Lead in the Environment

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T. G. Lovering, *Editor*

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A compilation of papers on the
abundance and distribution of
lead in rocks, soils, plants,
and the atmosphere, and on methods
of analysis for lead used by the
U.S. Geological Survey

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LEAD IN THE ENVIRONMENT—SUMMARY

By T. G. LOVERING

Lead is a soft, heavy, malleable, relatively inert metal with a low melting point (327.4°C), which has been known and used by man since ancient times. It has the chemical symbol Pb (from its Latin name plumbum), atomic number 82, and atomic weight of 207.2, making it the heaviest of the common metals. It is the stable end product formed by the radioactive decay of uranium.

Metallic lead was used in antiquity for jewelry, plumbing, and cooking utensils. In modern times metallic lead and lead alloys are extensively used for storage battery plates, sheathing for electrical cables, small-caliber ammunition, shielding for X-ray apparatus and atomic reactors, type metal, bearing metal, and solder. Lead compounds are also important as components in the manufacture of paint, ceramics, and glass and as an antiknock additive in gasoline. In 1970 the United States produced about 570,000 tons of lead and consumed about 1,380,000 tons. Much of the excess consumption was derived from recycled scrap metal, and the rest was imported chiefly from Canada and Mexico.

Ores of lead and zinc are often closely associated in deposits formed by replacement of limestone or dolomite. Lead ore is commonly present together with ores of copper, zinc, silver, arsenic, and antimony in complex vein deposits that are genetically related to silicious igneous intrusive rocks, but lead ore may occur in a variety of igneous, metamorphic, and sedimentary host rocks.

Although both metallic lead and the common lead minerals are nearly insoluble in pure water, they are appreciably soluble in certain organic acids; likewise, some of the lead compounds produced industrially are also considerably more water soluble than the element. If lead enters the human body in soluble form it accumulates there and can cause lead poisoning.

Airborne lead in smoke from smelters, or from the coking of coal with a high lead content, may produce toxic effects in plants, grazing animals, and humans exposed to the smoke for a long time. Lead poisoning may also result from the ingestion of lead-bearing paint by small children or of lead leached from pottery glazes by the citric acid in fruit juices.

Lead compounds released into the atmosphere in the exhaust fumes of automobiles have produced abnormally high concentrations of lead in the blood of individuals continuously exposed to these fumes for long periods of time, but as yet there is no established instance of lead poisoning resulting directly from this source.

MIGRATION OF LEAD IN THE NATURAL ENVIRONMENT

Natural concentrations of lead in lead ore deposits do not normally move appreciably in normal ground or surface water, because any lead dissolved from primary sulfide ore tends to combine with carbonate or sulfate ions to form insoluble lead carbonate or lead sulfate or else to be adsorbed by ferric hydroxide. Mechanical disintegration and transportation of these insoluble lead compounds can remove lead from the surface of lead ore bodies and disperse it to some extent. Lead can also be leached by acid waters, particularly those that are rich in organic material, and travel in solution as soluble lead organic complexes. In this form it can be taken up by plants and enter the food chain, but examples are rare. In regions characterized by alkaline, neutral, or saline waters and soils, naturally occurring forms of lead do not enter either water or plants except in very minute traces. Lead minerals in a nonreactive host rock such as sandstone or quartzite have been known to dissolve in acid waters in amounts toxic to vegetation in a small area, but there are no known instances of lead poisoning in humans related to the natural occurrence of lead.

ABUNDANCE OF LEAD IN ROCKS, SEDIMENTS, FOSSIL FUELS, AND MINERALS

The average abundance of lead in the Earth's crust is approximately 15 ppm (parts per million), which is equivalent to half an ounce of lead per ton of rock. The lead contents of the common rock types that make up the crust of the earth range from about 30 ppm for granitic rocks, rhyolite, and black shale to about 1 ppm for evaporite sediments, basalt, and the ultramafic igneous rocks such as dunite, which are rich in iron and magnesium and poor in silica (table 36).

Unconsolidated continental sediments have a mean lead content very close to the mean crustal abundance of 15 ppm, but unconsolidated deep sea muds are appreciably richer in lead, containing an average of about 60 ppm lead, and concentrations as high as 0.2 percent lead have been reported in sediments precipitated from hot brines in the Red Sea (table 36).

Coal contains an average lead concentration of about 10 ppm, and petroleum an average of less than 1 ppm of lead (table 36). Most of the lead in these fossil fuels concentrates in their ash when they are burned, although it has been estimated that during industrial burning coal may release as much as 6 percent of its original lead content into the atmosphere. Petroleum produces far less ash than coal, and inorganic constituents are much more highly concentrated in its ash.

Although lead is a major constituent of more than 200 known minerals (table 37), most of these are very rare, and only three are commonly found in sufficient abundance to form minable lead deposits. These three are galena, the simple sulfide of lead (PbS); anglesite, the lead sulfate ($PbSO_4$); and cerrusite, the lead carbonate ($PbCO_3$). Galena is a common primary constituent of sulfide ore deposits; anglesite and cerrusite normally form by the oxidation of galena close to the surface.

Lead is also present in trace amounts in many of the common rock-forming minerals (table 36). The amount of lead in any one of these minerals varies widely, and the greater the normal lead content of such a mineral, the greater the observed variation is likely to be. For instance, potash feldspar (orthoclase or microcline) generally contains the most lead of any of the common silicate minerals; yet, whereas samples from one group of pegmatite dikes in Norway yielded 280 ppm lead, similar samples from another group of pegmatite dikes in the same region contained less than 10 ppm. The maximum amount of lead this mineral can contain is unknown, but 2,800 ppm lead has been reported in a sample of a green variety of microcline called amazonite.

The common silicate minerals found in igneous rocks, in order of decreasing lead content, are (1) potash feldspar; (2) plagioclase feldspar and muscovite mica; (3) pyroxenes, amphiboles, and biotite mica; and (4) quartz. The common minerals of chemically precipitated sedimentary rocks (calcite, dolomite, gypsum, and halite) all normally contain less than 10 ppm lead. The lead content of the sedimentary clay minerals is extremely variable but is commonly on the order of 10–20 ppm.

NATURAL ABUNDANCE OF LEAD IN WATER

The concentration of lead in river water is low under natural conditions (table 36). Although small amounts of lead are widely distributed as a minor constituent in rock and soil minerals, lead is only slowly released by weathering processes. Even where the element is concentrated in ore deposits, the low solubility of lead in water that contains dissolved carbon dioxide species and has a pH near neutrality generally will maintain concentrations of lead in solution below a few tenths of a milligram per litre. The waterborne element tends to be complexed by relatively insoluble organic matter and may also be extracted from water by organisms.

The median concentration of lead in river and lake water of the United States is about 2 μg/l (micrograms per litre). Concentrations of lead in seawater range from a few hundredths of a microgram per litre (a value of 0.03 μg/l is widely quoted) in the deeper parts of the ocean basins to 0.4 μg/l observed at several places both nearshore and far offshore in surface waters of the Pacific Ocean. The higher nearshore and near-surface concentrations, however, are ascribable to atmospheric fallout of lead particles or washing out of such particles by rainfall. Concentrations of lead in rainfall over the United States have been reported to average 34 μg/l over a 7-month period in 1966 and 1967, with a median value of about 10 μg/l. When the distribution of sampling points is correlated with reported concentrations, results show strongly the effects of industrial air pollution near cities.

ABUNDANCE OF LEAD IN SOILS

Soil samples collected from nearly a thousand localities throughout the conterminous United States ranged in lead content from <10 to 700 ppm and had a mean lead concentration of 16 ppm (Shacklette, 1971); only 6 percent of these samples contained more than 30 ppm of lead (table 36). Many of the soil samples with lead content in excess of 100 ppm were obtained from localities in western Colorado, but others came from widely scattered isolated sites.

Lead content of young residual soils is strongly influenced by that of the parent rock from which they are derived; however, this relationship is modified, and may be obscured, by other factors in mature soils developed on deeply weathered parent material. These factors include oxidation and reduction reactions, linking of organic compounds by lead ions (chelation), base exchange reactions by clay, adsorption of lead by hydroxides of iron and manganese, local solution and transportation by organic acids, and cycling by vegetation. In general, lead is more mobile in acid soils than in alkaline soils, tending to be leached out of the former and to form residual concentrations in the latter. Relatively high total-lead concentrations in alkaline soil may reflect residual concentration of lead in an insoluble form, which is not available to plants.

LEAD IN VEGETATION

Lead occurs naturally in small amounts in all plants (table 36). The concentration of lead in vegetation varies not only with the individual species, but also as a complex function of climatic variations, parts of the plant, composition of the soil in which the plant grows and of the rock from which this soil is derived, and finally the effects of artificial contamination of both the water that nourishes the plant and the air that surrounds it.

Anomalously high concentrations of lead in plants may reflect natural contamination from lead dsposits or artificial contamination of the plant's environment by man. Extensive analyses of plants from primitive areas, unaffected by either of these sources of contamination, are required to establish normal background values for lead in natural vegetation.

Median concentrations of lead in the ash of uncontaminated natural vegetation are highest for lichens (1,000 ppm), an order of magnitude lower in mosses (100 ppm), about 30-50 ppm in evergreen trees, and about 15-30 ppm in deciduous trees, shrubs and grasses; however, all of these types of vegetation exhibit a wide range in lead content (commonly an order of magnitude) on both sides of the median. The ash of uncontaminated domestic fruit and vegetable samples from the United States has a median lead content close to 10 ppm, which is the lower limit of the analytical method. The observed range for lead in the ash of these foods is from <10 to 100 ppm. The lead content of these plants expressed in dry weight varies from about one-fourth to less than one-tenth the lead content of the ash. Thus the highest observed lead-in-ash content of 100 ppm, for a tomato sample, corresponds to a dry-weight lead content of about 7 ppm and to a lead content for a fresh tomato of less than 1 ppm.

Studies of seasonal variation in the lead content of trees suggest that lead concentration is highest in early spring at the beginning of the growing season, declines during the summer, and rises again in the fall. Lead also tends to concentrate in certain parts of a growing plant. In trees, the highest lead concentrations are usually found in the older twigs; somewhat less lead occurs in the young twigs, seeds, and trunk wood, still less in the leaves or needles, and least of all in the roots. On the other hand, lead content of the leaves of certain vegetables appears to be higher than that of their stems, and the lead in fruits and root vegetables is largely concentrated in the skin or peel.

There appears to be a general tendency for lead to be more abundant in plant ash than in the soil, and more abundant in the soil than in the bedrock, but there are many exceptions.

The knowledge that certain plant species have the ability to absorb anomalous amounts of lead from lead-rich soils and their underlying parent materials has been used as a biogeochemical tool in prospecting for lead deposits for a quarter of a century. These accumulator plants include certain species of both evergreen and deciduous trees, as well as many shrubs and smaller plants.

Contamination of food and forage crops by artificial lead compounds contained in insecticide sprays, automobile exhaust fumes, and industrial smoke is a matter of concern to public health workers. Anomalously high lead concentrations have been found in leafy vegetables and grasses grown in proximity to major highways, in crops grown on soil with a long history of treatment with lead-bearing insecticides, and in crops exposed to fallout from smelter smoke.

LEAD IN THE ATMOSPHERE

Lead enters the atmosphere largely in the exhaust fumes from internal combustion engines and, to a lesser extent, from the smoke produced by large-scale industrial burning of coal. Consequently the lead content of the air is highest in urban industrial areas and lowest in rural areas (table 36). The average lead concentration in the air of large metropolitan areas is about 2.5 $\mu g/m^3$. In rural areas it is less than 0.5 $\mu g/m^3$. The amount of lead present in the air at any particular place varies with traffic density, air temperature, and atmospheric conditions. The lead-bearing particles in the air are heavy and tend to collect in low areas with poor air circulation; lead concentrations greater than 40 $\mu g/m^3$ have been measured in the air of vehicular tunnels. In spite of this tendency of lead to accumulate close to the ground, traces of it enter the upper atmosphere and are carried widely around the earth to return to the surface in rain or snow. The lead content of a snow sample collected in 1965 from the Greenland ice cap was approximately 0.4 $\mu g/l$ of melted snow as compared to about 0.05 $\mu g/l$ in melted ice that had formed in 1864.

METHODS FOR DETECTION OF LEAD

Lead may be determined in water, soil, and rock, and in the ash of plants and organic fuels by a wide variety of methods. The analytical methods employed for both water and solids in the laboratories of the U.S. Geological Survey include optical emission spectrography and atomic absorption spectrophotometry. In addition, X-ray, spectrographic, and colorimetric methods are employed for the analysis of rock, mineral, and soil samples; electron microprobe analysis of polished ore samples is used for the nondestructive determination of lead in high concentrations in small mineral grains.

Water samples are filtered to remove solid particles and are then acidified. In the atomic absorption method a lead-scavenging organic compound is first added to the water and then extracted with an insoluble organic fluid (methyl isobutyl ketone); this fluid is then introduced into the flame of the atomic absorption spectrophotometer. In the emission spectrographic method, lead and other metals are first precipitated by adding a suitable reagent to the water sample. The precipitate is filtered, dried, and introduced into the arc of the emission spectrograph for the simultaneous determination of the metals present.

The optical emission spectrograph is the most widely used laboratory tool for chemical analysis of solid samples that do not contain large amounts of organic carbon, because this method provides a simultaneous analysis for a large number of elements on a very small quantity of sample material. In routine operation it will normally determine lead in concentrations as low as 5 ppm. Specific analyses for small traces of lead in such materials are made by the atomic absorption method, which, in routine operation, will give good results for lead in amounts as small as 1 ppm, and, with special sample preparation, this method can be used to detect even smaller amounts. Colorimetric methods with a sensitivity to about 20 ppm of lead are used for rapid field tests in reconnaissance geochemical exploration.

UNITS AND NOTATION

The amount of lead in natural materials is expressed in different ways for different substances by the authors of this report. Lead concentrations are generally reported in the following units:

For water—
  μg/l=micrograms per litre
  mg/l=milligrams per litre
For solids—
  ppb=parts per billion
  ppm=parts per million
  μg/g=micrograms per gram
  oz/ton=ounces per ton
For air—
  ng/m^3=nanograms per cubic metre
  μg/m^3=micrograms per cubic metre
  g/ha=grams per hectare
Conversion factors—
  1 ng=1 nanogram=0.000000001 gram
  1 μg=1 microgram=0.000001 gram
  1 mg=1 milligram=0.001 gram
  1 ppb=1 part per billion=0.000001 percent
  1 ppm=1 part per million=0.0001 percent
    1 part per thousand=0.1 percent
  1 oz/ton=31 parts per million=0.0031 percent
  1 g/metric ton (t)=1 part per million=0.0001 percent
  1 ha=1 hectare=1,000 square metres
Symbols
  >=greater than
  <=less than
  ≈ =approximately

INORGANIC CHEMISTRY OF LEAD IN WATER

By J. D. Hem

The concentration of dissolved lead in most natural water systems, which usually contain dissolved carbon dioxide and have a pH near 7, is very low—commonly less than 10 μg/l—partly because lead combines readily with carbonates, sulfates, and hydroxides normally present in such waters to form compounds of low solubility. Highly saline waters or strongly acid waters may contain appreciably higher concentrations of lead in solution, but such waters tend to be very restricted in distribution.

