is 327.4°C and its boiling point is 1744°C. It is a poor conductor of electricity and is remarkably impervious to ionizing radiation. It is the final decomposition product of some radioactive disintegrations.

Lead, which is located in Group IV and series 9 of the periodic table, has an atomic number of 82, an atomic weight of 207.21, and a valence of +2 or +4. Its divalent or plumbous compounds are common and stable; the quadrivalent or plumbic compounds occur only under unusual,

Table 3-1. SAMPLE COMPOSITION DETERMINED BY ELECTRON MICROPROBE

Sample	Percentage of total particles counted as:														
	$PbCl_2$	$PbBr_2$	PbBrCl	Pb(OH) Cl	Pb(OH) Br	$(PbO)_2$ $PbBr_2$	$(PbO)_2$ $PbBr_2$	$(PbO)_2$ PbBrCl	$PbCO_3$	Pb_3 $(PO_4)_2$	PbO_x	$(PbO)_2$ $PbCO_3$	PbO $PbSO_4$	$PbSO_4$
Black bag														
Zero time	10.4	5.5	32.0	7.7	2.2	5.2	1.1	31.4	1.2	---	2.2	1.0	---	0.1
18 hr	8.3	0.5	12.0	7.2	0.1	5.6	0.1	1.6	13.8	---	21.2	29.6	0.1	---
Near road	11.2	4.0	4.4	4.0	2.0	2.8	0.7	2.0	15.6	0.2	12.0	37.9	1.0	2.2
400 yards	10.5	0.7	0.6	8.8	1.1	5.6	0.3	0.6	14.6	0.3	25.0	21.3	4.6	6.0
Rural site	5.4	0.1	1.6	4.0	---	1.5	---	1.0	30.2	---	20.5	27.5	5.0	3.2

would be formed; or if the atmosphere were reducing, sulfide. Since the automobile is the principal source of airborne lead[1] it is of interest that the chief lead products in the automobile exhausts have been found to be lead halides and ammonium lead halides, and that lead chlorobromide is the principal component.[1]

In a study of the particulates formed from automobile exhausts, material discharged into a black bag from an automobile exhaust was examined at zero time and again after 18 hours.[2] The material collected near a roadway somewhat more distant from that site and at a very rural site was also examined. The analyses, made with an electron microprobe, are shown in Table 3-1. This information was obtained by noting the ratios of elements found in the vicinity of each other by the electron microprobe. Other work[3] has shown that it is difficult, nearly impossible, to identify lead compounds in atmospheric samples because of the amorphous nature of the material, which defeats attempts at diffraction studies, and the very low concentrations that exist in atmospheric particulate matter.

Of particular interest, lead bromochloride has been shown to decrease from a third of the initial amount of material to about an eighth over an 18-hour period; lead oxybromochloride decreases from 31.4 percent to 1.6 percent over an 18-hour period; and carbonate increases from 1.2 to 13.8 percent. These data suggest that the original exhaust, which is a mixture primarily of lead bromochloride and oxybromochloride (these two species account for about 63 percent of the total mixture), apparently changes to lead carbonate, oxides, or oxycarbonates over the 18-hour period. It would seem, then, that the compounds of lead in the air

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2. Ter Haar, G. L. and M. A. Bayard. Composition of Airborne Lead Particles. Nature. 232:553-554, 1971.
3. Robinson, E., and E. L. Ludwig. Particle Size Distribution of Urban Lead Aerosols. J. Air Poll. Control Assoc. 17:664, 1967.
4. Personal communication to R. J. Thompson, U. S. Environmental Protection Agency, from Ursula Cowgill.

depend to some extent upon the age of the particles, with the long-lived particles being preponderantly carbonate, oxide, or oxycarbonate. Since these chemical reactions occurred in a black bag, photolytic processes are not the mechanism responsible for the decrease in the halides observed.

3.2.2 Chemical Forms of Lead in Water

Chemical species of lead in water can be estimated from the known chemical properties of lead. However, the species to be found in any given situation in solution depend strongly upon other constituents in the same solution. The chemistry of lead in aqueous media is complex in that the element can be found in a multiplicity of complexed forms. Simple general statements are probably not very useful.

If certain anions, e.g., sulfate, carbonate, hydroxide, or halide, are present in sufficient concentrations, lead can be precipitated from the solution in various forms. Such forms might precipitate out in lakes, for example. In some sediments[4] of lakes lead bromide has, in fact, been detected. This would suggest the influence of the automobile on some of the chemistry of the lake.

3.2.3 Chemical Forms of Lead in Soil

Presented in Table 3-1 are analyses of some surface soil taken near highways in various locations. It is easily seen that the predominant species have been identified as carbonate, the oxycarbonate, or the oxide. There are certainly clear parallels between the results from the aged sample taken in the black bag and the analyses of the soil found near the roadways. In natural deposits, lead could be formed in a variety of ways, and has been found there as the sulfide, the oxide, the hydroxide, the carbonate, the halide, and the sulfate.

fluorescence (XRF) analyses. An alternative to the high volume sampler was needed since the high volume sampler collects particles in a single size range and is not designed to accommodate the membrane filters that are required for XRF analyzers. Moreover, the dichotomous sampler was developed to collect particles using the principle of virtual impaction in order to alleviate the problem of particle bounce errors that is characteristic of conventional cascade impactors.[1] These samplers collect particles smaller than the fractionation cut-point diameter on one filter and collects particles larger than the fractionation cut-point diameter on another filter. Dichotomous samplers with cut-point diameters between 2.0 and 3.5 μm have been evaluated. Since 1973 the development of a dichotomous sampler has gone through an evolutionary process in which each successive prototype model was improved. A manual version is now commercially available from Sierra Corporation, Palo Alto, California.

A prototype dichotomous sampler was evaluated in St. Louis at a site on the Washington University campus between August 26-31, 1973.[2] X-ray analyses of samples collected for a 23-hr period on August 30-31, 1973, indicated that particulate lead was concentrated in the size range below 2 μm. Of the total particulate lead collected, 460 ± 50 ng/m^3 was in particles $\leq$ 2 μm and 110 ± 12 ng/m^3 was in particles 2.5 to 10 μm in diameter.

Eight dichotomous samplers were performance-tested beside high volume samplers for 20 days during August and September 1975 at a rural and an urban site at St. Louis, Missouri.[3] Table 4-1 shows the results of the XRF and gravimetric analyses of the fine (less than 2 μm in diameter)

4. SAMPLING, PREPARATION, AND ANALYSIS

4.1 ENVIRONMENTAL MEASUREMENTS

4.1.1 Air

4.1.1.1 Sampling Methods--Except in the vicinity of sites where volatile lead compounds, such as tetraethyl lead used in gasoline, are produced or used, stationary sources contribute lead to the atmosphere principally in the inorganic particulate form. Particulate lead in air can be sampled for subsequent analysis by filtration through a porous medium or by impaction on a suitable non-porous plate.

4.1.1.1.1 Particulate lead--In EPA's National Air Surveillance Network (NASN), glass fiber filters in standard high volume samplers are used to collect suspended particulate matter from ambient air. The retention of particles $\geq$ 0.3 μm in diameter by these filters is excellent (>99.99 percent) at air flows of 1.4 to 1.6 m^3/min (50 to 60 ft^3/min). Commercial glass fiber filters may contain impurities that can interfere with analysis for particulate lead retained by the filter. In addition, the sampling network of the NASN collects suspended particulate matter from ambient air by filtration at 0.14 m^3/min (5 ft^3/min) through 10.16-cm (4-in.) cellulose acetate membranes that have a nominal pore size of 0.45 μm. An Andersen impactor, which uses aluminum impaction plates and a membrane filter for the terminal stage, has also been used to collect suspended particulate matter and to separate the particles by size.

In 1973, a program was undertaken by EPA to develop a dichotomous sampler capable of fractionating the respirable and nonrespirable fractions of atmospheric aerosols for subsequent gravimetric, chemical, and x-ray

A sampler has recently been developed by EPA which can obtain atmospheric particulate samples that are sized and in approximately gram quantities. The device uses impactor and electrostatic precipitator plates that have been coated with Teflon in order to reduce the problem of substrate contamination of the material collected.

The sampler collects particles smaller than 20 μm in size since the larger particles are removed first by a cyclone separator. The first collection stage consists of a slitted impactor that collects particles with a mean size of 3.5 μm. The second stage collects materials with a mean size of 1.7 μm; and the electrostatic precipitator collects the remaining particles.

Samples obtained at the Los Angeles Catalyst Site A (see Section 5.2.1.3.8) by such a collector are undergoing analysis. The sampler is expected to be the prototype for samplers used in future health studies, inasmuch as a gram of material can be obtained from ambient air. This is enough to permit determination of the species of lead and other elements present and to permit biological testing of sized partiuclate fractions.

4.1.1.1.2 Vapor-phase lead--Alkyl lead vapor (organic lead) is not an expected component of the atmosphere at stationary sources other than at sites where lead is produced or used. Sites where lead is used would include locations with high automobile densities where some organic lead emissions from evaporation are produced. Values of about 0.02 to 0.05 $\mu g/m^3$ were reported in London.[7] Organic lead may be collected by iodine crystals, activated carbon, or iodine monochloride.

and coarse (2 μm to 10 μm in diameter) particles collected at an urban and a rural site. These data again indicate that most of the lead is found in the fine particle fraction. Table 4-2 shows the comparability of four dichotomous samplers run simultaneously at an urban site. For sulfur, lead, and total mass, the standard deviation for the fine particles is quite small. However, the standard deviation for the coarse particles is somewhat large. Subsequent laboratory investigations revealed that the deposits of the coarse particles were not uniform, which led to an improved sampler design that does produce uniform deposits.[3] Figure 4-1 shows a comparison between the dichotomous samplers and the high volume samplers for the total (fine plus coarse) mass concentrations. These results indicate the potential of the dichotomous sampler as an alternative to the high volume sampler. However, the dichotomous sampler generally has a 20 μm upper cutoff diameter and further studies are required to determine the effect of particles larger than 20 μm on such comparisons.

In April 1975, a network of ten automated dichotomous samplers began operation as part of the Regional Air Pollution Study in St. Louis Missouri, to test the accuracy and reliability of the automatic aerosol sampling system under realistic ambient conditions.[4] In addtion, an interlaboratory comparison study of aerosol sampling and analysis methods is currently under way.[5] This study includes high volume, manual and automated dichotomous, Two Mass,[6] streaker, and Lundgren samplers. The samples will be analyzed for lead in addition to other trace elements. The air sampling will be conducted at a single site in Charleston, West Virginia.

TABLE 4-2. COMPARABILITY OF FOUR DICHOTOMOUS PARTICLE SAMPLERS RUN SIMULTANEOUSLY AT AN URBAN SITE[a] IN ST. LOUIS, MISSOURI

Parameter/ Element	Fine particles		Coarse particles	
	σ, $\mu g/m^3$[a]	σ, %[b]	σ, $\mu g/m^3$[a]	σ, %[b]
Mass	2	7	4	18
S	0.2	5	0.06	19
Ca	0.06	30	0.05	29
Pb	0.04	6	0.03	26

[a]Located at the Missouri Botanical Garden in St. Louis.

[b]Standard deviation (σ) expressed in micrograms per cubic meter and as a percentage of the average concentration.

Table 4-1. MASS AND PERCENTAGE COMPOSITION OF SIZE-FRACTIONATED AEROSOL COLLECTED AT ST. LOUIS, MISSOURI, AVERAGED OVER THE PERIOD AUGUST 18 TO SEPTEMBER 7, 1975

	Urban[a]		Rural[b]	
Element	Fine (29 $\mu g/m^3$), %	Coarse (22 $\mu g/m^3$), %	Fine (26 $\mu g/m^3$), %	Coarse (15 $\mu g/m^3$), %
Si	1	8	0.5	4
S	12.5	1.4	12.6	0.9
K	0.4	1.2	0.3	0.9
Ca	0.7	8.2	0.5	4.2
Ti	1.1	2.0	<0.1	0.2
Fe	1.4	4.8	0.3	1.3
Zn	0.35	0.20	0.13	0.15
Br	0.33	0.16	0.06	0.04
Pb	2.2	0.60	0.51	0.11

[a]Located at the Missouri Botanical Garden in St. Louis.

[b]Located in the agricultural area in Illinois, 40 km south of St. Louis.

Recent reports[8,9] have presented data suggesting that large quantities of lead pass through cellulose acetate membrane filters. No attempts were made to identify the lead species passing through the filters even though Robinson and Wolcott[8] used the designation "molecular lead" in their report. To date, other workers have not been able to verify these findings.[10]

Harrison et al.[7] have reported a method for collecting and analyzing organic lead. A 0.02 m^3 sample of air is drawn through a 0.22 μm Millipore filter into an adsorption tube packed with gas chromatographic packing material. The air passes through a short section wrapped with heating coil to ensure that condensation of vapors will occur in the lower part of the U-shaped tube; this lower section is immersed in liquid nitrogen. Particulate lead is determined by analysis of the Millipore filter. The vapor-phase lead is determined by equilibrating the sealed adsorption tube in an oven and eluting the contents with nitrogen, by means of a switching valve, into the combustion air stream of an atomic absorption spectrophotometer. The method is reported to have a detection limit of 0.2 ng Pb, corresponding to 0.01 μg organic Pb/m^3 in a sample of 0.02 m^3 of air. The method appears free of errors from background absorption, matrix effects, and interference from other pollutants.[7]

4.1.1.2 Sample Preparation--The lead in suspended particulate matter collected by the NASN is obtained in a form amenable to analysis by oxidation in a low-temperature asher, followed by extraction with a 4:1 mixture of distilled nitric acid:hydrochloric acid under reflux. The solution (freed from glass fibers, if necessary) is concentrated and

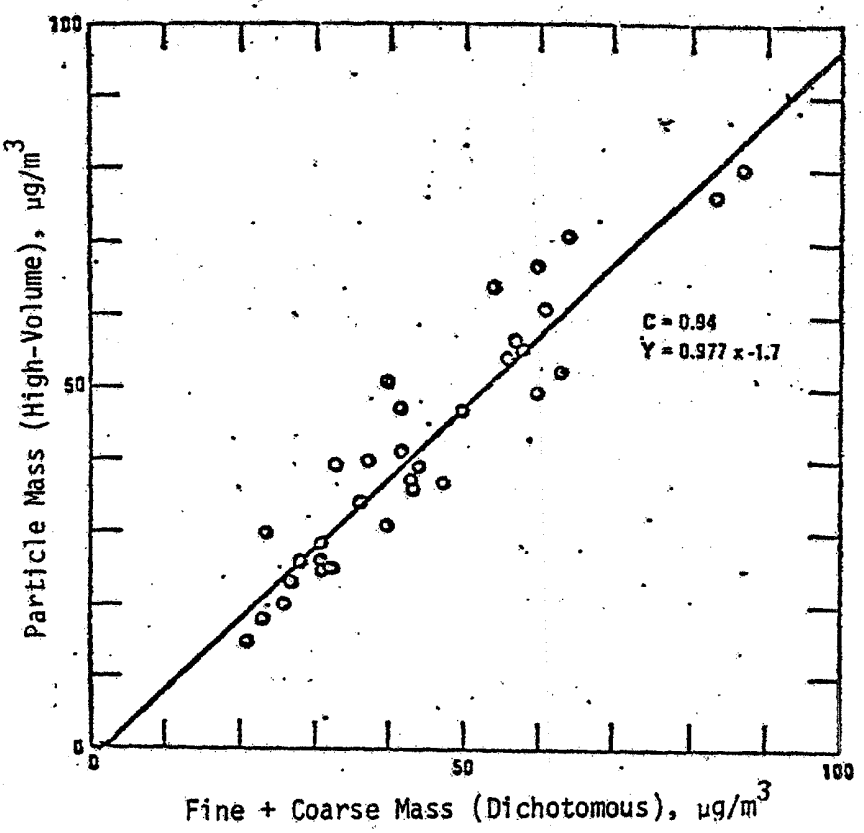

Figure 4-1. Comparison of total mass particle concentrations determined using high volume and dichotomous samplers.