STABILITY FIELDS OF INORGANIC LEAD COMPOUNDS IN NATURAL WATER SYSTEMS

An outstanding characteristic of lead is its tendency to form compounds of low solubility with the major anions of natural water. The hydroxide, carbonate, sulfide, and more rarely, the sulfate of lead may act as solubility controls. Over most of the Eh-pH region, in which water is stable at 25°C and 1 atm (atmosphere) pressure, the divalent form, Pb^{+2}, is the stable species of lead. The more oxidized solid PbO^2, in which lead has a +4 charge, is stable only in a highly oxidizing environment; thus Pb^{+4} probably has very little significance in controlling the behavior of lead in aqueous geochemical systems. If sulfur activity is very low, metallic lead can be a stable phase in alkaline or near-neutral reducing conditions in the presence of water.

Fields of stability for solid species of lead in the system $Pb+H_2O$ at 25°C are shown in figure 1. A dissolved activity of solute lead species of $10^{-8.32}$ mol/l (equivalent to 1 g/l) was used to locate solid-solute boundaries. The stability fields of solids in the Eh-pH diagram would be enlarged at the expense of the areas of Pb^{+2} and $Pb(OH)_3^-$ if a higher dissolved lead activity were assumed.

The boundaries in figure 1 were calculated from thermodynamic data for lead assembled in table 1. The data were selected from published literature, mostly from the compilation of Wagman and others (1968). The range of published free energy values is rather large for some of the species of lead important in this study, and the choice of values can influence stability and solubility calculations substantially. Standard Gibbs free energy values compiled in the National Bureau of Standards Technical Notes (Wagman and others, 1968) should be mutually compatible, but for a few of the lead species either no values are given or values in other publications appeared to be in better agreement with the consensus of published solubility information. Free energy values for PbS and $PbCO_3$ in table 1 were taken from Robie and Waldbaum (1968) because they seemed to give solubilities nearer those reported by most investigators, as quoted by Sillén and Martell (1964).

No value for the hydroxy-carbonate solid or $PbSO_4$ aq is given in either the compilation by Robie and Waldbaum or that of Wagman and others. The value given by Wagman and others for $PbOH^+$ is not compatible with stability data for this complex given by Sillén and Martell (1964). The value chosen here is calculated from a stability constant published by Faucherre (1954), which agrees better with the considerable number of values for this ion determined by other investigators, even though it was calculated at 20°C rather than 25°C. The discrepancy introduced by this deviation from standard temperature is negligible. Faucherre's data were obtained for a solution of 0.06 ionic strength, and have been adjusted to zero ionic strength using the Debye-Hückel equation. Faucherre's work also provided data for the polynuclear ion $Pb_4(OH)_4^{+4}$. Latimer's (1952) compilation of free energy data gave a value for $Pb(OH)_2$c nearly 8 kcal less negative than the one given in table 1. The rather wide range in thermodynamic data adds a considerable factor of uncertainty to the solubility calculations.

The mixed oxide Pb_3O_4 c apparently is less stable than $Pb(OH)_2$ c in the system specified for figure 1 and does not appear in the Eh-pH diagram. The $Pb(OH)_2$ c value given in table 1 results in a large domain for this species in the Eh-pH diagram and almost eliminates the mixed hydroxy carbonate from consideration. The natural occurrence of this mineral, however, does suggest that the difference between the stabilities of mixtures of $PbCO_3$ and $Pb(OH)_2$ and of the basic carbonate likely favors the basic carbonate. If the free energy value of Latimer is used for the basic carbonate, the species has a narrow stability field near pH 8, and this field would be considerably enlarged if the carbon dioxide species concentration were assumed to be higher than the 10^{-3} mol/l used in drawing the boundaries in figure 2.

The system specified for figure 1 is highly simplified. To be more applicable to systems involving ordinary surface or underground water, the effects of dissolved carbon dioxide and sulfur species must be included. If a fixed total activity of dissolved carbon dioxide species and a fixed total activity of dissolved sulfur species are specified, stability fields of lead carbonate, sulfate, and sulfide can be shown. Figure 2 is an Eh-pH diagram for the system $Pb\text{-}CO_2\text{-}H_2O\text{-}S$ at 25°C and 1 atm pressure. Total activities of dissolved CO_2 and sulfur species are both 10^{-3} molar. Areas of stability of solids and the solubility of lead are shown in figure 2. Table 2 gives equations used for the solubility calculations in that part of the diagram where $Pb(OH)_2$ c and carbonate or hydroxy carbonate are dominant.

As specified here, the activities of these dissolved carbon dioxide species do not necessarily involve a gas phase. Specifying a fixed partial pressure of carbon dioxide, as is sometimes done in solubility calculations of this type, tends to lead to a very high, probably unrealistic, concentration of carbonate in solution at the higher pH's.

From figure 2 it is evident that the solubility of lead is very low (less than 1 μg/l) between pH 8.5 and 11, and is also low in all strongly reducing systems down to pH 2. However, between pH 6 and 8 the solubility of lead is a rather complex function of pH and total dissolved CO_2 and sulfur species. Lead can be relatively soluble in a dilute natural water below pH 6.5. In such a solution if the activity of dissolved CO_2 species were lower than 10^{-3} molar, the lead solubility would be greater than shown in the diagram. Some dilute river waters thus could be a favorable chemical environment for the solution of lead.

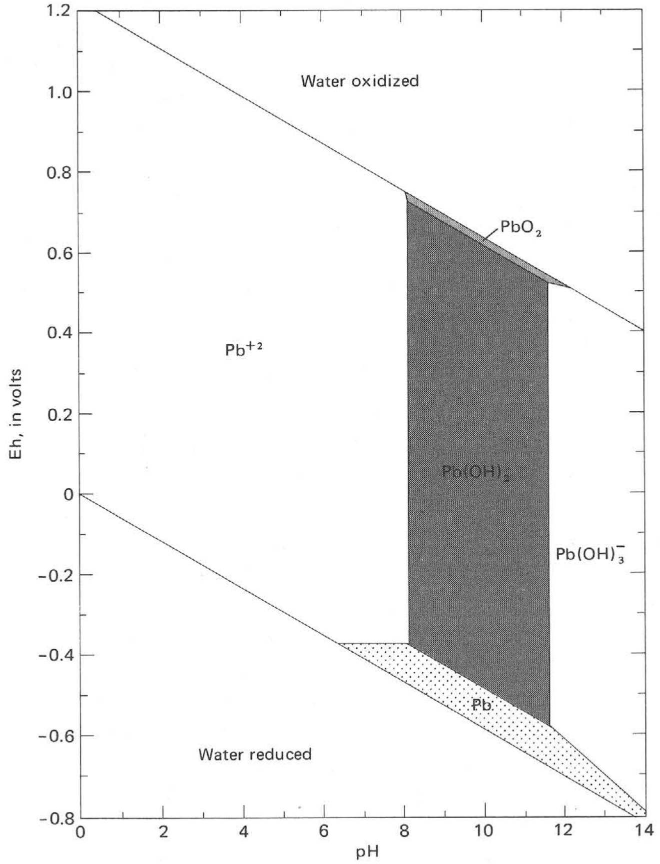

FIGURE 1.—Fields of stability for solids species (c; patterned) and dominant solute species in system $Pb+H_2O$ as functions of pH and redox potential. Dissolved lead activity $10^{-8.32}$ mol/l at 25°C and 1 atm pressure.

TABLE 1.—*Standard Gibbs free energies of formation of lead species and related solutes.*

[c, solid state; aq, dissolved]

Formula	Free energies $\Delta G°f$ (kcal/mol)	Source of data
Pb^{+2} aq	-5.83	Wagman and others (1968).
$PbOH^+$ aq	-51.4[1]	Calculated from Faucherre (1954).
$Pb(OH)_2$ aq	-95.8	Wagman and others (1968).
$Pb(OH)_3^-$ aq	-137.6	Do.
$Pb_4(OH)_4^{+4}$ aq	-225.6[1]	Calculated from Faucherre (1954).
$PbCl^+$ aq	-39.39	Wagman and others (1968).
$PbCl^2$ aq	-71.03	Do.
$PbSO_4$ aq	-187.38	Calculated from Kolthoff, Perlich, and Weiblen (1942).
PbO c[2]	-44.91	Wagman and others (1968).
PbO c[3]	-45.16	Do.
$Pb(OH)_2$ c	-108.1	Do.
PbS c	-22.96	Robie and Waldbaum (1968).
$PbCO_3$ c	-150.3	Do.
$Pb_3(OH)_2(CO_3)_2$c	-409.1	Latimer (1952).
$PbSO_4$ c	-194.36	Wagman and others (1968).
PbO_2 c	-51.95	Do.
Pb_3O_4 c	-143.7	Do.
H_2O[4]	-56.69	Do.
OH^- aq	-37.59	Do.
H_2S aq	-6.66	Do.
HS^- aq	2.88	Do.
SO_4^{-2} aq	-177.97	Do.
HSO_4^- aq	-180.69	Do.
H_2CO_3 aq	-148.94	Do.
HCO_3^- aq	-140.26	Do.
CO_3^{-2} aq	-126.17	Do.

[1] At 20°C.
[2] Yellow.
[3] Red.
[4] Liquid.

Within the field of stability for $PbSO_4$, the solubility of lead is a function of the total sulfate concentration. This control is most effective at rather low pH and when sulfate concentrations are high. The dissolved ion-pair $PbSO_4$ aq is not a dominant form of dissolved lead unless sulfate activity exceed $10^{-2.62}$ mol/l. In a solution of this type ionic strength would be rather high, requiring a stoichiometric sulfate concentration of at least 500 mg/l to produce the specified activity of SO^{4-2} ions. The $PbSO^4$ aq complex does influence the solubility of lead shown in fugure 2, however, and was taken into account in locating the solubility lines. The solubility of lead is near 5 mg/l in most of the $PbSO_4$ c field; within this area solubility is constant above pH 2 because of the specified constant sulfur activity. Below pH 2 the lead solubility increases because some of the sulfate is converted to HSO_4^- at very

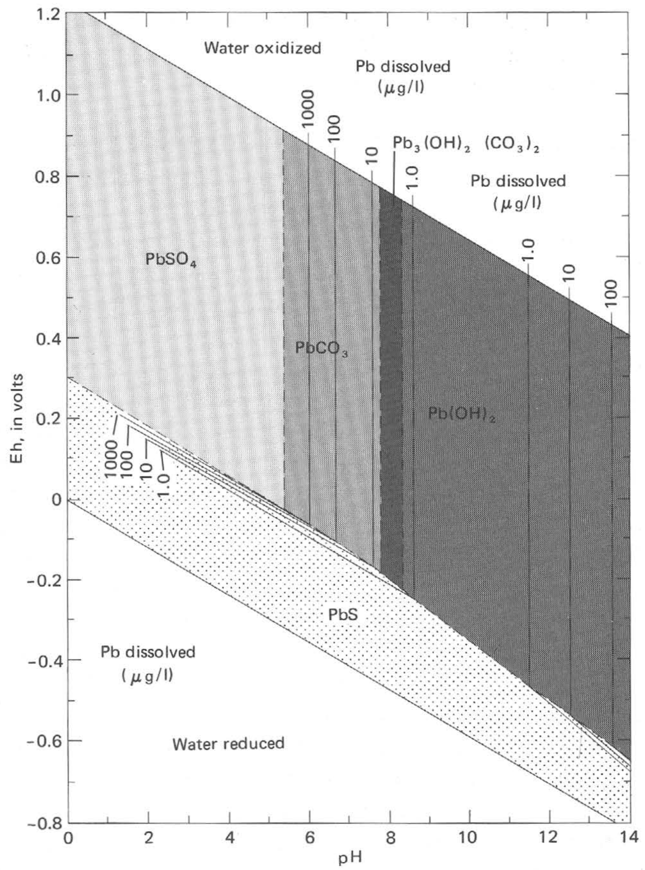

FIGURE 2.—Fields of stability for solids (c, patterned) and solubility of lead in system $Pb+CO_2+S+H_2O$ at 25°C and 1 atm pressure. Ionic strength 0.005.

low pH. Under reduced conditions the stable solid is galena, PbS, which has a very low solubility above pH 2.

The lead solubilities and regions of stability of solids shown in figures 1 and 2 are derived from theoretical chemistry, and certain variables are artificially fixed so that the results can be expressed on a two-dimensional graph. In effect, the defined systems retains only two degrees of freedom. Although some natural systems—for example, ground water in a mineralogically homogeneous aquifer—may have constraints enough to conform to a simple equilibrium model, the usual river or lake water is subject to changing conditions that increase the number of degrees of freedom, and a close conformance to equilibrium is unusual. However, the strong influence on lead solubility of the pH and alkalinity of the water may be reflected in analyses of river water, because the effect may be strong enough to be discerned even if equilibrium is not attained. Although available data are neither entirely reliable nor adequate in quantity, the best current information suggests that many surface waters in the United States carry concentrations of lead in solution whose values are close to those predicted from solubility calculations such as those represented in figure 2.

TABLE 2.—*Chemical equilibria and solubility equations for lead species in hydroxide and carbonate domains*

Chemical equilibria

Equation		Source of constant
$[Pb^{+2}][H^+]^{-2}$	$= 10^{8.15}$	Calculated from data in table 1.
$[PbOH^+][H^+][Pb^{+2}]^{-1}$	$= 10^{-8.12}$	Do.
$[Pb(OH)_2][H^+]^2[Pb^{+2}]^{-1}$	$= 10^{-17.16}$	Do.
$[Pb(OH)_3^-][H^+]^3[Pb^{+2}]^{-1}$	$= 10^{-28.08}$	Do.
$[Pb_4(OH)_4^{+4}][H^+]^4[Pb^{+2}]^{-4}$	$= 10^{17.95}$	Do.
$[Pb^{+2}][HCO_3^-][H^+]^{-1}$	$= 10^{-3.09}$	Do.
$[PbSO_4][SO_4^{-2}]^{-1}[Pb^{+2}]^{-1}$	$= 10^{2.62}$	Do.
$[HCO_3^-][H^+][H_2CO_3]^{-1}$	$= 10^{-6.35}$	Garrels and Christ (1965).
$[CO_3^{-2}][H][HCO_3^-]^{-1}$	$= 10^{-10.33}$	Do.
$[H_2CO_3]pCO_2^{-1}$	$= 10^{-1.47}$	Do.

Solubility equations

$$\Sigma CO_{2,\ diss.} = [H_2CO_3] + \frac{[HCO_3^-]}{\gamma HCO_3^-} + \frac{[CO_3^{-2}]}{\gamma CO_3^{-2}}$$

$$\Sigma Pb_{diss.} = \frac{[Pb^{+2}]}{\gamma Pb^{+2}} + \frac{[PbOH^+]}{\gamma PbOH^+} + \frac{4[Pb_4(OH)_4^{+4}]}{\gamma Pb_4(OH)_4^{+4}} + [Pb(OH)_2] + \frac{[Pb(OH)_3^-]}{\gamma Pb(OH)_3^-} + [PbSO_4]$$

Obtaining the solubility of $Pb(OH)_2$ c by the use of data in table 1 leads to elimination of stability regions for several lead oxides shown in similar diagrams published by others. The field for PbO_2 is so small that it has very little significance, and it is not shown in figure 2. There are no areas of stability for the mixed valence oxide Pb_3O_4 or for the anhydrous PbO species. The low solubility of lead shown on the diagram, however, is a function of both hydroxide and carbonate effects and is likely to be real.