Organic lead has been collected from a filtered air stream using iodine monochloride, with the methyl isobutyl ketone extract of the ammonium pyrrolidine-dithiocarbamate complex analyzed by atomic absorption.[15] Using this method, the average concentration of lead at sites of high auto-mobile density was found to be 0.2 $\mu g/m^3$; in an underground parking garage, the average was 1.9 $\mu g/m^3$. The atomic absorption/carbon rod technique has been used for the continous monitoring of lead at levels higher than ambient in urban areas.

X-ray fluorescence (XRF) has been used for determining micro and trace quantities of lead in a wide varity of samples.[2,16,17] Ambient air samples collected on filters can be used for lead measurements without prior sample preparation. The quality of the XRF results is dependent on calibration procedure, particle size, and interelemental matrix effects. When combined with a dichotomous sampling approach, XRF analysis is capable of yielding quantitative data for more than 70 elements on samples that have been segregated into respirable and nonrespirable size fractions.

An intercomparison study[18] involving twenty-two investigators who collectively used six different analytical techniques to analyze trace elements in simulated and real air particulate samples showed that energy-dispersive x-ray fluorescence spectrometry is a reliable technique for multielement analysis of particulate matter collected on filter media. This technique showed the highest number of elemental determinations per person-hour invested and provided satisfactory accuracy for the quantitative determination of elements potassium (Z=19) and above, with somewhat larger errors for elements down to aluminum (Z=13). Non-x-ray techniques were neither well represented nor strongly supported by the study.

made up to volume for subsequent analysis. The recovery of lead by this procedure is essentially quantitative, whereas the muffle furnace technique that was used for the determination of lead in NASN samples collected prior to 1968 yielded only about 50 percent of the lead actually present in the samples.[11]

4.1.1.3 Analytic Methods--The lead in samples collected by the NASN prior to 1967 was analyzed on a routine basis with an emission spectrograph. The photographic plate technique yielded only semi-quantitative data. Since 1967, direct reading instrument has been used for the analysis of samples; the instrument has been optimized and yields data for NASN samples that are accurate within 10 percent of the data obtained by atomic absorption spectrometry.[12] The latter allows direct analysis of the acid extract from the sample preparation (4.1.1.2) and yields elemental compositional data for some 25 metals contained in particulate matter. The atomic absorption technique has proved to be quite precise and presumably accurate for the determination of lead in particulate matter samples. The average recovery of lead from spiked samples (that is, samples to which a known amount of lead is added to facilitate determination of percentage recovery) was 93 ± 7 percent; 160 duplicates from a year of sampling (containing 1.4 μg Pb/m^3 air) showed a mean relative deviation of 1.5 percent.[13]

The dithizone technique has been used to extract lead from acidic digestion or extraction mixtures; the colored lead complex formed is determined colorimetrically. The dithizone method can yield excellent results but the technique is tedious and demanding, and the reagent is sensitive to light.[14]

American Society for Testing and Materials, Philadelphia, Pa., and the Association of Official Analytical Chemists, Washington, D.C. Current methods for water analysis are published by the American Public Health Association, Washington, D. C.

4.2 SOURCE MEASUREMENTS

4.2.1 Stationary Sources

4.2.1.1 Introduction--Several investigations have been conducted to develop and evaluate methods for testing emissions from stationary sources for lead. Stanford Research Institute (SRI) has surveyed and evaluated existing manual methods for measuring emission concentrations of lead and other toxic materials.[12] Arthur D. Little, Inc., (ADL) has developed methods and conducted laboratory and field tests to assess the accuracy, reproducibility, sensitivity, and specificity of selected methods for nine pollutants, including lead. A review of analytical technology available for continously monitoring stationary source emissions of lead has been prepared by Monsanto Research Corporation.[20]

4.2.1.2 Sampling Procedures--The procedures recommended by SRI[12] for source sampling for lead utilize a sampling train very similar to that specified by EPA for determination of particulate emissions (Method 5).[21] The sampling train consists of glass-lined probe, a holder for glass-fiber or membrane filters, a system of impingers, a metering system, and a pump. Glass-fiber filters may contain an undesirable lead background, but their use may be necessary in the case of high-temperature sampling. At lower (about 220°F or less) temperatures, organic membrane filters, which have a much lower metallic content, may be used. The collection

The method proposed as a tentative reference method for the determination of lead in suspended particulate matter collected from ambient air involves particulate collection on glass-fiber filters by a high-volume sampler. A portion of the filter is then extracted with acid in an ultrasonic bath. The resulting solution is quantitated with an appropriate analytical instrument such as an atomic absorption spectrophotometer or an optical emission spectrometer.

4.1.2 Other Materials

In monitoring for lead in vegetation, careful study of pertinent variables should be made so that they can be controlled or measured. In addition, the plant variety and part should be selected on the basis of the ultimate use of the data. For example, if human food content is the purpose of study, then the parts (fruits, seeds, leaves, or roots) that are eaten should be selected and processed (peeled, hulled, washed, or pitted) in order to obtain valid information. If the food of grazing animals is of concern, unwashed pasture plants and/or forage crops such as hay should be examined. For studying the influence of sources on the environment, ubiquitous local species, such as grasses, should be chosen and examined, both washed and unwashed, with due attention paid to growth and age status.

Analysis for lead in biological materials and in soil and dust specimens is reviewed in a National Academy of Sciences report,[19] which also describes the special methods of collection and storage required to avoid the contamination of animal tissues.

Methods of analysis for lead and other metals--particularly those that offer greater sensitivity--are currently undergoing development. Additional sources for current methods are the publications of the

Except in preparation for x-ray spectrometry, the samples are either removed from the the filter with acid or ashed to remove organic matter and treated with acid. Of the wet chemical methods, analysis by atomic absorption was selected as the most practical by SRI and ADL because of availability, ease of operation, and adequate sensitivity. Although interferences (such as phosphate or carbonate) that can enhance or suppress the response might exist, most can be eliminated in sample preparation or in the measurement procedures.

The application of x-ray fluorescence analysis to a large number of particulate samples collected from a variety of stationary sources and from ambient air has demonstrated that the method is rapid and economical.[22] Little sample preparation is required and the method is essentially non-destructive. Detection limits for lead samples collected on membrane filter paper and analyzed with a wavelength-dispersive spectrometer, with 100-second counting times, are of the order of 30 ng/cm^2. Problems of matrix effects and high background interference are minimized by the collection of thin sample depositions on high-purity filters made from low-atomic-number materials.

4.2.1.4 Continuous Monitoring--Several techniques have been applied to the continuous monitoring of lead vapor emissions (principally as organo-lead compounds), but no single method has been tested sufficiently to qualify as a continuous monitor for total lead vapor and particulate.[20] A technique that might be considered for development is non-flame atomic absorption spectrometry, which would have to be preceded by steps to chemically or thermally decompose the lead compounds to elemental lead

solution in the impingers recommended by SRI is 6 N HNO_3. Iodine monochloride impinger solution, which is more efficient than the Method 5 solution for trapping organo-lead compounds, has been suggested for use if organic lead is suspected to be present in the emissions. Lead may be present in stack emissions in a variety of chemical forms and may be emitted as fume, dust, or organic vapors. In order to resolve the question of whether a fine-particulate emission standard would make a lead emissions standard unnecessary, it would be essential to know what fraction, if any, of the lead penetrates the filters of the sampling train. It is most important, therefore, to obtain efficient collection in the impingers following the filters if there is indication that any elusive form of lead is passing through the filters.

The collection procedure proposed and tested by ADL is also similar to the Method 5 train except that a high-purity quartz filter which has an extremely low lead content is used. The filter is followed by two impingers containing 0.1 N HNO_3. Comparative tests showed that 0.1 N HNO_3 is essentially as effective as 6 N HNO_3 and is much less dangerous to use in field testing. Analysis of probe wash, filter extractions, and impinger solutions is by an air/acetylene flame atomic absorption procedure. A series of nine replicate measurements made with samples collected from the stack gas of an oil-fired source simulator unit yielded an 8.9 percent relative standard deviation for the lead determinations. The trace metals were added to the fuel in known amounts (Pb as lead octanoate).

4.2.1.3 Analytical Methods--Among the methods that have been used to determine the lead concentration in air pollution samples are atomic absorption spectroscopy, x-ray spectrometry, polarography, and colorimetry.

4.2.2.2 Sampling Procedures--A variety of procedures have been used to obtain samples of auto exhaust aerosols for subsequent analysis for lead compounds. Pioneering work in this area was done by Habibi at DuPont[23] and Ter Haar at Ethyl.[24] Subsequent efforts were performed by Moran and by Gentel and Manary at Dow under EPA contract,[25,26] by Springer at the University of Michigan under an EPA grant,[27,28] and by Trayser et al. at Battelle Memorial Institute under CRC sponsorship.[29]

Habibi developed a procedure, using a large horizontal air dilution tube, designed to segregate fine combustion-derived aerosols from larger lead particles ablated from combustion chamber and exhaust deposits. In this procedure, hot exhaust was ducted into a 22-in.-diameter, 40-ft-, long air dilution tunnel and mixed with filtered ambient air at an 8-in.-diameter mixing baffle in a concurrent flow arrangement. Total exhaust and dilution air flow rates were 1000 to 1300 ft^3/min, which produced a residence time of about 5 sec. in the tunnel. At the downstream end of the tunnel, samples of the aerosol could be obtained through isokinetic probes facing upstream, using filters or cascade impactors. Properly designed air dilution tubes of this type have very few aerosol losses for particles smaller than about 2 μm,[2] those which can be carried into human lungs.[30]

Ter Haar et al. reported the accumulation of air-diluted aerosols from cyclic emissions tests in a large plastic bag. Filtration or impaction of aerosols from the bag samples produced filter or impaction stage samples suitable for lead analysis.[24] Because of the rather lengthy residence time, there have been some fears expressed that the bag technique results in large aerosol sizes because of condensation of low-vapor-pressure organic substances on the lead particles.

and maintain the lead as vapor. Other potential methods include emission spectroscopy and x-ray emission spectrometry. With the latter approach, some means must be developed to collect vapors on filter media if gaseous lead compounds are present in the sample.

4.2.2 Mobile Sources

4.2.2.1 Introduction--The major source of lead aerosols in the environment is the combustion of gasoline containing lead antiknock compounds, mainly in automobiles. Lead antiknock mixtures commonly used include tetraethyl lead, tetramethyl lead, and intermediate lead alkyls together with ethylene dichloride, ethylene dibromide, dyes, and antioxidants. Commercial anti-knock mixtures contain a stoichiometric amount of chlorine in the form of ethylene dichloride to convert the lead completely to $C/_2$, and one-half the stoichiometric amount of bromine as ethylene dibromide.

The lead antiknock compounds are thermally unstable at combustion chamber temperatures; in the burning fuel-air mixtures, these organo-lead compounds break down to form atomic lead, which is then rapidly converted to PbO. The oxide form seems to be necessary for antiknock action. In the presence of HCl, Cl_2, HBr, and Br_2 (products of the organo-halide combustion) PbO is subsequently converted to the more volatile lead halides, principally PbClBr. Thus, the principal form in which lead is emitted from automobiles is an aerosol of PbClBr dispersed in tailpipe exhaust gases.

Sampling and analytical procedures used for lead compounds have been designed to obtain representative samples of the tailpipe emissions and to cope with the various other exhaust aerosol constituents as potential interferences.

at about 1-foot intervals.[25] Trayser et al. have used tunnels similar in dimension to those of Habibi with a centrifugal fan located upstream rather than a downstream positive displacement pump.[30] This geometry produces a slight positive pressure in the tunnel and expedites transfer of the aerosol to holding chambers for studies of aerosol growth. Since the total exhaust plus dilution air flow is not held constant in this system, there may be slight sample misproportionation. However, these errors can be minimized by maintaining a very high dilution-air/exhaust flow ratio.[30]

There have also been a number of studies performed using total filtration of the exhaust stream to arrive at material balances for lead. Hirschler and Gilbert[31] Springer,[27] and Habibi[32] have constructed rather low back-pressure metal filters. Habibi has stated that the cylindrical filtration unit used in his studies is better than 99 percent effective in retaining lead particles. Supporting data for lead balances seem to confirm this conclusion.[33]

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

4.2.2.3 Analytical Procedures--The two most commonly applied analytical procedures for lead in filtration or impactor stage samples of auto exhaust aerosols are atomic absorption spectroscopy and x-ray fluorescence

Any source sampling technique which maintains tailpipe emissions in more concentrated air-diluted form than would occur in normal vehicle use is likely to produce greater-than-normal condensation of low-to-moderate vapor pressure organics. Thus, it is important to realize that conclusions based on measurements of very low vapor pressure components, such as lead salts, are far more relevant to ambient air inventories than are estimates of organic aerosol constituents.

Springer has used a very low residence time sampling system based on proportional sampling of raw exhaust, followed by air dilution and filtration or impaction.[27,28] Because of high sampling rates of the raw exhaust, a relatively large sample of metallic aerosol constituents can be obtained quite conveniently with this technique. Because of the requirement for maintaining a constant proportion of the sample flow to the total exhaust flow, this technique may be limited by the response time of the equipment to operating cycles which have relatively small transients in the exhaust flow rate. Gauley and Springer have used the technique primarily with the relatively mild seven-mode cycle used for emissions testing prior to 1972.

Most research on aerosol emissions in recent years has used various configurations of the Habibi horizontal air dilution tunnel. Several polyvinyl cholride dilution tunnels have been used at Dow and at EPA with good success.[25,26,30] These 18-in.-diameter tunnels of varying lengths have been limited by diluted exhaust temperatures to total flows above about 400 cfm. Build-up of electrostatic charge on the walls of these plastic systems can cause abnormally high wall losses, but these can be avoided by wrapping the tunnel with a grounded conductive cable

of 0.26 degrees corresponding to ΔE of 154 eV.[37] This line may also be satisfactory in some high-resolution energy-dispersive instruments.[38] In real exhaust emission filter samples, no significant non-linearities in deposit thickness have been observed in the x-ray fluorescence determination of lead at loadings of 150 μg/cm.^{2} Using the criterion of Rhodes,[39] none would be expected below about 1000 μg/cm,^{2} a loading which would cause filter plugging in virtually every application. Therefore, deposit thickness is unimportant. In terms of speed, cost, and effectiveness, x-ray fluorescence determination of lead mass emissions appears to be the preferred method. Multistage impactor samples are more difficult to handle in XRF because of the spatially non-uniform distribution. This is particularly the case for single-jet impactors where thin-film standards are probably not applicable. In these cases or for glass-fiber filters, where medium thickness may present difficulties, atomic absorption spectroscopy appears to be the preferred method.

spectroscopy. Both techniques are also used in ambient air lead analysis and the sample preparation and handling procedures for both applications are nearly the same.