The basic lead carbonate $Pb_3(OH)_2\ (CO_3)_2$, because of the rather low CO_2 concentration specified, has a small field of stability in the system defined in figure 2. However, there is only a small difference in free energy of formation between the actual double compound and a mixture of lead hydroxide and lead carbonate. The determination of which species might be formed in the vicinity of pH 8 by precipitation from a supersaturated solution could be mainly a matter of relative rates of reaction. Whether the stable solid is basic carbonate or a mixture of hydroxide and carbonate, the calculated equilibrium solubility of lead is essentially the same.

Other solids mentioned in the literature include hydroxy sulfates, nitrates, and chlorides of lead, none of which are stable in the system as defined. The solubility of lead phosphate is low enough to be a factor in some natural waters; generally, phosphate ionic species are not present in sufficient amounts in river and lake water to control the solubility of lead.

Other possibly significant solute species of lead have been described in the literature. The chloride complex $PbCl^+$ will not be significant in solutions having less than about 1,000 mg/l of chloride. It could be a significant factor in saline water. A considerable amount of data has been obtained on polynuclear hydroxide complexes of lead such as $Pb_4(OH)_4{}^{+4}$ and $Pb_3(OH_4{}^{+2}$ For the most part, such species have been studied in more concentrated solutions of lead than the upper limit represented in figure 2. From the thermodynamic data it can be shown that polynuclear hydroxide species are not dominant factors in the aqueous chemistry of lead unless the concentration of lead is over 10^{-2} molar (Faucherre, 1954) and other complexing anions, such as sulfate and chloride are absent or in low concentrations. It seems reasonably certain that such conditions are rarely, if ever, attained in natural geochemical systems. Carbonate complexes such as $PbCO_3$ aq may be important in some waters but are not considered here.

EFFECTS OF TEMPERATURE AND IONIC STRENGTH

Except as noted, all the thermodynamic data in tables 1 and 2 are for a temperature of 25°C. This standard temperature is somewhat higher than that of most stream waters in the United States. At lower temperatures the solubilities of most minerals are somewhat decreased. However, the solubility of some carbonates increases as temperature declines. In a system having a CO_2 gas phase, the solubility of CO_2 also increases as temperature goes down and the dissociation reactions are affected.

Strictly speaking, solubility calculations made for 25°C are applicable only to systems at that temperature. If one is interested in testing a solution for adherence to equilibrium solubility at some other temperature, for example, at 5°, all the measurements on the system that would be affected by temperature should be made at 5°, and the results compared with solubility calculations adjusted to apply at 5°. Approximate temperature corrections for equilibrium constants can be made using standard chemical thermodynamic relationships. The alkalinity and pH measurements are seldom all made at the field temperature, however. Converting such values to ones that would represent some other temperature is not a simple matter.

Alkaline-earth metal carbonates decrease in solubility as temperature increases. The effect of temperature on solubility of lead carbonate does not appear to have been closely studied. A few stability constants quoted by Sillén and Martell (1964, p. 140, 141) suggest the solubility of lead carbonate may decrease with decreasing temperature, but temperature effects do not appear to be large. It does not seem worthwhile to calculate the solubility of lead at temperatures below 25° until more study has been given. However, the effect is probably not very large between 25° and 0°C, when compared to other factors that influence field application of solubility calculations.

Solutions of high ionic strength may retain substantially more lead in solution than do more dilute waters. Ion pairing effects also become increasingly important at high ionic strength. The calculations given here do not apply to solutions whose total dissolved-solids concentration is much above 5,000 mg/l.

INORGANIC CONTROLS OF LEAD SOLUBILITY

As noted earlier in this discussion, lead forms carbonate, sulfate, sulfide, hydroxide compounds of low solubility. It is possible to show by equilibrium solubility calculations (fig. 2) that the concentration of lead species in solution should be less than 10 μg/l at ordinary Earth-surface temperatures when HCO_3 concentration is 61 mg/l or more and pH is between 7.6 and 12.6. A great many natural surface and ground waters are in this concentration range. If the pH is constant and bicarbonate alkalinity is increased, the solubility is proportionately decreased throughout the pH range characteristic of most freshwater. Calculations described by Hem and Durum (1973) showed that many river waters in the United States have lead concentrations near the solubility limits imposed by their pH levels and contents of dissolved CO_2 species.

The comparison of observed lead concentrations with theoretically calculated ones can never be expected to give more than a very approximate indication of what is happening in river water. The influences of changing temperature and pH on solubility may be substantial. It is not unlikely that apparent supersaturation could occur, perhaps as the result of kinetic barriers to crystallization of small particles. Close adherence to a solubility model can be expected to be rare or nonexistent; however, some waters have a so much greater capacity for lead solution than others that even a crude model can be useful. Although many waters do not have sufficient contact with lead compounds to be able to attain saturation, the opportunity for such contact is particularly favorable in urbanized areas or wherever there is heavy automobile traffic and extensive utilization of leaded gasoline. In such areas, the rainfall itself, along with dry fallout of particulate material from the atmosphere, can supply enough lead so that surface runoff reaching streams could contain substantial amounts—enough to reach saturation at times.

Lazrus, Lorange, and Lodge (1970) calculated that as much as 138 g of lead is deposited by rainfall per month on each hectare (10^4 m^2) in some parts of the northeastern United States. If the runoff in such an area is at a rate of about 50 cm of water annually (a commonly observed rate), the runoff would have to have an average lead concentration of 330 μg/l to remove lead at a rate of 138 g/ha/mo. Higher or lower concentrations could be calculated for other areas and conditions. This figure for average concentration does indicate, however, that a large potential supply of lead is available for transport in runoff. Concentrations as high as 330 μg/l could be stable in water having a pH near 6.5 and an alkalinity of about 25 mg/l HCO_3. Water having these properties is common in runoff from areas in New York and New England. Thus, the potential for high lead concentrations in river and lake waters does exist in some places, and careful monitoring of river and ground water quality is desirable.

In some other areas the composition of runoff water will be less favorable for lead solution. In many places the average pH and alkalinity are so high that less than 1 μg of lead could be retained in solution at equilibrium.

The most comprehensive data on lead concentrations in river water of the United States are included in a report by Durum, Hem, and Heidel (1971). However, their compilation does not include either the bicarbonate or pH determinations needed to apply solubility calculations in testing for adherence to equilibrium conditions. Some of the sampling sites were points at which pH and alkalinity measurements are regularly made, and some applicable measurements were found in the computer-stored data for water quality stations.

Of the 720 samples obtained for the Durum, Hem, and Heidel study, 70 could be correlated with applicable pH and alkalinity determinations that had been made either on a sample obtained the same day as the sample for lead, or on one obtained within a few days, if the composition of the source was relatively constant (as in large lakes, for example). Lead was detectable in 39 of these samples, as shown in table 3.

This table gives a calculated range of lead concentration for each sample, based on pH and alkalinity. The lower number is the solubility in a very dilute solution; the

TABLE 3.—*Observed and calculated saturation concentrations of lead in U.S. surface waters collected during October and November 1970*

[Modified from Durum, Hem, and Heidel, 1971, and unpublished USGS records]

Sample source	Date sample collected (Oct. 1970, except as noted)	ΣHCO_3 (Mg/l)	ΣHCO_3 (log mol/l)	pH	Pb (μg/l)	
					Calculated range	Observed
Raritan River near Manville, N.J	12	75	−2.85	7.5	5.0– 15.0	3
Millstone River near Manville, N.J	12	48	−3.09	7.4	12.0– 35.0	5
Manasquan River at Squankum, N.J	13	60	−2.96	7.1	18.0– 60.0	4
Delaware River at Trenton, N.J	13	45	−3.12	7.7	4.0– 9.0	5
St. Johns River near Melbourne, Fla	14	113	−2.66	7.6	3.0– 9.0	1
St. Johns River at Jacksonville, Fla	2	103	−2.75	7.9	2.0– 5.0	2
Plantation Road Canal near Fort Lauderdale, Fla	29	167	−2.49	7.6	2.0– 6.0	4
Caloosahatchee River near Olga, Fla	29	199	−2.43	8.2	.6– 1.5	1
Peace River at Arcadia, Fla	Nov. 6, 1970	51	−3.05	7.9	3.0– 10.0	3
Phillipi Creek at Sarasota, Fla	6	158	−2.56	8.0	1.2– 3.0	1
Alifia River at Lithia, Fla	7	42	−3.09	7.2	15.0– 50.0	1
Swift Creek at Facil, Fla	6	15	−3.42	6.7	150.0– 400.0	1
Ochlockonee River near Havana, Fla	15	32	−3.21	7.1	25.0– 80.0	4
Coosa River at Childersburg, Ala	14	77	−2.83	7.4	5.0– 20.0	4
Alabama River at Claiborne, Ala	9	50	−3.06	7.5	9.0– 25.0	9
Sipsey Fork near Grayson, Ala	22	38	−3.05	6.8	40.0– 150.0	6
Mahoning River, Ohio-Pennsylvania boundary	8	88	−2.85	7.3	8.0– 25.0	1
Cataloochee Creek near Cataloochee, N.C	13	9	−3.53	7.2	40.0– 100.0	20
Tennessee River at Kentucky Dam, Ky. (near Paducah)	16	66	−2.90	7.5	6.0– 18.0	4
Washington Creek at Windigo, Mich	15	68	−2.87	7.4	6.5– 20.0	2
St. Marys River, Sault Ste. Marie, Mich	12	50	−3.04	7.7	5.0– 12.0	6
St. Clair River at Port Huron, Mich	19	95	−2.79	8.3	1.0– 4.0	5
Detroit River at Detroit, Mich	16	98	−2.78	8.2	1.5– 4.5	4
Missouri River at St. Joseph, Mo	14	186	−2.45	8.0	.9– 2.5	5
Mississippi River at East St. Louis, Ill	13	229	−2.39	8.0	.8– 2.5	7
North Sylamore Creek near Fifty Six, Ark	30	146	−2.54	7.3	4.0– 12.0	10
Arkansas River below Little Rock, Ark	7	100	−2.72	7.6	3.5– 10.0	11
Kiamichi River near Big Cedar, Okla	6	10	−3.74	7.9	20.0– 60.0	84
Las Vegas Wash near Boulder City, Nev	Nov. 19, 1970	258	−2.33	8.0	.8– 2.0	2
Santa Ana River below Prado Dam, Calif	8	318	−2.40	8.2	.5– 1.2	34
Merced River, Happy Isles Branch, Yosemite, Calif	20	9	−3.76	7.1	100.0– 300.0	2
Elder Creek near Branscomb, Calif	7	75	−2.80	7.5	4.5– 12.0	2
North Fork Quinault River, near Amanda Park, Wash	15	44	−3.08	7.4	10.0– 30.0	2
South Fork Coeur d'Alene River near Smelterville, Idaho	8	7	−3.24	5.8	1000.0–5000.0	5
Hayden Creek near Hayden Lake, Idaho	21	47	−3.07	7.7	5.0– 15.0	3
Snake River near Shelley, Idaho	6	150	−2.57	8.2	.8– 2.0	3
Rock Creek near Twin Falls, Idaho	19	335	−2.24	7.8	1.0– 3.0	2
Campbell Creek near Spenard, Alaska	16	48	−3.06	7.9	5.0– 10.0	2
Ship Creek near Anchorage, Alaska	16	59	−2.90	7.9	5.0– 15.0	1

higher represents the effect of increased ionic strength. Temperature effects are not directly recorded, but will generally have the effect of slightly decreasing the solubility of carbonates as temperature decreases. Most samples probably were 10°–15° cooler than the standard 25°C used in the calculations. The influence of temperature on lead solubility in these systems needs more investigation.

Of the 39 concentrations of lead determined, 12 are within the predicted solubility range and an additional 10 are reasonably close (within a factor of 2) to upper or lower limits.

The possible experimental and sampling errors are probably enough to explain these discrepancies. The remaining 17 samples include 15 that are well below saturation, a condition to be expected in a high percentage of the samples, owing to lack of sufficient opportunity to dissolve lead. There were only two samples in which a substantial degree of supersaturation occurred—one from the Mississippi River at East St. Louis, which was sampled during a high stage and may have been carrying colloidal particulate lead that could pass through the filter used in clarifying the sample, and the other from the Santa Ana River below Prado Dam, in the Los Angeles area of California, where lead fallout rates are probably very high, causing a situation also conducive to accumulation of colloidal particulate lead.

The principal value of these solubility calculations is in the aid they give to understanding the freshwater part of the geochemical cycle of lead and in the suggestion that hazards of increased lead in water supplies may be most severe in areas where runoff has both a relatively low dissolved-solids concentration and a low pH. It is not intended to imply that the equilibrium aspects of lead chemistry are the only important ones. Factors not considered here may be operating to prevent high lead concentrations from being reached in solutions that are below saturation. However, until more evidence is obtained that such factors are preventing lead from appearing in runoff, it seems obvious that lead concentrations in river and lake water require close attention.

NONSOLUTE LEAD IN WATER

A significant fraction of the total content of lead carried by river water may be in an undissolved state. This nonsolute lead can consist of colloidal particles in a hydrosolic suspension, a characteristic form of many metals having sparingly soluble hydroxides. It may also be present as larger undissolved particles of lead carbonate, oxide, hydroxide, or other lead compound, and can be incorporated in other components of the particulate lead of the runoff, either as sorbed ions or as surface coatings on sediment mineral particles. It can also be carried as a part of organic suspended matter in both living and nonliving forms.

The concentrations of lead usually reported represent an arbitrarily defined solute fraction, separated from the nonsolute fraction by filtration. Most filtration techniques cannot be relied upon to remove all colloidal-size particles, and on acidification of the filtered sample, as usually is done for preservation before analysis, the colloidal material that passed through is dissolved and is reported in that form. Usually the solids removed from a surface water sample by filtration are not analyzed for lead. Exceptions are the analyses reported for rivers in the USSR by Konovalov, Ivanova, and Kolesnikov (1968), for which the only determinations of lead were on material removed by filtration. Their assumption appears to have been that solute lead was insignificant. Samples of ground water are not generally filtered before analysis. Content of colloidal material in such waters is probably negligible, however, owing to natural filtration effects during recharge and movement through the aquifer.

Even the lead in rainfall can be mainly particulate. Samples of rain were collected at the U.S. Geological Survey in Menlo Park, Calif., during the period January–April 1971. Filtration through membranes with 0.10- μm-diameter pores removed as much as 90 percent of the lead. Several samples of runoff from a small stream draining part of the city of Palo Alto, Calif., were collected during this period. One of these contained 90 μg/l of lead, about 90 percent of which could be removed by filtration. The sediment contained 0.11 percent lead.

Kopp and Kroner (1970, p. 14) reported lead in only 5 of 228 samples of suspended material obtained from composited river and lake samples. In one of these, however, the concentration was equivalent to 120 μg/l in the original composite.