Sample preparation for atomic absorption spectroscopy varies somewhat with particle collection medium. Glass-fiber filters are commonly subjected to low-temperature ashing to destroy the organic matrix and are extracted with hot 10 percent nitric acid.[34] Cellulose acetate-nitrate membrane filters are normally wet-ashed and extracted. Cascade impactor stages may be either glass or stainless steel or glass-fiber filters.[35] These are generally wet-ashed also.

There are few significant interferences in atomic absorption determination of exhaust-derived lead. Phosphate and carbonate interfere with the determination but both are essentially absent in auto exhaust particles. For example, DuPont has reported that only 3 percent of the lead obtained from a lead trap is present as the phosphate.[33] No carbonate compounds have been found by either DuPont or Dow.[25,33] Therefore, it is believed that no significant interferences exist in this method. The detection limit for lead is approximately 0.02 μg/ml.[36]

Membrane filters or film impactor collection stages may also be analyzed for lead and for halides by x-ray fluorescence (XRF) spectroscopy. DuPont, Ethyl, and Dow have all reported x-ray diffraction results from similar samples.[25,26,33] X-Ray fluorescence analysis is conveniently performed using the Pb Lα fluorescence line at 10.55 keV. Millipore, Fluoropore, and Nuclepore filters have all been found satisfactory in this application. Lead Lα fluorescence can be determined without significant interference in a wavelength-dispersive instrument with a resolution

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are indicated in Figure 5-1. Lead is mined primarily as the sulfide ore, galena, which is often associated with minor amounts of other minerals, including zinc, cadmium, copper, bismuth, gold, and silver. Approximately 80 percent of the primary lead produced in this country is from native mines.[6] Missouri ore deposits provide about 60 percent of the domestic production.

The reported consumption of lead, major forms of which are listed in Table 5-1,[6] reached nearly 1.2 million metric tons in 1975. Lead with a high degree of recoverability as secondary lead may be found in certain products, especially batteries, cables, plumbing, weights, metal products, and ballast. This reserve of lead in use is estimated at 3.8 million megagrams (Mg) (metric tons (MT)). Lead in pigments, gasoline additives, chemicals, and low-lead alloys, however, is widely dispersed and economically unrecoverable.

Although mobile and stationary emission sources of lead are found throughout the nation, they tend to be concentrated in areas of high population density, except for some smelters. Figure 5-2 shows the approximate locations of mining districts, primary smelters, and lead alkyl plants. Battery plants are also given by number for each state.

Lead or its compounds may enter the environment at any step during its mining, smelting, processing, use, or disposal. A diagrammatic presentation is given in Figure 5-3. Recent estimates of the contributions of major sources of lead emissions indicate that the major contamination of the environment from man-made sources is to the atmosphere, and by far the largest component is found in motor vehicle exhaust as a

5. ENVIRONMENTAL APPRAISAL

5.1 ORIGIN AND ABUNDANCE

5.1.1 Natural Occurrence

Lead is a natural component of the earth's crust. It also occurs naturally in water and air as a result of erosion, dust formation from soil, and diffusion of gases from the earth's crust.[1-4] Because man has mined and used lead for centuries, it is difficult to determine the natural background of lead in our contemporary environment. Calculations of natural contributions, made on the basis of geochemical information, indicate that natural sources contribute relatively small amounts of lead to the environment. Natural concentrations in the air have been estimated[4] to be about 0.0006 $\mu g/m^3$, resulting mainly from airborne dust containing 10 to 15 ppm of lead.[2] The presence of radioactive lead-210 in the atmosphere is caused by the release of radon gases from the earth.[5] The lead content of soils and rocks averages 10 to 15 ppm.[3]

Lead is a ubiquitous element that is widely distributed in small amounts, particularly in soil and in all living things. In addition, occasional concentrated deposits of lead compounds occur in the earth's crust. These deposits, which have been discovered and mined, are the source of the large quantities of lead that have been redistributed in the environment as a result of human activities.

5.1.2 Man-made Sources

5.1.2.1 General Comments--Lead occupies an important position in the United States economy. The patterns of its flow through the economy

Table 5-1. LEAD CONSUMPTION IN UNITED STATES

(megagrams (metric tons))

Product	Year		
	1968	1971	1975
Metal products			
Ammunition	74,549	79,423	58,113
Bearing metals	16,726	14,770	11,053
Brass and bronze	19,066	18,361	12,160
Cable covering	48,484	47,998	20,048
Casting metals	7,884	6,603	6,995
Collapisble tubes	8,444	9,107	2,010
Foil	5,545	4,006	2,908
Pipes, traps, and bends	19,136	16,484	12,912
Sheet lead	25,642	25,039	22,552
Type metal	25,379	18,876	14,707
Weights and ballast	15,208	15,830	18,160
Solder	67,185	63,502	52,022
Subtotal	333,250	319,821	243,640
Storage batteries			
Grids and posts	226,867	292,268	296,395
Oxides	239,061	324,313	338,113
Subtotal	465,928	616,581	634,508
Coatings and miscellaneous			
Caulking lead	45,094	27,203	12,969
Annealing	3,803	3,690	2,385
Galvanizing	1,592	1,265	1,114
Plating	353	528	341
Terne metal	1,294	1,278	1,371
Other	16,257	14,286	19,252
Subtotal	68,394	48,250	37,432
Pigments			
White lead	5,312	4,291	2,266
Red lead and litharge	78,437	56,087	59,383
Pigment colors	12,846	12,622	9,633
Zinc oxide	2,933	701	453
Subtotal	99,529	73,701	71,735
Chemicals			
Gasoline additives	237,539	239,666	189,246
Miscellaneous chemicals	570	364	164
Subtotal	238,681	239,866	189,410
Total	1,205,783	1,298,383	1,176,725

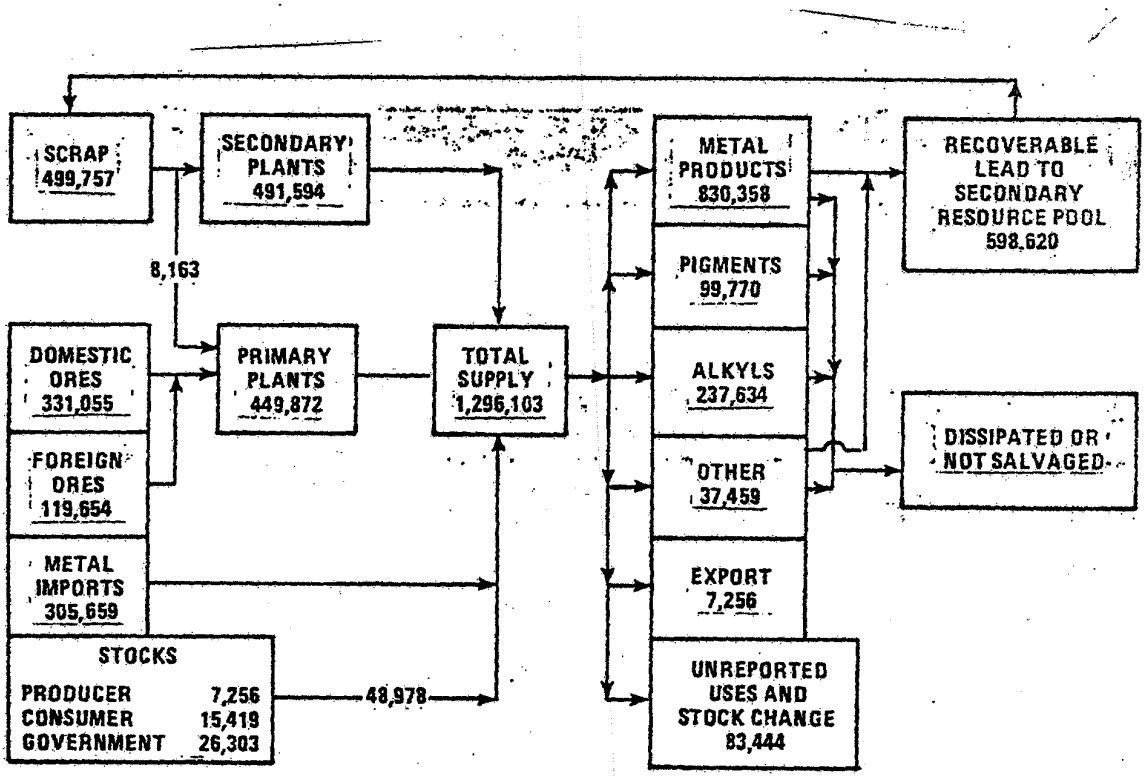

Figure 5-1. Flow of lead in United States, megagrams (metric tons).[6]