Dry atmospheric fallout of lead was measured during May and June of 1971 at Menlo Park, Calif. These measurements were made by exposing, for 1–2 weeks on the building roof, a large shallow polyethylene container in which distilled water was maintained at a depth of a few centimetres. The water and sediment accumulated were then analyzed for dissolved and particulate lead. This particulate fallout consistently contained 0.09 to about 0.10 percent of lead, and the fallout rate of lead ranged from 30 to 66 g/ha/mo. No measurable amount of rain fell during this period. Rates and composition of fallout obtained in this set of observations are similar to those reported earlier by Chow and Earl (1970) for the San Diego, Calif., area.

Before a meaningful estimate can be made of the effectiveness of runoff in transporting lead away from areas where it has been deposited by atmospheric fallout and rain, it will be necessary to obtain more information on the amounts of lead transported in nonsolute form, especially during periods when runoff rates are high, as well as corresponding information on the amount carried in solution. At present such data are almost totally nonexistent. A laboratory study of sorption of lead by cation exchange (Hem, 1976) indicated that a major part of the lead in stream water may be adsorbed on suspended sediment.

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ORGANIC CHEMISTRY OF LEAD IN NATURAL WATER SYSTEMS

By R. L. WERSHAW

Natural soil-water and sediment-water systems are extremely complex, consisting of a myriad of interacting organic and inorganic components. In this section we shall be concerned with the interaction of one of the inorganic components, lead, with the organic components of these systems.

The organic components of a soil-water system are an extremely diverse group of compounds (Saxby, 1969), including carbohydrates, amino acids, phenolic and quinonic compounds, organic acids, nucleic acids, enzymes, porphyrins and other heterocyclic compounds, lipids, terpinoids, and humic materials. (See Saxby, 1969; Spakhov and Spakhova, 1970; Greaves and Wilson, 1969; Kowalenko and McKercher, 1971; Ivarson and Sowden, 1969; and Kononova, 1966, for more complete discussions of the organic compounds in soils.)

In addition to the natural organic compounds present in soil, streams and lakes contain organic sediments and suspended solids that have been derived from municipal, agricultural, and industrial wastes. These wastes are made up of carbohydrates, proteins, nucleic acids, enzymes, lipids, and many of the other organic compounds of living systems. Oils, plasticizers, polymers, and an enormous number of other organic compounds are discharged to natural waterways by manufacturing and chemical industries.

The interaction of lead with the organic components of soil-water and sediment-water systems is still not well understood, but we shall review the work that has been done and attempt to draw what conclusions we can from the data available.

A number of studies have shown that the organic matter of soils and stream sediments apparently binds metals and reduces their mobility. However, as Mortensen (1963) has pointed out, although many workers have suggested that soil organic matter forms complexes with metals, and that these complexes are important in soil formation and plant nutrition, the evidence for existence of metal-soil organic matter complexes in nature is largely circumstantial.

Although a relatively large number of publications are available on the interaction of metals with organic materials of soils and waters (see Mortensen, 1963; Saxby, 1969), very few of the papers have dealt with interactions of lead and organic material, and of these, most have been concerned with lead in soil-water systems; there are very few on the interaction of lead with organic materials in streams and lakes.

SURFACE WATER–SEDIMENT SYSTEMS

Herrig (1969) and Hellman (1970a, b, 1971) have studied the heavy metals in the waters and sediments of the Rhine River and its tributaries. Herrig found that both inorganic and organic lead compounds were being introduced into rivers as industrial and municipal wastes; the most common of these were lead oxide, metallic lead, lead stearate, lead palmitate and tetraethyl lead. Much of this lead was concentrated in the suspended and bottom sediments of high organic content. The sediments were more effective in removing lead than in removing copper or zinc (Hellman, 1970a).

The sediments of the lower Rhine contained about 10 times the amount of heavy metals found in those of the upper Rhine and its tributaries. Lead concentrations as high as 0.2 percent were found in some of the sediments; high heavy-metal concentrations in the sediments were associated with high concentrations in the river water. The high concentrations are orders of magnitude higher than the natural background levels and can only be due to municipal and industrial pollution. The high concentration of lead in sewage sludge indicates that municipal waste can be a major contributor of lead pollution in some streams (Gross, 1970). Even though the sediments remove large quantities of heavy metals from the water of rivers, they are still not efficient enough to totally decontaminate the water, and therefore the river water often contains high heavy-metal concentrations. Hellman (1970a) measured lead concentrations in the water as high as 85 μg/l, and the average for the length of the Rhine river was 51 μg/l.

The lead in the organic components of a sediment enters the sediment from two sources: (1) The plant and animal remains that provide the organic compounds to the sediment, and (2) the water that comes into contact with the sediment. The chelation of lead by the chemical components of living organisms tends to cause lead to accumulate in living tissue (MacLean and others, 1969;

Danielson, 1970; Bryce-Smith, 1971). This accumulation of lead is no doubt a major source of lead in organic sediments. However, both the organic and inorganic components of sediments will also remove lead from water. Therefore, as has been pointed out by Hellman (1970a), organic sediments will tend to decontaminate surface waters contaminated with lead and other heavy metals. However, one must also remember that sediments will tend to supply lead to waters with low lead concentrations in order to maintain chemical equilibrium. Therefore, even if the lead pollution of a surface water were to cease immediately, the sediments would continue to supply lead to the water and to its fauna and flora.

CHEMISTRY OF THE INTERACTIONS

Saxby (1969) has reviewed the literature of metal-organic chemistry in the geochemical cycle. He found that lead has been detected in the carbonaceous fractions of soils, coals, petroleum, bituminous rocks and asphalts, shales, sedimentary sulfides, and phosphate rocks. In general, however, very little is known about the molecular associations of metals in geological materials. Therefore, in our discussion we shall have to draw heavily upon studies that have been made on synthetic organic systems and medically important biological systems; however, the general chemical principles elucidated in these studies should also hold true for natural soil-water systems.

Two different types of organic lead compounds may be found in nature: (1) the so-called organo-lead compounds, in which the lead is covalently bonded to carbon atoms and the metal complexes, and (2) chelates, in which the lead is ionically bonded to organic ligands.

Lead normally exhibits both divalent and tetravalent states in organic compounds. When lead is covalently bonded to carbon it is generally more stable in the tetravalent state; relatively stable divalent lead derivatives are known, however. (See Shapiro and Frey, 1968, for a more complete discussion of lead bonding in organic compounds.)

Covalently bonded organo-lead compounds in natural systems undergo slow oxidation by air and photolysis when exposed to light. Most of these compounds except those in which the lead-carbon bonds are highly polar, such as the perfluoroalkyl lead compounds and R_3PbX and R_2PbX compounds in which X is an anion, are not hydrolyzed by water. In coordination compounds, such as metal complexes and chelates, ionic lead is normally divalent; however, organo-lead cations in which the lead is tetravalent may also be complexed by organic ligands.

Most of the detailed studies on the complexing of lead and other metals by organic ligands have been conducted by biochemists on the components of living systems; the same ligands however are present in the organic material of soils, natural waters, and sewage effluents.

Lead is generally most strongly bound to sulfur containing ligands and to phosphoryl groups (Passow, 1970), but it also forms coordination bonds with other ligands.

Vallee and Wacker (1970) have reviewed the chemistry of metalloproteins and have pointed out that lead interacts with proteins and enzymes by binding to carboxyl groups or sulfhydryl groups. The binding of lead and other heavy metals to a wide variety of enzymes inhibits the activity of the enzymes (Morrow and others, 1969; Hernberg and Nikkanen, 1970; Vallee and Wacker, 1970). Li and Manning (1955) have demonstrated that, in general, lead forms more stable complexes with proteins than do cadmium, zinc, or copper.

The binding of lead to enzymes and the consequent inhibition of enzymatic activity will undoubtably affect the biological reactions that take place in streams, soils, and sewage treatment facilities, but unfortunately there are very few data on the interactions of lead with soil and water biochemical systems. However, the poisoning of enzyme systems in natural waters by heavy metals can be expected to drastically alter the rates of decomposition of organic wastes in these systems.

Heavy-metal cations may not always act as enzyme poisons in soil systems. Ladd and Butler (1970) have shown that divalent cations are effective in reducing the inhibition of the enzyme protease by humic acid. It appears that the humic acid binds to the enzyme, thereby preventing it from combining with substrate. If metal cations are present in the system, active sites on the humic acid will apparently preferentially bind to the cations and be unavailable for binding the enzyme. Lead also interacts with polynucleotides and viruses. Lead ions will cause the depolymerization of some polynucleotides such as ribonucleic acid (RNA) (Farkas, 1968) and deoxyribonucleic acid (Eichhorn, 1962; Izatt and others, 1971). In the depolymerization of RNA it appears that the lead binds the phosphate groups. This neutralizes the charge on the phosphate groups and renders the phosphodiester bonds more susceptible to hydrolysis by hydroxyl groups (Farkas, 1968). In the binding of lead to tobacco mosaic virus molecules the lead may displace protons of the hydroxyl groups (Fraenkel-Conrat, 1965).

In α amino acids, in more complex molecules containing α amino acids, and in molecules similar to 8-hydroxyquinoline and quinoline acid, lead and many other metals form five-membered chelate rings with reactive ligands. Charles and Freiser (1952), in their work on five-membered chelate rings, have measured the stability constants of lead chelates of *o*-aminophenol and *o*-aminobenzenethiol. Their data indicate that the order of decreasing stability for metal *o*-aminophenol is as follows: Cu, Ni, Zn, Co, Pb; for *o*-aminobenzenethiol, however, the order is Cu, Ni, Pb, Zn, Co. Lead forms more stable complexes with *o*-aminobenzenethiol than with *o*-

aminophenol, apparently because the lead-sulfur bond is stronger than the lead-oxygen bond.

Other groups of compounds such as carbohydrates, carboxylic acids, lipids, phenols, and oxygenated isoprenoids that have electron donor ligands similar to those of the proteins mentioned above would also be expected to complex lead. In this regard Hoogeveen (1970) has demonstrated that lead is bound by phospholipids. Martin, Ervin, and Shepherd (1966) and Martin and Richards (1969) have shown that copper, zinc, iron, and aluminum form complexes with soil polysaccharides. These metal-polysaccharide complexes are generally more resistant to decomposition in soils than are uncomplexed polysaccharides. Although there are no experimental data on lead-polysaccharide complexes in soil, one would expect them to have properties similar to those of other heavy-metal polysaccharide complexes.

It is well established that soil humic materials such as humic acid and fulvic acid form complexes with metals (Kononova, 1966). Aleksandrova (1967) has classified the interactions of metals with humic materials into three categories: (1) Formation of heteropolar salts (an ion exchange phenomenon between strong bases and humic materials), (2) formation of coordination complexes, (3) formation of adsorption complexes with nonsilicate sesquioxides (adsorption of humus on sesquioxide gels). Most of the interactions of lead with humic materials that have been studied fall under the second category.

Humic acids and fulvic acids form stable complexes with lead (II) ions and other metal ions; these complexes may be separated from a mixture of humic acid or fulvic acid metal complexes by gel permeation chromatography (Mücke and Kleist, 1965; Klöcking and Mücke, 1969). Therefore, it should be possible to isolate intact, humic-metal complexes from soils and sediments.

Bondarenko (1968) found that the presence of fulvic acid in water increased the rate of solution of lead sulfide 10–60 times over a water solution at the same pH that did not contain fulvic acid. At pH values near 7, soluble lead-fulvic acid complexes were present in solution; at initial pH values between 7.4 and about 9, the lead-fulvic complexes partially decomposed, and lead hydroxide and carbonate were precipitated. At initial pH values of about 10, the amount of lead-fulvic acid complexes again increased. Bondarenko (1968) attributed this increase to dissociation of phenolic groups at high pH values, a phenomenon which increases the complexing capacity of the fulvic acid.

In addition to interactions in which a lead ion is bound by a single organic molecule, a single metal ion can be bound by two different organic molecules. It has been demonstrated, for example, that polyvalent cations act as bridges between clay minerals and humic and fulvic acids (Greenland, 1971).

SUMMARY AND CONCLUSIONS

The complexing of lead by most of the common sulfur-, phosphorus-, oxygen- and nitrogen-containing ligands means that lead will accumulate in both the living and nonliving organic components of soil-water and sediment-water systems. The living and non-living organic components are not independent of each other, but are constantly interacting, as the living components metabolize the nonliving components of the system and then die, contributing their remains to the pool of non-living compounds in the system. Some of the lower forms of life are consumed in the process by the higher forms of life and in this way chemical elements from the sediments are introduced into the food chain of the system; this food chain often ends with man. The fate of heavy metals in this process has not been elucidated; however, the sediment in a contaminated surface-water body will serve as a large reservoir which can provide lead and other metals to the biota of the system even after heavy metal pollutants have ceased to be introduced into the system. Unfortunately, in the case of heavy metals, much more attention has been paid to heavy metals dissolved in the water phase of surface water than to the complexed metals in the sediment phase which, in general, probably contain a considerably higher amount of metals than the water. The sediments will also act as a reservoir for providing dissolved heavy metals to the water when contamination levels are low.

High concentrations of lead in soils and sediments will have a marked effect upon enzyme systems, acting in some instances to reduce inhibition by other components of the systems. The alteration of the activity of some of the most basic components of living systems is certain to have a profound effect upon the biological and chemical processes taking place in natural systems.

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DISTRIBUTION OF PRINCIPAL LEAD DEPOSITS IN THE CONTINENTAL UNITED STATES

By A. V. Heyl

The principal lead deposits in the continental United States are shown in figure 3. Most of the deposits and depositional districts are located within a few major tectonic and geographic regions of the United States. They are, from east to west, (1) the Appalachian foldbelt (Blue Ridge, Ridge and Valley, and Piedmont provinces) extending from Maine to Alabama; (2) several low domed uplifts within the little-disturbed craton of the greater Mississippi Valley (Central Lowland); (3) the Ouachita Mountains foldbelt (Ozark Plateaus) of Arkansas and Oklahoma; (4) the Rocky Mountains belt from Mexico and western Texas northward to western Wyoming and eastern Idaho (Middle and Southern Rocky Mountains); (5) the cordillera, which includes the Basin and Range province of New Mexico, Arizona, Nevada, western Utah, southeastern California, and southern Idaho, as well as the Sierra Nevada, Oregon Plateaus (Columbia Plateaus), Northern Rocky Mountains, and Cascade Mountains, and the main mountain ranges of Alaska (Pacific Mountain System); and (6) the Pacific foldbelt (Pacific Border province), which forms a narrow band in western California.

The deposits in the Mississippi Valley region (Central Lowland and Ozark Plateaus), Rocky Mountain belt (Northern and Southern Rocky Mountains provinces), and the cordillera (Basin and Range province) are the largest in the United States and have produced most of the commercial lead during the history of the United States. It is worthy of note, however, that the actual areas of lead deposits in these three regions are so small that even if all are taken into account they probably would not markedly increase the total crustal abundance of lead within these three regions. The deposits outside of these three regions are locally numerous, but they have not been major commercial sources of lead.

Lead is commonly associated with zinc and silver, and less commonly with gold, copper, fluorine, barium, cadmium, antimony, bismuth, and arsenic. In most districts lead is subordinate to zinc in total tonnage. The most notable exception is the southeastern Missouri district where lead is far more abundant than zinc (fig. 3, loc. 1). This district has been our major source of lead since the 1870's.

Most of the major districts in Utah also have more abundant lead than zinc and silver has been a major byproduct. Likewise, in the Coeur d'Alene district of northern Idaho (fig. 3, loc. 3), which dominates lead production in the West, total lead production also exceeds that of zinc; this district is also the major source of silver in the United States.

Silver is associated with lead in most deposits in the western States, the quantity ranging from a minor byproduct to a major value of the ore. Many of the lead deposits mined in the foldbelts of the southern Rocky Mountains and in the Basin and Range region of the cordillera during the 19th and early 20th centuries were oxidized silver-enriched deposits worked mainly for their silver content.

The deposits in the Appalachian foldbelt (Blue Ridge, Piedmont, and Ridge and Valley provinces) are mainly zinc or copper-zinc deposits with relatively minor lead. A few of the largest deposits, such as the most productive zinc deposits in New Jersey, Pennsylvania, Maine, and east Tennessee, are almost free of lead. A few deposits, such as those at Edwards and Balmat, N.Y. (fig. 3, loc. 5), Blue Hill, Maine, and Austinville, Va. (fig. 3, loc. 6), contain enough lead to provide a commercial byproduct. Hundreds of other small deposits that contain lead are known throughout the Appalachian foldbelt.

The deposits in the Ouachita Mountain belt (Ozark Plateaus province) have also produced mainly zinc in the past, and lead is locally only abundant enough to provide a minor byproduct.

The cordillera and Rocky Mountain belt (Basin and Range and Southern Rocky Mountains provinces) contain many silver-bearing lead and lead-zinc deposits, and local concentrations of deposits are widely scattered throughout these regions. In the southern Rocky Mountains they are most abundant in the Colorado mineral belt (fig. 3, loc. 9), the San Juan Mountains, Colo. (fig. 3, loc. 10), and the Wasatch Range, northern Utah. In the cordillera, deposits are scattered throughout the Basin and Range and the

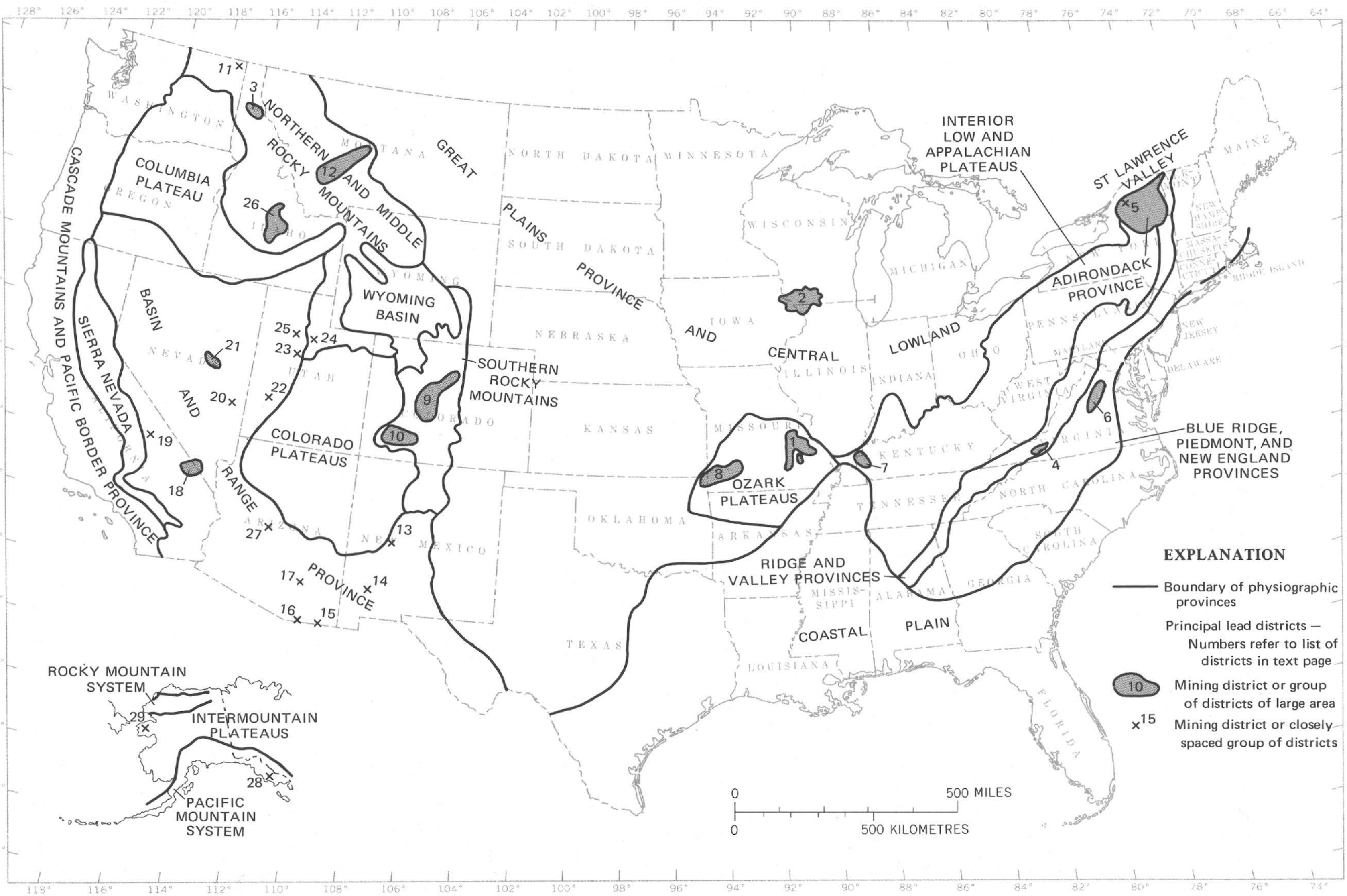

FIGURE 3.—Lead deposits in the United States that have produced or are known to contain more than 100,000 tons of lead. Districts or areas are listed in order of decreasing lead content. Compiled by A. V. Heyl, 1973.

1. Southeast Missouri
2. Upper Mississippi Valley (Wisconsin, Illinois, Iowa)
3. Coeur d'Alene, Idaho
4. Austinville-Ivanhoe, Va.
5. Balmat-Edwards, N.Y.
6. The massive sulfide deposits of the Piedmont region, Virginia.
7. Illinois-Kentucky district
8. Tri-State district, Missouri, Oklahoma, and Kansas
9. Leadville, Red Cliff, Aspen, and other districts, Colorado mineral belt
10. San Juan Mountains region, Colorado
11. Northport, Deep Creek, and Metaline districts, northeast Washington
12. Barker, Neihart, Butte, Bryant, and Colorado districts, western Montana
13. Magdalena district, New Mexico
14. Central, Hanover, and nearby districts, New Mexico
15. Bisbee district, Arizona
16. Harshaw and nearby districts, Arizona
17. Mammoth and nearby districts, Arizona
18. Yellow Pine, Nevada, and nearby Resting Springs and Kingston Range districts, California
19. Darwin and nearby districts in Inyo County, Calif.
20. Pioche and nearby districts, Nevada
21. White Pine and Eureka districts, Nevada
22. San Francisco and Star districts, Utah
23. The Tintic and nearby districts, Utah
24. Park City and Cottonwood region, Utah
25. West Mountain, Bingham, Rush Valley, and Ophir districts, Utah
26. Warm Springs, Bayhorse, Alder Creek, and Wood River districts, Idaho
27. Big Bug and nearby districts, Arizona
28. Ground Hog, Glacier Bay, and Tracy districts, Alaska
29. Kugruk River, Alaska

Northern Rocky Mountains provinces, but the greatest concentrations are in northern Idaho and adjacent eastern Washington. Similarly the wide cordillera belt that extends northward and westward through Alaska (Pacific Mountain System) contains most of the lead deposits known in that State.

Very few important lead-bearing deposits occur in the part of the Pacific foldbelt within the conterminous United States (Cascade and Pacific Border province), although potentially important deposits are common in the Alaskan part of the Pacific foldbelt (Pacific Mountain System). Zinc deposits containing some lead occur on Santa Catalina Island and in other parts of southern California, in the Shasta copper district in northern California, and in Lane County, Oreg.

MIGRATION OF LEAD DURING OXIDATION AND WEATHERING OF LEAD DEPOSITS

By LYMAN C. HUFF

Lead deposits, like deposits of other ore metals, commonly are surrounded by a zone in which the earth materials are enriched with the ore metal. During the oxidation and weathering of lead ore, some lead becomes incorporated in the soil, stream sediment, drainage waters, and plants. This dispersion of lead has been studied in detail around many lead deposits because it serves as a useful means of prospecting (Hawkes and Webb, 1962). Such studies show that some earth materials and plants near ore deposits may contain highly anomalous concentrations of lead and that such anomalous concentrations may extend outward from the ore deposits. These geochemical halos are an important factor in evaluating the lead content of our environment.

The lead content of most lead ores averages about 8 percent whereas the lead content of unmineralized rock is only about 15 ppm. This high contrast (about 5,000:1) indicates that, during weathering and erosion, the lead from the ore can be disseminated in earth materials in anomalous amounts throughout an area that is quite large by comparison with the original ore deposits. We will consider here the effects of supergene processes upon primary lead deposits and identify, insofar as they can be determined, the most important means of lead dispersal.

WEATHERING OF LEAD ORE

Geologic study has provided much information on the behavior of lead during oxidation and weathering of lead deposits. The predominant lead mineral in the primary ore is the sulfide, galena. During weathering, galena is slowly oxidized by atmospheric oxygen to either the sulfate (anglesite) or the carbonate (cerussite), as indicated by the following equations:

$$\underset{\text{Galena}}{PbS}+2O_2 \longrightarrow \underset{\text{Anglesite}}{PbSO_4}$$

$$\underset{\text{Galena}}{PbS}+CO_2+H_2O+2O_2 \longrightarrow \underset{\text{Cerussite}}{PbCO_3}+H_2SO_4$$

Cerussite usually is formed at a pH above 6 and anglesite at a pH below 6 (Garrels, 1960, p. 170–171). Where pyrite is present, Fe^{+3} in solution may facilitate oxidation of the galena. The CO_2 required in the formation of cerussite is provided by the carbon dioxide content of soil gas or, in many instances, by the carbonate content of nearby limestones. Part of the lead may also be incorporated in clay minerals or in iron oxide coatings of complex composition. If the primary ore is rich in pyrite, a large part of the lead may become incorporated in the iron-oxide-rich gossans which characterize the weathered outcrops of such deposits.

The common supergene lead minerals are quite insoluble in natural waters. In weathered ore, dark-colored fragments of galena commonly are coated with a light-colored layer of anglesite or cerussite, showing the process of oxidation in progress. These oxidation products of lead do not leach away in soil moisture, but remain in the weathered rock. Many lead deposits have a high content of zinc, which oxidizes to soluble products that do leach away from the weathered ore. The behavior of lead during weathering thus contrasts sharply with that of zinc, sulfur, and other soluble oxidation components of the original ore. The lead content of weathered lead ore commonly is just as high as that of the original unweathered ore.

In the lead mining district of southwestern Wisconsin, residual concentrations of weathered galena fragments were found over some of the lead veins (Huff, 1952). These residual concentrations were left by the decomposition and mechanical washing away of the lighter minerals. As these residual concentrations had a high lead content and were easy to mine, they formed an important source of ore during the early development of this district. Such residual concentrations of lead are not common, but they do show the characteristic insolubility and limited leaching of lead minerals during weathering.

LEAD IN SOILS NEAR ORE DEPOSITS

As the weathered outcrops of lead deposits contain a large amount of lead, it might be suspected that soils on or near such deposits also would have a high lead content. Study in many places has shown this to be true. Some representative data (table 4) show that lead contents of 1,000 to 10,000 ppm are common in soils near outcrops of lead deposits.

TABLE 4.—*Range of copper, lead, and zinc content of soils collected near ore veins*

[Veins are classified in order of decreasing grade as C, commercial; SC, subcommercial; and M, mineralized (Huff, 1952, p. 536)]

Vein	Classification	Copper			Lead			Zinc		
		High (ppm)	Low (ppm)	High/low ratio	High (ppm)	Low (ppm)	High/low ratio	High (ppm)	Low (ppm)	High/low ratio
Unnamed vein, Porters Grove Range, Iowa County, Wis.	SC	......	......	......	4,400	110	44	2,600	400	6
Iron King vein, Yavapai County, Ariz.	SC	720	180	4	7,000	200	35	5,500	520	11
Collins East vein, Mammoth St. Anthony mine, Pinal County, Ariz.	C	......	......	......	4,500	430	10	......	......	......
Unnamed copper vein, Pima County, Ariz.	M	930	170	5	......	......	......	......	......	......
Apache vein, Gila County, Ariz.	M	......	......	......	220	15	14	......	......	......
Pittsburgh vein, Coeur d'Alene district, Shoshone County, Idaho:										
Upper traverse	C	......	......	......	12,000	70	170	580	200	3
Lower traverse	C	......	......	......	13,000	130	100	1,800	230	8
Chicago vein, Blackbird district, Lemhi County, Idaho	C	1,600	220	7	......	......	......	......	......	......
Malachite vein, Jefferson County, Colo:										
West traverse	SC	5,300	50	106	......	......	......	500	80	5
East traverse	M	400	50	8	......	......	......	......	......	......
Union Copper veins, Gold Hill district, Cabarrus County, N.C.	SC	720	150	5	2,500	150	17	680	220	3

Most supergene lead minerals are soft and disintegrate mechanically during weathering, so that much of the lead probably is concentrated in the fine-size fraction of the soil. Most geochemical exploration studies of soil are based upon analysis of a fine-size fraction, such as the minus-80-mesh fraction. These studies yield high lead values, indicating concentrations in the fines. Few analyses of all size fractions of soil have been made, however, and so little data are available on the relative concentration of lead in the various size fractions.

The dispersion of lead in residual soil is demonstrated effectively by study of soil samples collected near lead-rich veins (Huff, 1952). Soil samples collected across a lead-zinc vein in Wisconsin (fig. 4) show maximum lead content immediately over the vein. Soil on the hillside above the vein contains background amounts of lead. On the hillside below the vein, the lead content of the soil gradually decreases away from the vein through dilution as the soil creeps downhill. The distribution of zinc in the soil is somewhat different than that of lead. Probably this difference is caused by partial dispersion of zinc by solution in soil moisture, whereas the dispersion of lead is almost completely mechanical.

Some of the ore metals show a marked tendency to leach from the surface or A horizon of residual soils and to concentrate in the lower or B horizon, so that the B horizon attains a higher metal content than the A. Such leaching and redeposition has been recognized for zinc and copper but not for lead. Wherever such comparisons have been made the A horizon contains as much or more lead than does the B (see Keith, 1969, table 1).

In the southwestern Wisconsin lead-zinc district residual soil derived from lead deposits is overlain by a silty layer of eolian loess. This loess is believed to be largely of Pleistocene age. Although the loess has been in contact with lead-rich residual soil for thousands of years, study shows that there has been little, if any, diffusion of lead in solution from the lead-rich soil into the loess (Kennedy, 1956, p. 187–223). Similar studies made where glacial till overlies lead ore show little or no diffusion of lead in solution upward into the glacial till.