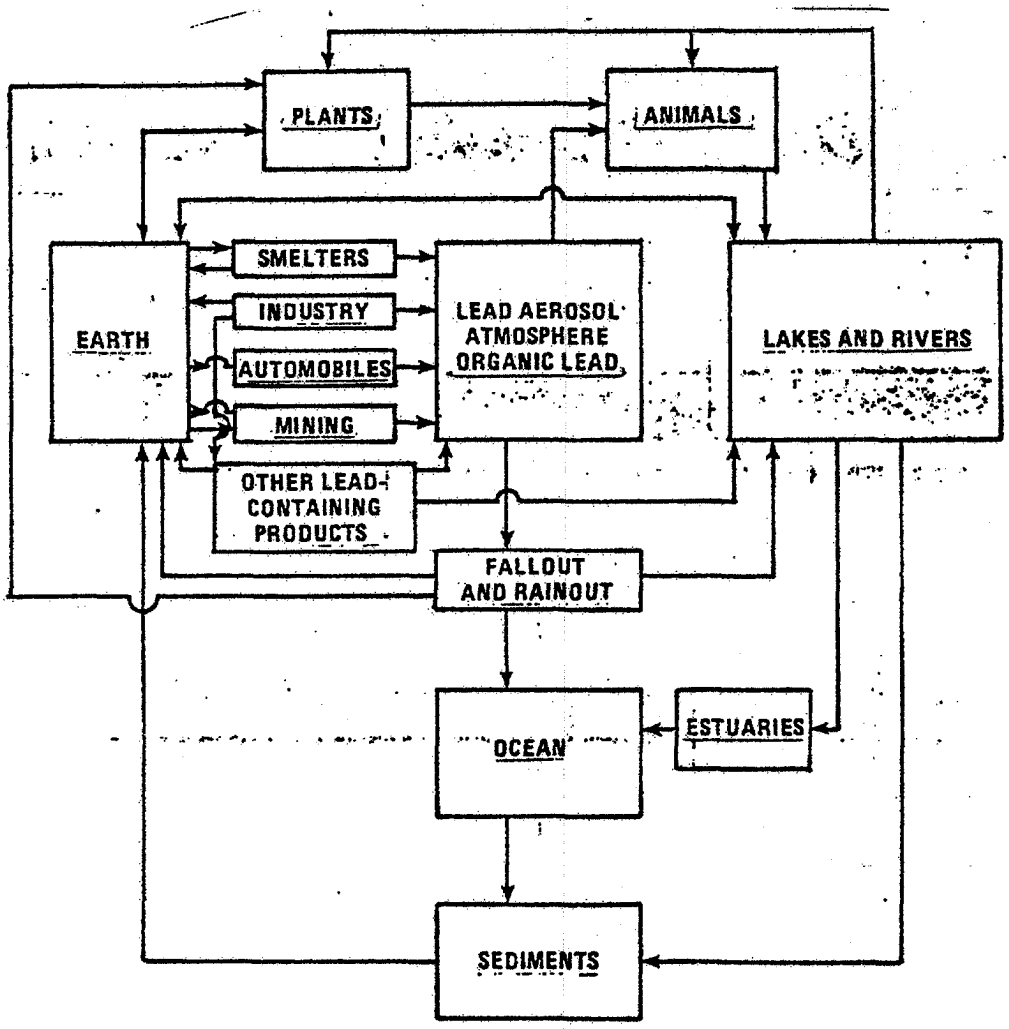

Figure 5-3. Ecological flow chart for lead showing possible cycling pathways and compartments.[3]

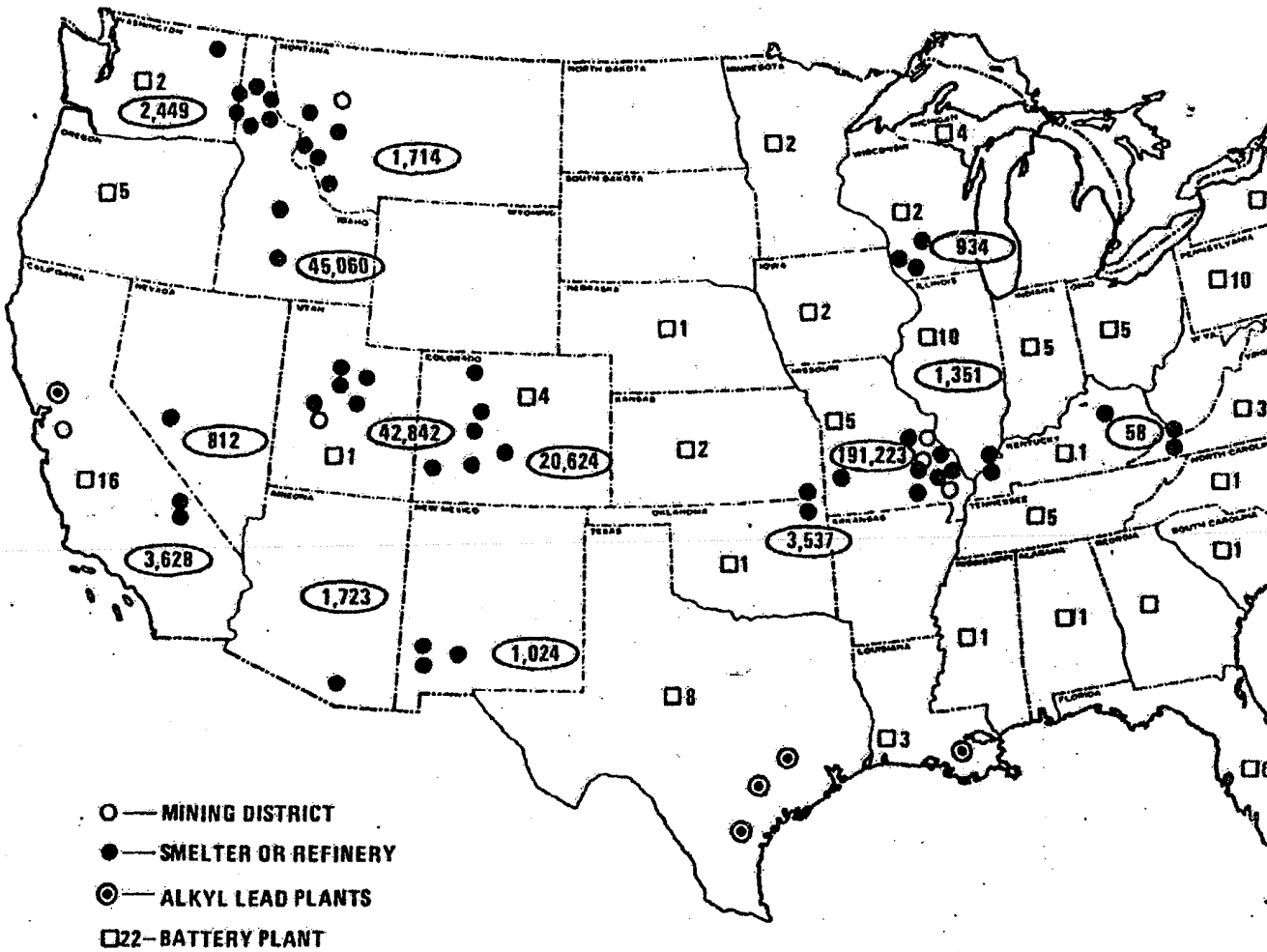

Figure 5-2. Location of major lead operations.