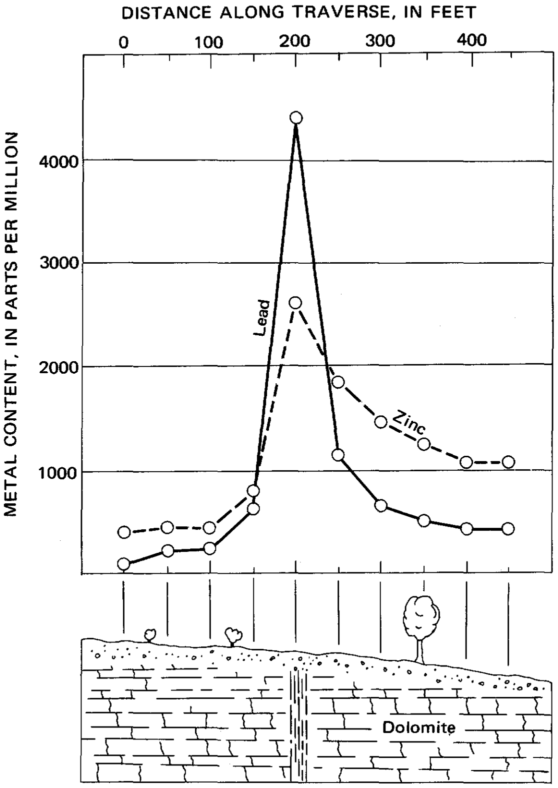

FIGURE 4.—Relationship between unnamed vein and geochemical anomaly in residual soil, Porters Grove Range, Iowa County, Wis. From Huff (1952, p. 524).

Surface soils may contain highly anomalous amounts of lead for 5 miles (8 km) or more from a major source of contamination such as a lead smelter. (Canney, 1959). In Yugoslavia, near a lead smelter which has operated for centuries, as much as 24,000 ppm lead has been measured in contaminated soil (Djurić and others, 1972). These high concentrations result from airborne dust particles rich in lead which have been incorporated in the soil. The minimal leaching rate of lead from soils indicates that most of the lead added to surface soils from contaminating sources will remain in these soils indefinitely.

LEAD IN STREAM SEDIMENTS

In most mining districts the lead which creeps downhill in soils eventually is transported to creeks, or washes, where it is incorporated by running water into stream sediments.

Geochemical exploration studies show that stream sediments containing anomalous amounts of lead from mineralized areas can be traced downstream several miles from the source of the lead. It is assumed that the lead in such sediments, like that in soils, is mostly concentrated in the fine particles. Here again few analyses have been made of different size fractions to determine the extent of concentration in the fine particles.

Several studies of panning concentrates indicate that lead may also be concentrated in part in heavy minerals. In one area in New Mexico the heavy minerals containing lead have been identified (Griffitts and Alminas, 1968, p. 8) as fragments of limonite and wulfenite. Anglesite and cerussite are too soft to survive stream transportation as sand grains and are rarely found in heavy-mineral concentrates.

Reconnaissance mineral exploration of many large areas has been accomplished by sampling stream sediments and by analyzing these samples for lead as well as for other ore metals. A good example is a study in New Brunswick (Boyle and others, 1966). Stream-sediment samples commonly contain less than 100 ppm of lead (in the minus-80-mesh-size fraction); near known lead deposits they may contain more than 5,000 ppm of lead. Representative data for stream sediments collected by the author near Tombstone, Ariz., are given in table 5.

TABLE 5.—*Ore-metal content of stream-sediment samples (minus 80-mesh) collected in and downstream from the Tombstone district, Arizona*

[N.a., not analyzed]

Sample No	Sample locality	Metal content (ppm)				
		Lead	Zinc	Silver	Molybdenum	Copper
	Tombstone Gulch:					
1	Near town and rich mines	4,500	4,300	26.0	120	175
33	0.5 mi (0.8 km) downstream from Sample 1	5,000	7,000	33.0	30	300
3	0.7 mi (1.1 km) downstream from Sample 1	5,500	6,000	46.0	16	500
2	1.9 mi (3.0 km) downstream from Sample 1	850	720	9.1	4	80
32	2.6 mi (4.2 km) downstream from Sample 1 and 0.4 mi (0.6 km) above Walnut Creek	550	460	4.1	<4	30
	Walnut Creek:					
18	0.8 mi (1.3 km) below mouth of Tombstone Gulch	118	130	N.a.	N.a.	30
7	1.4 mi (2.2 km) below mouth of Tombstone Gulch	90	83	1.3	<4	N.a.

LEAD IN MINE DRAINAGE

Measurable amounts of lead are rarely detected in either mine waters or drainage from mines. Representative data obtained near lead and zinc deposits in New Brunswick indicate a lead content of as much as 3,300 ppm in stream sediments but less than 0.001 ppm in stream waters. The water sample with the highest lead content, 2 ppm, was collected within a mine (Boyle and others, 1966, p. 24). In the same waters, the zinc content is as much as 1,000 ppm. The contrast shows the relative insolubility of lead. These results and other available data indicate that during weathering and erosion, little if any lead is removed in solution from lead deposits.

PLANTS

Plants growing in lead-rich soil absorb some lead from the soil. Later, when the plants die and decay, this lead is returned to the soil. The renowned geochemist V. M. Goldschmidt, after his chemical studies of coal ashes (1937), theorized that lead, as well as many other trace elements present in soil, tends to be absorbed by plants and plant humus. Thus, wherever soils are rich in lead, the plants also are likely to be rich in lead.

The extent to which plants accumulate lead from the soil (Webb and Millman, 1951; Worthington, 1955; and Malyuga, 1964) can be judged by the lead content of plants growing near areas of lead mineralization. Some studies have indicated an anomalous lead content in some plants but not in others (Cannon, 1960, table 3). Relative amounts of lead accumulated by various species can be evaluated by comparing the lead content of plant ash (which contains nearly all the inorganic constituents) with the lead content of the soil in which the plants are growing. Table 6 gives data of this type for three areas.

In most of these areas the lead content of plants is higher than that of the soil in the nonmineralized areas and lower than that of the soil in the mineralized area. In other words, the plants show less accumulation of lead from lead-rich soils. The reasons for this relationship between soils and plants with respect to lead is not completely understood. However, it does indicate that the ability of plants to accumulate lead from soils is limited.

Data given in another section of this report indicate considerable differences among plant species in ability to accumulate lead. Considering the large number of plant species, it is quite possible that some common plants which have never been investigated accumulate large amounts of lead. The mineralized areas, with high lead content in their soils, provide excellent environments to study the lead content of common, non-agricultural plant species. Because of the current interest in lead dispersion, additional studies of common plants in mineralized areas seem desirable to identify all species which accumulate lead.

TABLE 6.—*Mean lead contents of plants compared with mean lead contents of associated soils in both nonmineralized and mineralized areas*

[Data from the Mississippi Valley district from Keith (1969, p. 353-356); data from Alaska from Shacklette (1960, p. B102-B103); data from the Tombstone district collected by the author]

	Lead (ppm)	
	Nonmineralized area	Mineralized area
Upper Mississippi Valley		
Soils:		
Residual, A horizon	18	124
Plant ash:		
Elm, stems	102	78
Maple, stems	119	135
Oak, stems	150	99
Mahoney Creek lead-zinc deposit, Alaska		
Soils	20	1,300
Ash of all plant species sampled	90	160
Tombstone district, Arizona		
Soils:		
Alluvial	35	3,905
Plant ash:		
Mesquite, stems	53	239

CONCLUSIONS

The supergene dispersal of lead, unlike that of some other ore metals, takes place mostly by mechanical processes. Chemical changes are involved in weathering but the weathered products are relatively insoluble and are not leached from the rock by soil moisture. These soft insoluble lead minerals are incorporated in the fine-size fractions of the soil and stream sediments. They are dispersed by gravity and can be traced in ever-diminishing concentrations a long distance from their source.

The low solubility of the supergene lead minerals limits the amount of lead which dissolves in mine waters or is accumulated by plants. Available data on the lead content of mine waters indicate that it is normally very low. Some plants accumulate lead from lead-rich soil near ore deposits; this accumulation varies according to species and may amount to several hundred parts per million in the ash of some species. However, as shown elsewhere in this report, high concentrations in plants have also been observed near lead smelters and near highways where plants absorb lead from industrial and automobile exhaust fumes.

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LEAD IN IGNEOUS AND METAMORPHIC ROCKS AND IN THEIR ROCK-FORMING MINERALS

By Michael Fleischer

LEAD IN IGNEOUS AND METAMORPHIC ROCKS

Most of the recent estimates of the lead content of igneous and metamorphic rocks (table 7) are based principally on the spectrographic analyses by Wedepohl (1956). Since the publication of his work, several hundred determinations by a variety of methods have been published. These are summarized in table 8 and are shown graphically for selected rock types in figure 5, in which the rocks analyzed have been classified under the names given by the respective authors. The data are in good general agreement with the averages previously proposed by Wedepohl and other researchers. It will be noted that the median values are generally slightly lower than the arithmetic averages, a consequence of the inclusion of a few very high determinations; thus, it is believed that the median value is generally more meaningful than the arithmetic average.

The data indicate that, within the probable error of the averages, the lead contents of plutonic rocks are generally about the same as those of their volcanic equivalents (table 8), granites correspond to rhyolites, diorites to andesites, and alkalic rocks to trachytes and phonolites.

Table 7.—*Published estimates of lead contents of igneous and metamorphic rocks*

Rock Type	Lead (ppm)
Silicic rocks (granite, rhyolite)	[1]20.0
Granite	[2]20.0
Granite, high Ca	[3]15.0
Granite, low Ca	[3]19.0
Granodiorite	[2]15.0
Intermediate rocks (diorite, andesite)	[1]15.0
Quartz diorite	[2] 8.0
Diorite	[2]10.0
Alkalic rocks	[2] [3]12.0
Ultramafic rocks	[2] 3.0 [1] .1 [3] 1.0
Rhyolite and obsidian	[2]21.0
Dacite	[2]11.0
Basalt and gabbro	[2] 6.0 [1] 8.0 [3] 6.0

[1] Vinogradov (1956, 1962).
[2] Wedepohl (1956).
[3] Turekian and Wedepohl (1961).

The lead contents increase with increasing silica content and, in general, with content of potassium, but even within a single pluton or igneous complex correlations such as Pb/K, Pb/Rb, and Pb/Ba show wide variations. It is very doubtful that these ratios are useful as a tool for correlation. They are even less useful as a basis for prediction of lead contents. A few typical examples from recent papers for the variation of the Ba/Pb ratio are listed in table 9.

The average lead content for gneiss in table 8 is slightly lower than that for granitic rocks, but there are not sufficient data to permit drawing any conclusions as to whether lead is gained or lost during metamorphism, except to say that metasomatic reactions leading to the development of K-feldspar result in increased lead content. Milovskiy and Matveyeva (1970) studied three instances of granitization and found increases of average lead content in two, where lead increased from 13 to 30 ppm and from 8 to 18 ppm; in a third example the lead content remained constant at 40 ppm Pb.

The distribution of analyses for granite, granodiorite, basalt, and gneiss is shown in figure 5.

LEAD IN ROCK-FORMING MINERALS OF IGNEOUS AND METAMORPHIC ROCKS

From consideration of the ionic radii of the rock-forming elements of igneous rocks (values are from those of Whittaker and Muntus, 1970, for coordination number 6), one would expect lead (Pb^{+2}, 0.126 nanometres) to be concentrated in minerals of potassium (K , 0.146 nm), such as K-feldspars, biotite, and muscovite, and to occur to a lesser degree in minerals of calcium (Ca^{+2}, 0.108 nm) and sodium (Na^{+}, 0.108 nm). In igneous rocks one would also expect very close geochemical coherence between lead and barium (Ba^{+2}, 0.144 nm) and between lead and strontium (Sr^{+2}, 0.121 nm), and fair coherence of lead with rubidium (Rb^{+}, 0.157 nm).

In reality, however, although there is a general parallelism between the contents of lead and potassium,

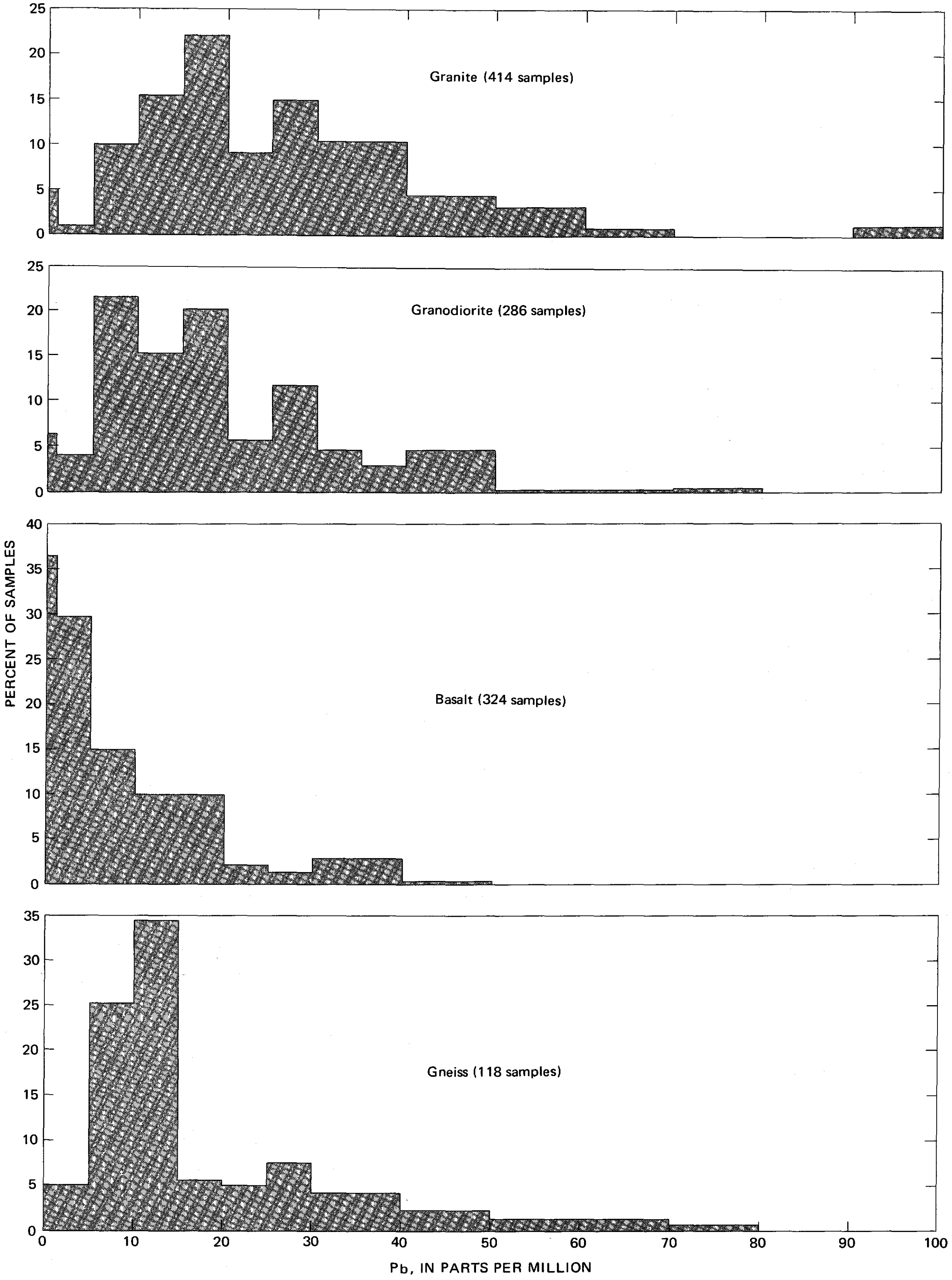

FIGURE 5.—Histograms of lead distribution in granite, granodiorite, basalt, and gneiss.