5.1.2.3 Stationary Sources--The major emissions of lead to the environment are to the atmosphere. As shown in Table 5-2, based upon 1970 data, metallurgical industries, waste incineration, and consumer product manufacturing are some of the principal stationary sources emitting lead. Since 1970, the quantity of lead emissions from the metallurgical industry has decreased somewhat because of the application of control technology and the closing of several plants, particularly in the zinc pyrometallurgical industry. The manufacturing of consumer products such as lead glass, storage batteries, and lead additives to gasoline, also contribute a significant amount of stationary source lead emissions. Based upon the available 1970 data, waste oil and municipal solid waste incineration contribute the largest quantity of lead emissions (31 percent) from stationary sources.

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. Another possible source of land or water media contamination is the disposal of particulate lead collected by air pollution control systems. The non-air media impact of the disposal of dusts collected by various control systems has not been quantified to date.

The lead-containing particles emitted from stationary sources occur in various sizes. Those emitted from uncontrolled stationary sources are generally larger than 2 μm mass mean diameter, and, therefore, tend to settle out in large part on land, water, and buildings near the source. These large-particle emissions add considerable lead to the dust, soil, and vegetation in the neighborhood of the source. These sources also contribute smaller-diameter particles to the atmosphere,

result of combustion of lead additives in gasoline.[7] This amounts to somewhat more than 163,260 Mg (MT) per year, which is 70 percent of the lead used in additives. The fate of the remainder is discussed in subsection 5.1.2.4. Atmospheric emissions of lead from stationary sources are estimated to be about 16,326 Mg (MT) per year.[8] In addition to these, pesticide contamination of crops and soil by 2721 Mg (MT) of lead annually [4081 Mg (MT) of lead arsenate] has been reported.[9]

5.1.2.2 Historical Changes--Perhaps the most impressive data on the magnitude of environmental contamination by lead, and its increase over time, are to be found in a small group of recent historical studies. Some of the most useful records on the increasing distribution of lead caused by man have been obtained by analyzing the layers of snow and ice from Greenland.[10] Annual ice layers from the interior of northern Greenland indicate that lead concentrations have increased from less than 0.001 µg/kg of ice in 800 B.C. to more than 0.2 µg/kg in 1965, an increase of approximately 200 times. This increase began in the early 18th century with the onset of the industrial revolution. The rate of increase remained about the same from that period until after the 1930's, when it rose more abruptly with the increasing use of lead gasoline additives. Jaworowski,[11] in a study of European glaciers, noted similar findings. Likewise Ruhling and Tyler,[12] in an examination of historical collections of Swedish mosses, observed an increase in lead content in samples taken from the period 1860 to the present.

Table 5-2 (Continued). ESTIMATED LEAD EMISSIONS FROM STATIONARY SOURCES IN UNITED STATES, 1970[8]

Source category	Emissions, megagrams (metric tons)	Emissions, %
Coal mining	589	3.6
Oil refining	82	0.5
Iron and steel industries	1,360	8.3
Gray-iron foundries	2,086	12.7
Ferroalloy industries	63	0.4
Cement plants	453	2.9
Total	16,371	100.0

Table 5-2. ESTIMATED LEAD EMISSIONS FROM STATIONARY SOURCES IN UNITED STATES, 1970[8]

Source category	Emissions, megagrams (metric tons)	Emissions %
Mining and milling	54	0.3
Metallurgical industries		
Primary lead	1,542	
Primary copper	1,542	
Primary zinc	218	
Secondary lead	199	
Subtotal	3,501	21.4
Lead oxide production	127	0.8
Consumer product manufacturing		
Storage Batteries	435	
Gasoline additives	1,723	
Pigments	190	
Solder	100	
Cablecovering	45	
Type metal	181	
Brass and bronze	36	
Metallic lead products	82	
Subtotal	2,793	17.0
Waste incineration		
Waste oil	2,902	
Municipal incineration	2,177	
Sewage and sludge incineration	181	
Subtotal	5,260	32.1

larger size ranges appears to depend upon a number of factors, including the particular driving pattern being followed by the vehicle and its past driving history. As an overall average, however, it has been estimated[13] that over the lifetime of the vehicle approximately 35 percent of the lead contained in the gasoline burned by the vehicle will be emitted as fine particulate, while approximately 40 percent will be emitted as coarse particulate. The total emission of about 75 percent of the lead contained in the gasoline burned by the vehicle corresponds roughly to the figure mentioned earlier of about 70 percent of the lead in gasoline additives being emitted in the vehicle exhaust.

The remainder of the lead consumed in gasoline is stored as deposits 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. The fate of this spent oil and its lead content is of considerable interest, and will be discussed further below. Meanwhile, some measure of its significance can be seen in Table 5-2 under the item "waste oil". Some lead which has been deposited in the exhaust system gradually flakes off, is emitted in the exhaust as extremely large particles, and rapidly falls into the streets and roads where it is incorporated into the dust and washed into sewers or onto adjacent soil.

The use of lead additives in gasoline, which has been increasing in total volume for many years, is now being reversed as cars designed to use low-lead or lead-free gasoline are making up a larger portion of the total automotive population (see Section 5.2.1.2, Figure 5-5). Regulations promulgated by EPA[14] that limit the average concentration of lead additives

where long-range transport may occur. When controls are applied to stationary sources, the total mass of the emissions is reduced significantly; however, the number of particles being emitted may not be affected greatly if the particle size is small. This is because current particulate control technology methods are usually more effective in removing the larger-diameter particles (> 2 μm mass mean diameter); e.g., those particles with the greatest mass. The smaller-diameter particles (which may range in size from 2 μm down to a few hundredths of a micrometer) may be far greater in number than the larger, more massive particles, and may escape collection altogether. These "fine particles" have less tendency to settle and therefore will be transported longer distances. Generally speaking, control methods are applied to emissions from stacks, vents, and other process outlets; however, lead-containing particles may also be emitted as fugitive dusts in the larger size range (> 2 μm diameter).

5.1.2.4 Mobile Sources--Lead particulates emitted in automotive exhaust fall into two rough size classes. Particles initially formed by condensation of lead compounds in the combustion gases are quite small in size, well under 0.1 μm in diameter. Particles in this size category which become airborne can remain suspended in the atmosphere for long periods and travel substantial distances from the original source. Larger particles are also emitted, which form as a result of agglomeration of smaller condensation particles. These larger particles, which may be tens of micrometers or larger in diameter, behave in the atmosphere more like the larger lead particulates associated with most stationary sources, and fall to the ground in the vicinity of the traffic producing them. The distribution of lead exhaust particles between the smaller and

in gasoline on an increasingly stringent schedule with time will also contribute to a reduction in future automotive lead emissions. Implementation of these limitations is currently suspended, pending the outcome of legal challenges.

5.2 CONCENTRATIONS

5.2.1 Air

5.2.1.1 Introduction--Some attempts have been made to evaluate the impact of major lead sources on the ambient air in their immediate vicinity. Many data relating to the extent of lead pollution have been acquired from monitoring aimed at the general definition of the nature and extent of air pollution on a national scale and, in some instances, on a local scale.

5.2.1.2 Ambient Lead Monitoring--Data collected by the National Air Surveillance Network (NASN) from 1957 to 1974, used to illustrate the nationwide distribution of lead over urban areas, are presented below.