TABLE 8.—*Summary of published analyses of lead content of igneous and metamorphic rocks.*

[Leaders (...) indicate not determined]

Rock type	Number of analyses	Lead content (ppm)		
		Range	Arithmetic average	Median
Granitic rocks	536	0–200	25.0	18
Granodiorite, adamellite	317	0– 80	22.0	16
Diorite, quartz diorite	122	0– 76	14.0	11
Alkalic rocks	153	0–500	22.0	16
Ultramafic rocks	34	0– 37	2.0	...
Rhyolite, obsidian	273	0–200	21.0	18
Latite, quartz latite	49	0– 50	25.0	21
Dacite, rhyodacite	121	0–300	12.0	11
Andesite	203	0–150	12.0	8
Basalt, gabbro, diabase	372	0–100	7.5	4
Trachyte, phonolite	33	0– 60	18.0	16
Gneiss	274	0– 80	20.0	12
Schist	81	0–100	15.0	15
Amphibolite	51	0– 50	11.0	9

both in igneous rocks and in the individual minerals of those rocks, examination in detail shows extremely wide and unsystematic variations in the K/Pb ratio. The same may be said of the relation between lead and rubidium contents; likewise, the ratios of lead to barium and lead to strontium vary over an extremely wide range and show no systematic relation to crystallization trends.

In discussing this problem, Heier (1962 p. 426) stated,

> Lead does not show any simple relation to any of the other elements substituting for potassium in K-feldspars. Because Pb^{+2} is both divalent and smaller than K^{+}, it should be strongly captured according to classical distribution rules. However, the data * * * show that lead tends to be enriched in the most fractionated (pegmatite) K-feldspars. This contradiction to Goldschmidt's rule is related to the large electronegativity value of Pb^{+2}, and the consequent increased covalent nature of the Pb-O bonds as compared to the K-O bonds.

DISTRIBUTION OF LEAD AMONG ROCK-FORMING MINERALS

Less than a dozen analyses have been published in which lead content has been determined for all the constituents of a given rock, and the material balances for these are not very good, presumably because of the low spectrographic sensitivity for lead. The few available analyses (Nockolds and Mitchell, 1948; Tauson and Kravchenko, 1956; Zlobin and Gorshkova, 1961) all show that 70–95 percent of the total. lead in the rocks is present in K-feldspar plus plagioclase.

It should be noted that some of the accessory minerals of granitic rocks, especially those containing radioactive elements (for example, monazite, xenotime, uraninite, thorite, zircon, allanite, titanite), commonly contain far greater concentrations of lead than major rock-forming minerals; the contribution of accessory minerals to the total lead content of the rock, however, is generally small.

TABLE 9.—*Range of variation of Ba/Pb ratio in igneous and metamorphic rocks*

Rock type	Range of Ba/Pb ratio	Reference
Rhyolite:		
Pitchstone	60–300	Carmichael and McDonald (1961).
Pantellerite	4– 56	Gibson (1972).
Andesite	20– 44	Peltz and others (1971).
Do	30–153	Taylor and others (1969).
Olivine basalt	36–129	Cummings (1972).
Ankaramite	75–360	Gunn and others (1970).
Dolerite	8– 35	Walker (1969).
Granodiorite	17–210	Savu and others (1971).
Granite	23– 76	Do.
Do	2– 90	Saha and others (1968).
Gneiss	7–132	Khaffagy (1971).

Because galena occurs in small amounts in many rocks, attempts have been made (Arnaudov and others, 1967; Arnaudov and Pavlova, 1971) to measure "sulfide lead" (by leaching with a solution containing 25 percent NaCl+0.5N HCl) and "sulfate lead" (by leaching with a solution containing 25 percent NaCl); these experiments show that in nearly all samples of feldspars and muscovites, 70–95 percent of the lead present is in the silicate molecule.

LEAD CONTENT OF ROCK-FORMING MINERALS

The feldspars, as stated previously, are the principal carriers of lead in igneous and metamorphic rocks. Their contents of lead vary widely from locality to locality, and even in different samples from a single locality, but general trends are evident from table 10 and figure 6, where data for orthoclase and microline are grouped together.

For rocks of granodiorite composition the content of lead is only slightly greater in K-feldspar than in coexisting plagioclase (indeed, a few analyses show more lead in the plagioclase), but the lead content of the plagioclase decreases with decreasing content of calcium. Consequently, the ratio of lead in K-feldspar to lead in plagioclase increases towards the granites proper and

TABLE 10.—*Lead content of feldspars*

[Leaders (...) indicate not determined]

Rock type	Number of analyses	Pb(ppm)		
		Range	Average	Median
K-feldspars (microcline and orthoclase)				
Rhyolite, latite, quartz latite[1]	162	2– 115	47	....
Granitic rocks[2]	344	0– 150	36	20
Granitic pegmatite[3]	428	0– 560	72	30
Amazonite, granitic pegmatite	174	<5–13,500	477	200
Plagioclase				
Rhyolite, latite, quartz latite	3	13–14	14	14
Granitic rocks[2]	128	1–52	13	10
Granitic pegmatite	90	<5–148	46	35

[1] These are mostly sanidine.

[2] Granite, granodiorite, adamellite, gneiss.

[3] Excluding amazonite.

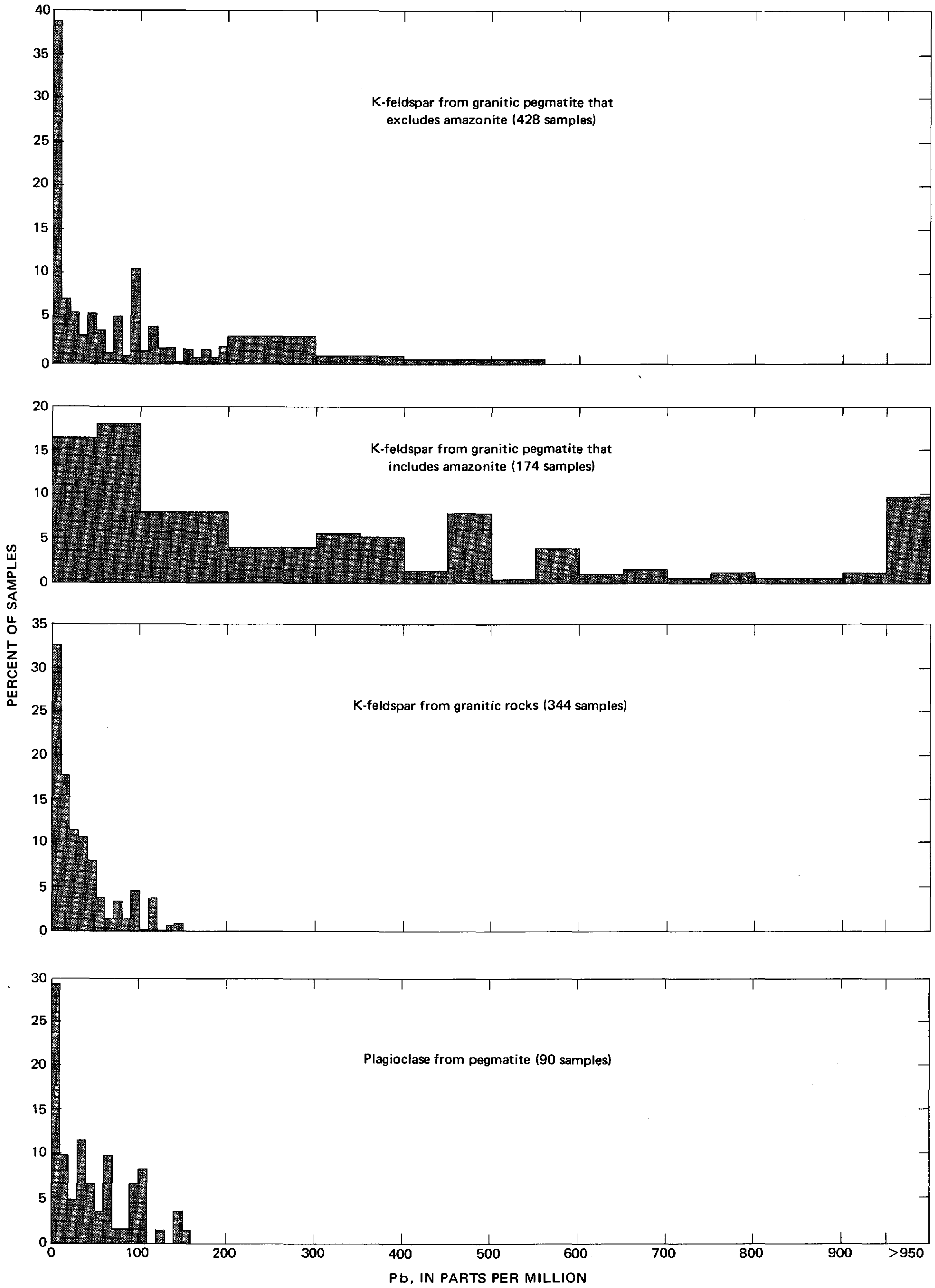

FIGURE 6.—Frequency of occurrence (percent of total samples) If lead in K-feldspar from granitic pegmatite that excludes amazonite, from granitic pegmatite that includes amazonite, and from granitic rocks, and in plagioclase from pegmatite.

further increases in the feldspars of granitic pegmatite. The K-feldspars of very late stages of granitic pegmatite (including the amazonite) show very high contents of lead, reaching maximum levels of 1.35 percent for amazonite (Alker, 1959) and 1.10 for green orthoclase (Cech and others, 1971).

Plots correlating lead content with Rb/Pb and Ba/Pb ratios show that these ratios tend to decrease as lead content increases, but the data scatter is so great that these ratios probably are not useful for correlation or prediction.

Data on other rock-forming minerals are assembled in table 11. Most of the data on muscovite are from Bradshaw (1967), who found significantly higher contents of lead in samples from granites associated with mineralization. The data of Parry and Nackowski (1963) and of Lovering (1969, 1972) indicate that the lead content of biotites from mineralized granitic rocks is slightly higher than in those from unmineralized granitic rocks; it is possible, however, that some of the variation is due to regional differences not connected with processes of mineralization. The average for chlorites seems to be higher than would have been anticipated; it may reflect introduction of lead during hydrothermal alteration, but more work is clearly needed. The low contents in quartz, pyroxene, amphibole, garnet, and olivine are as expected.

Very little work has been done on the fate of lead in the weathering of igneous rocks. The data of Butler (1953, 1954), however, indicate that most of the lead is taken up by minerals of the clay-size fraction.

SUMMARY

Averages for lead in the major types of igneous and metamorphic rocks as shown by recent analyses are in good agreement with the averages suggested by Wedepohl (1956). In the normal igneous or metamorphic rock series, the lead content increases with silica content and there is a rough correlation between contents of lead and potassium, but the variations are so great that ratios of lead to potassium, rubidium, or barium are not of much value for correlation or prediction. No distinct differences were noted between extrusive rocks and their intrusive equivalents.

The data do not clearly show whether lead is gained or lost during metamorphism, but indicate gain of lead during feldspathization or other types of potassium-metasomatism.

Most of the lead in igneous and metamorphic rocks is contained in feldspar; although some minor accessory minerals commonly contain more lead, their contribution to the total lead content of the rock is small. Late-stage K-feldspars of granitic pegmatite usually have the highest lead content of the common rock-forming minerals. The lead content of the late micaceous minerals (muscovite, biotite, and chlorite) is generally lower than that of the feldspars, but higher than that of the other common rock-forming minerals. Micas from mineralized granitic rocks appear to contain slightly more lead than those from unmineralized rocks of similar composition.

TABLE 11.—*Lead content of other rock-forming minerals*

Mineral and rock type	Number of analyses	Pb (ppm)	
		Range	Average
Muscovite:			
Granitic rocks:			
Mineralized[1]	55	4–100	21
Unmineralized[1]	99	1–450	7
Granite pegmatite	21	9– 34	18
Schist	8	<10– 77	42
Eclogite	2	(2)	10
Biotite:			
Granitic rocks	585	< 1–450	29
Silicic volcanic rocks	17	<10– 50	10
Schist	73	5–120	20
Pyroxenite	1	None	9
Biotite and phlogopite:			
Granite pegmatite	11	no data	13
Chlorite[3]	39	7–220	64
Quartz	31	0– 50	3
Pyroxene	[4]196	0– 59	[3]5
Amphibole	[5]47	0– 34	[4]10
Garnet	21	1– 46	8
Olivine	9	0– 6	2

[1] Granite, granodiorite, gneiss.
[2] Both analyses yielded 10 ppm.
[3] Nearly all from granitic rocks.
[4] Excluding two analyses of 216 and 343 ppm Pb.
[5] Excluding one analysis of 150 ppm Pb.

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ABUNDANCE OF LEAD IN SEDIMENTARY ROCKS, SEDIMENTS, AND FOSSIL FUELS

By T. G. Lovering

SEDIMENTARY ROCKS AND SEDIMENTS

Lead is present in very small amounts in the common sedimentary rocks. Analytical data from the U.S. Geological Survey's rock analysis storage system for more than 2,500 sedimentary rock samples from various parts of the United States show average lead concentrations of about 32 ppm for carbonaceous shale, 23 ppm for siltstone, mudstone, claystone, and noncarbonaceous shale, 17 ppm for sandstone, and 11 ppm for limestone and dolomite. For all these rock types, median values are lower than the averages (fig. 7), and even the carbonaceous shale, which has the highest average lead content, contains only about 1 ounce of lead per ton (31 g/t) of average rock.

Comparable data on the lead content of these and other sedimentary rocks are found in the literature. Selected samples of carbonaceous shale from various formations in the Western United States contained from <10 to 70 ppm lead, with a median of 15 ppm (Davidson and Lakin, 1961, 1962). Vine (1966) collected four sets of black shale samples from various parts of the country and found median values in them ranging from 10 to 30 ppm of lead, and Wedepohl (1971) obtained an average lead value of 23.8 ppm from 200 bituminous shale samples taken from both the United States and Europe. Likewise, in an additional 73 samples of shale of Mesozoic to Holocene age, from Europe, Korea, Japan, the United States, and Trinidad, Wedepohl found an average of 23.8 ppm lead with a standard deviation of 15 ppm. Tourtelot (1962, pl. 4) found that the lead content of samples of Pierre Shale taken from widely separated localities in Montana, Wyoming, and South Dakota showed a narrow range of from 7 to 30 ppm with a median at 15 ppm. Krauskopf (1955, p. 416) gave an average value for lead in shale of 20 ppm; Newman (1962, p. 425) estimated the average lead content of Triassic mudstones on the Colorado Plateau as 13 ppm, and Cadigan (1971, p. 41–42) calculated a geometric mean of about 12 ppm lead for these rocks.