Table 5-3. CONCENTRATION RANGES OF LEAD IN GASOLINE SAMPLES COLLECTED IN 10 EPA REGIONS, 1972[13]

Sample collection location	Concentration range, g/gal[a]					
	No. samples	Premium gasoline	No. samples	Regular gasoline	No. samples	Low-lead gasoline
Boston	9	1.49 to 2.85	5	1.23 to 2.84	11	0.009 to 0.68
New York	9	0.85 to 1.31	11	0.72 to 1.08	5	0.018 to 0.29
Philadelphia	8	1.31 to 2.77	9	1.19 to 2.70	8	0.010 to 0.60
Atlanta	6	1.78 to 2.58	7	0.90 to 2.36	6	0.016 to 0.48
Chicago	11	1.09 to 2.72	7	0.98 to 2.43	7	0.008 to 1.70
Dallas	5	2.10 to 2.89	5	1.39 to 2.72	5	0.032 to 0.44
Kansas City	5	1.21 to 2.65	5	1.42 to 2.20	5	0.011 to 1.46
Denver	5	1.84 to 2.72	5	1.14 to 1.94	4	0.022 to 1.20
San Francisco	9	1.48 to 3.52	5	1.28 to 2.32	6	0.037 to 0.63
Seattle	4	1.80 to 2.65	7	1.62 to 3.40	3	0.020 to 0.50

[a] g/gal x 0.264 = g/liter.

Table 5-4. NUMBER OF NASN URBAN STATIONS WHOSE DATA[15,16] FALL WITHIN SELECTED ANNUAL AVERAGE LEAD CONCENTRATION INTERVALS, 1957-1974

Year		Concentration interval, $\mu g/m^3$					Total
		<0.5	0.5-0.99	1.0-1.9	2.0-3.9	4.0-5.3	
1957-1963	No. stations	81	102	84	15	1	283
	Percent	29	36	30	5		100
1964	No. stations	13	25	12	3		53
	Percent	25	47	23	5		100
1965	No stations	11	59	41	3	1	115
	Percent	9	51	35	2	1	100
1966	No. stations	9	40	40	6		95
	Percent	9	42	42	6		100
1967	No. stations	4	37	63	9		113
	Percent	3	32	55	7		100
1968	No. stations	14	67	54	10	1	146
	Percent	9	45	36	6	1	100
1969	No. stations	5	46	103	23	1	178
	Percent	2	25	57	12	1	100
1970	No. stations	9	54	80	15	1	159
	Percent	5	33	50	9	1	100
1971	No. stations		23	64	21	1	109
	Percent		21	58	19	1	100
1972	No. stations	16	67	84	12	1	180
	Percent	9	37	47	7	0	100
1973	No. stations	20	76	36	4	1	137
	Percent	15	55	26	3	1	100
1974	No. stations	19	69	38	4	0	130
	Percent	15	53	29	3	0	100
1957-1974 Total	No. stations	201	665	699	125	8	1698
	Percent	12	39	41	7	1	100

5.2.1.2.1 National Air Surveillance Network Data[15]--From 1957, samples of suspended particulate matter collected at some 300 urban and 30 nonurban NASN sites have been analyzed for trace metals, including lead. The emission spectrographic method employed in the analysis has sufficient sensitivity to permit detection of lead in all urban and most nonurban samples, thus providing a broad data base. (Data obtained before 1968 by this method are only semi-quantitative; see subsection 4.1.1.3.)

Summaries of the data for urban and nonurban NASN sites for 1957 through 1974 are presented in Tables 5-4 and 5-5, which categorize the sites by four different concentration ranges.[15,16] The majority of the urban sites (80 percent of the site-years) reported data that fall into the concentration interval 0.5 to 1.9 $\mu g/m^3$, and the majority of nonurban sites (85 percent of the site-years) reported data that fall into the concentration interval 0.03 to 0.19 $\mu g/m^3$. Tables 5-6 and 5-7 are listings of all urban and nonurban quarterly composite averages by year for 1970 through 1974.

NASN urban sites for which annual average concentrations have been 3.0 $\mu g/m^3$ or greater are listed in Table 5-8.[15,16] Highest concentrations for short averaging times have been included in order to show potential peak exposure conditions.

A large number of Southern California cities is included in the list because of the heavy automobile traffic in these areas. Both annual and maximum 24-hour, or quarterly, averages for Los Angeles County sites were consistently high, apparently because of location, topography, and meteorological conditions that favor retention of pollutants in the air over the area.

Table 5-6. URBAN CUMULATIVE FREQUENCY DISTRIBUTIONS BY YEAR, 1970 THROUGH 1974[16]
($\mu g/m^3$)

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

[a]LD = limit of detection.

Table 5-5. NUMBER OF NASN NONURBAN STATIONS WHOSE DATA[15,16] FALL WITHIN SELECTED ANNUAL AVERAGE LEAD CONCENTRATION INTERVALS, 1957-1974

Year		Concentration interval, $\mu g/m^3$				Total
		<0.03	0.03-0.099	0.10-0.19	0.20-0.45	
1959-1965	No. stations	5		8	3	16
	Percent	31		50	19	100
1966	No. stations		10	6	3	19
	Percent		52	32	16	100
1967	No. stations	1	7	10	2	20
	Percent	5	35	50	10	100
1968	No. stations	1	15	4		20
	Percent	5	75	20		100
1969	No. stations		11	9	1	21
	Percent		52	43	5	100
1970-1971	No. stations			7	3	10
	Percent			70	30	100
1972	No. stations	10	4	9	11	34
	Percent	29	12	26	33	100
1973	No. stations	9	7	6	1	23
	Percent	39	31	26	4	100
1974	No. stations	3	5	6	2	16
	Percent	19	31	38	12	100
1957-1974 Total	No. stations	29	59	65	26	179
	Percent	16	33	36	15	100

Table 5-8. NASN STATIONS[15,16] WITH ANNUAL AVERAGE LEAD CONCENTRATIONS $\geq$ 3.0 $\mu g/m^3$

Year	Station	Average	Maximum quarter	Maximum 24 hr
1962	Los Angeles, CA	4.2		17.0
	Pasadena, CA	3.5		
1965	Los Angeles, CA	4.6	9.7	
1966	Phoenix, AZ	3.2	8.1	
	Burbank, CA	3.7	6.0	
	Los Angeles, CA	3.6	11.0	
	Pasadena, CA	3.6	4.3	
1967	Los Angeles, CA	3.1	5.4	
1968	Burbank, CA	4.4		14.0
	Glendale, CA	3.0		7.5
	Long Beach, CA	3.3		12.0
	Los Angeles, CA	3.9		10.0
	Pasadena, CA	3.5		8.3
1969	Fairbanks, AK	3.2	4.8	
	Phoenix, AZ	3.1	7.1	
	Burbank, CA	3.5	4.7	
	Glendale, CA	3.1	4.5	
	Los Angeles, CA	4.6	5.7	
	San Juan, PR	3.8	4.2	
	Dallas, TX	3.0	5.2	
1970	Burbank, CA	4.8	6.7	
	Glendale, CA	3.3	4.2	
	Los Angeles, CA	3.8	5.6	
	San Juan, PR	3.0	3.9	
1971	Anaheim, CA	3.3	4.8	
	Burbank, CA	5.3	5.8	
	Pasadena, CA	3.4	4.8	
	Santa Ana, CA	3.5	4.7	
	Scranton, PA	3.3	5.0	
	Dallas, TX	3.0	3.3	
1972	Burbank, CA	3.2	6.7	
	Glendale, CA	3.5	5.2	
	Los Angeles, CA	3.1	4.8	
	San Juan, PR	5.0	6.9	
1973	Burbank, CA	4.0		

Table 5-7. NONURBAN CUMULATIVE FREQUENCY DISTRIBUTIONS BY YEAR, 1970 THROUGH 1974[16]
($\mu g/m^3$)

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