Published data on the lead content of normal sandstone are somewhat less abundant than those for shale and siltstone. Krauskopf (1955, p. 416) gave an average range of 10–40 ppm lead for sandstone. Wedepohl (1971, p. 241) found a mean value of 19.2 ppm lead in 45 Paleozoic and Mesozoic quartz sandstones from Germany. Lapchinskii and Lapchinskaya (1966, p. 123–127) reported an observed range of 16–52 ppm for lead in Carboniferous sandstone from Shebelinsk, Russia, and Razdorozhnyi (1966, p. 203–206) obtained a modal value of 10 ppm lead from sandstone samples of similar age from the Donets Basin of Russia.

Our data on normal lead in carbonate rocks (limestone and dolomite) are comparable with the average abundance of 8±4 ppm estimated by Graf (1960, p. 71) and with the average of 9 ppm given by Wedepohl (1971, p. 241) for 124 samples of European carbonate rocks.

Semiquantitative analyses of several hundred samples of phosphate rock from the Phosphoria Formation in Idaho (Sheldon and others, 1953; McKelvey and others, 1953) suggest that the normal lead content of this rock ranges from 10 to 100 ppm and that many of the samples contain >100 ppm of lead, indicating a slightly greater concentration of lead in phosphate rock than in carbonaceous shale. Bauxite, on the other hand, appears to be more comparable to the carbonate rocks in its lead content; samples of Arkansas bauxite had an average content of 7 ppm and a maximum content of 70 ppm lead (Gordon and Murata, 1952). However, some published analyses of European phosphorites and bauxites suggest the reverse relationship in the relative concentrations of lead in these two rocks. Orekhov (1968) reported a maximum value of 30 ppm lead in samples of lower Tertiary phosphorites of the Rostov region in Russia. Maksimovic (1968) found a range of 16–155 ppm, with an average of 69 ppm lead, in 120 samples of bauxite from Herzegovina, Yugoslavia. György (1957), however, gave lead concentrations in bauxite samples from western Hungary that are comparable to those reported for Arkansas bauxite.

The normal lead content of marine evaporite rocks appears to be even lower than that of the sedimentary carbonate rocks. Stewart (1963, p. Y33–Y39) presented several analyses of these marine rocks and of the chloride and sulfate minerals of which they are composed. The highest lead value he gave is 5.4 ppm for a core sample of halite (NaCl); most of the halite samples, and also those of potash evaporites, contained less than 1 ppm of lead. The low lead content of potash evaporite sediments is somewhat surprising in view of the tendency for lead to concentrate in the potash feldspars of igneous rocks.

The presence of available lead in the marine environment is indicated by relatively high lead concentrations in samples of unconsolidated marine sediments. Turekian and Wedepohl (1961, p. 186) reported an average of 45 ppm lead in deep sea clay from the Atlantic and 110 ppm in corresponding samples from the Pacific. Ericson, Ewing, Wollin, and Heezen (1961, p. 229–231) analyzed more than 100 argillaceous bottom sediments from the Atlantic Ocean and the Caribbean Sea. These samples gave a median lead value of 60 ppm and a maximum of 240 ppm. Riley and Skirrow (1965, p. 49) reported an average of 162 ppm of lead in deep sea clay samples; they believed more than half of this lead to have been derived from seawater (p. 57). Similarly, in deep sea nodules of iron and manganese oxides, they obtained nearly 1,000 ppm lead, which they thought was adsorbed from seawater by hydrous colloidal oxides of iron and manganese.

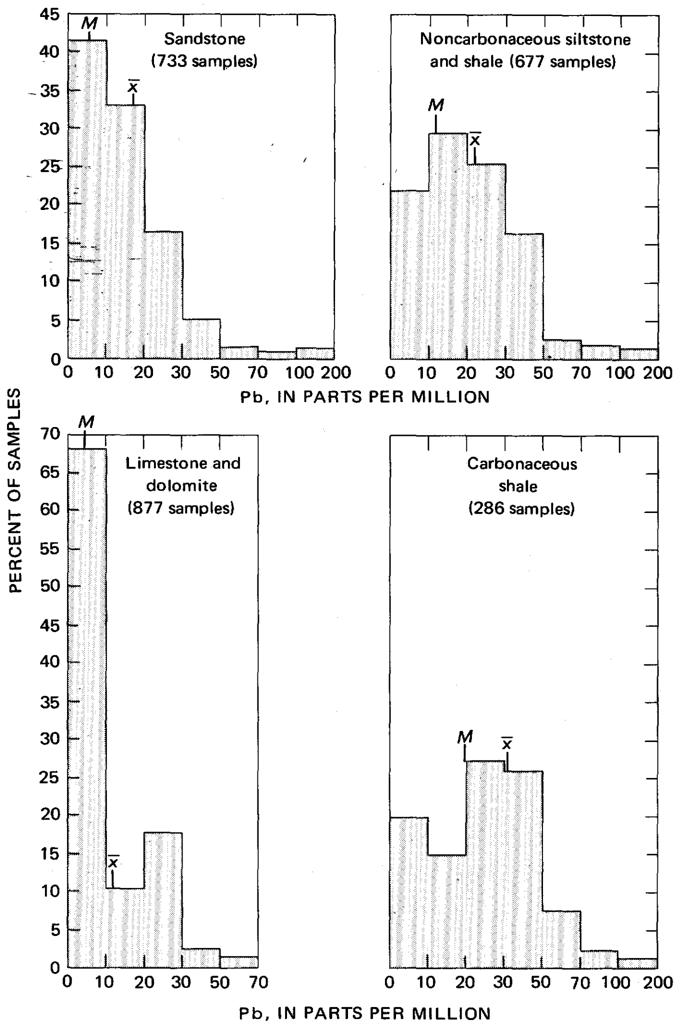

FIGURE 7.—Lead content of common sedimentary rocks (from U.S. Geological Survey's rock analysis storage system). *M*, median; $\bar{x}$, average.

Marine sediments deposited in shallow water appear to contain appreciably less lead than those deposited in deep water. Nearshore samples from the Pacific Ocean average only 20 ppm lead (Riley and Skirrow, 1965, p. 49), and similar lead contents are reported from Mediterranean Sea sediments (Bilyavskii, 1969), and Baltic Sea sediments (Lubchenko, 1970). However, in tectonically active areas, such as the Red Sea, where volcanic emanations and hydrothermal solutions mingle with marine water, lead content of the sediments can be greatly increased. Sediment samples from the bottom of hot brine pools in the Red Sea contain as much as 0.2 percent lead (Hendricks and others, 1969, p. 434).

This contrast between lead contents of deep and shallow marine sediments suggests that lead entering the marine environment has a tendency to move outward and downward toward the deeps. Such a theory would help to explain the low lead in evaporite sediments that formed in shallow basins; most of the lead may be presumed to have migrated seaward from these basins before the brines became sufficiently concentrated for the evaporite minerals to precipitate. Higher lead content of deep marine sediments may also be caused, in some places, by lead-bearing juvenile emanations entering the deep sea basins.

The normal lead content of unconsolidated terrestrial stream sediment appears to be comparable to that of shale. Holman (1963) found an average of 18 ppm lead in stream sediment samples from Nova Scotia. Analyses of more than 5,500 stream sediment samples from a large area in Maine yielded a mean of 25 ppm lead (F. C. Canney and Maurice Chaffee, written commun., 1971).

FOSSIL FUELS

The normal lead content of coal appears to be intermediate between that of shale and of the carbonate rocks, averaging about 10 ppm. Rao (1968) estimated that the lead content of Alaskan coal samples ranged from 1 to 50 ppm and averaged 10 ppm. Published lead analyses of organic fuels samples are normally given as percent lead in ash, inasmuch as lead cannot be determined by ordinary analytical methods in the presence of large amounts of organic carbon. The values given by Rao for the lead content of the ash of Alaskan coal samples are approximately one order of magnitude higher than his estimated values for the raw coal, ranging from 20 to 400 ppm and averaging 100 ppm. Abernathy, Peterson, and Gibson (1969) presented data on the lead content of the ash of large numbers of coal samples from the western, interior, and eastern coal provinces of the United States. The average lead in ash was given as 29 ppm for the western province, 131 ppm for the interior province, and 55 ppm for the eastern province.

The published data suggest that the lead content of coal tends to decrease as its rank increases. Duel and Annell (1956) found lead contents in ash of low-rank-coal samples ranging from 100 to 1,000 ppm. Nunn, Lovell, and Wright (1953, p. 56) estimated a range of 10–100 ppm in the lead content of anthracite ash; and Chow and Earl (1970, p. 46) found a range of 10.0–33.8 ppm of lead in the ash of anthracite samples from Pennsylvania and Rhode Island.

Headlee and Hunter (1955, p. 151–155) ran some experiments on the partitioning of lead in coal among the products of combustion. They concluded that the ashing techniques used in the laboratory retain essentially all of the lead in the ash, but that ordinary burning of coal in industrial processes volatilizes about 6 percent of the lead originally present in the coal. If we use this figure, and assume a lead content of 10 ppm (0.001 percent) in the coal, it would require the combustion of approximately 10,000 tons of coal to introduce 1 pound (0.45 kg) of volatilized lead into the atmosphere. Industrial burning of coal samples with a lead content of 0.037 percent in the ash produced soot with a lead-in-ash content of 0.4 percent, and the ash of coal tar derived from this coal contained 2.84 percent lead (Headlee and Hunter, 1955, p. 155).

The lead content of petroleum, although generally lower than that of coal, is extremely variable. Hyden (1961, p. 44–59) published extensive tables showing the lead content of crude oil samples from different parts of the country. Lead ranges from <0.001 to 11.4 ppm and averages 0.025 ppm in the oil, and it ranges from <0.0015 to 300 ppm and averages 20 ppm in the ash. Donnell, Tailleur, and Tourtelot (1967) reported a maximum lead content of 200 ppm in the ash of samples of Alaskan oil shale.

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LEAD CONTENT OF WATER

By M. J. Fishman and J. D. Hem

The lead content of water is usually described in terms of concentrations of the dissolved element. For research purposes, the U.S. Geological Survey, in testing water samples for trace elements, considers dissolved material to be particles small enough to pass through a 0.45- μm-pore-diameter membrane. Although this is an arbitrary operational definition and some colloidal material may pass through the filter, the 0.45- μm size limit is widely used. Where data are given here on dissolved lead, they may be assumed to represent material that passed through a 0.45- μm-porosity filter. Until recently very little attention has been given to the minor-element content of material caught on the filter, and it is not possible to obtain from published literature any clear indication of the importance of the suspended fraction in the total quantity of lead transported by streams. There is some evidence, however, that, at times, considerable amounts may be present in suspension in streams carrying direct runoff from urbanized areas.

LEAD IN SURFACE WATERS

A considerable amount of information on lead concentrations in surface waters has been obtained since the late 1950's. However, the observations tend to be sporadic and scattered, and the details of the chemical behavior of the element and its occurrence in any single stream have not been fully explored. Kleinkopf (1960) reported a mean lead concentration of 2.3 μg/l in waters from 440 lakes in the State of Maine, with a range of 0.03–115 μg/l. Durum, Heidel, and Tison (1960) reported concentrations of a suite of minor elements, including lead, for samples from major streams throughout the world. Data from their report and supplementary unpublished analyses in U.S. Geological Survey files show a range of lead concentrations from 0 to 200 μg/l, with an average of 8.4 μg/l. There were 93 samples in this group, representing 27 streams, mostly in North America. Lead occurred in concentrations above the detection limit in more than 90 percent of the samples. The samples in the study by Durum, Heidel, and Tison were filtered before analysis, but the filter only removed particles over 1 μm in diameter. Consequently these lead values may include some from material usually found in suspension as well as that in solution.

Since 1960, the U.S. Geological Survey has performed more than 1,600 lead determinations on surface-water samples collected throughout the United States. These samples were analyzed for lead by spectrographic and atomic-absorption techniques, which are discussed by M. J. Fishman (this report). Most of the samples were from one of three sources: (1) public water supplies, (2) water courses downstream from major municipal or industrial complexes, and (3) U.S. Geological Survey hydrologic bench-mark stations.

The dissolved-lead concentrations in these samples, representing surface waters in all 50 states as well as Washington, D.C., and Puerto Rico, range from "not detected" to 890 μg/l. However, lead only rarely occurs in amounts exceeding the U.S. Public Health Service (1963) drinking water standard of 50 μg/l lead. Only 13 of the more than 1,600 samples analyzed, or less than 1 percent, contained concentrations in excess of 50 μg/l. Of the 13 samples, only 3 contained more than 100 μg/l lead, or more than twice the U.S. Public Health Service limit. Eighty-six percent of the samples contained less than 10 μ g/l. Most surface waters, except for water courses downstream from major municipal and industrial complexes, evidently contain less than 10 μg/l of dissolved lead.

Table 12 summarizes, by States, the maximum and minimum concentrations of lead found in surface waters of the United States. Also included in the summary are the percentage of samples containing less than 10 μg/l and the number of samples that exceeded the U.S. Public Health Service drinking water limit. The data in this table, which cover the period from 1960 through 1971, were obtained from Durfor and Becker (1964), and Durum, Hem, and Heidel (1971), and from miscellaneous spectrographic data from analyses performed in the U.S. Geological Survey laboratory in Denver, Colo., under the direction of P. R. Barnett.

Table 13 shows lead concentrations in selected surface waters of the United States, as determined from miscellaneous spectrographic analyses.

Several in-depth studies of surface water in individual States and regions have also been carried out. Silvey (1967) reported an average concentration of 5.7 μg/l of lead in streams of California in which the element could be

TABLE 12.—*Maximum and minimum concentrations of lead found in surface waters of the United States and Puerto Rico from 1960 to 1971*

[ND, sought but not found]

	Number of samples	Number of samples equaling or exceeding mandatory maximum for drinking water[1]	Percent of samples having less than 10 μg/l	Lead concentration (μg/l) Maximum	Lead concentration (μg/l) Minimum
Alabama	76	1	96	50.0	ND
Alaska	9	0	100	5.0	< 1.0
Arizona	19	0	89	12.0	ND
Arkansas	32	0	81	20.0	< .8
California	40	0	68	34.0	< 1.0
Colorado	70	0	89	30.0	ND
Connecticut	50	1	72	50.0	< 1.0
Delaware	4	0	25	23.0	2.0
District of Columbia	4	0	100	5.8	< 1.0
Florida	37	0	100	6.0	< .7
Georgia	22	0	41	32.0	< 1.0
Hawaii	8	0	100	< 1.0	< 1.0
Idaho	26	0	100	6.0	< 1.0
Illinois	23	0	48	25.0	2.5
Indiana	46	0	89	20.0	ND
Iowa	14	0	100	5.7	< 1.0
Kansas	14	0	100	7.5	ND
Kentucky	10	0	60	20.0	< 1.0
Louisiana	19	0	95	11.0	< 1.0
Maine	7	1	57	890.0	5.0
Maryland	29	0	93	43.0	< 1.0
Massachusetts	24	1	75	87.0	1.3
Michigan	25	0	92	15.0	2.0
Minnesota	30	0	97	17.0	< 1.0
Mississippi	11	0	82	10.0	< 1.0
Missouri	103	0	84	38.0	< .5
Montana	25	0	96	23.0	< 1.0
Nebraska	21	0	81	40.0	< 1.0
Nevada	8	0	100	5.0	< 1.0
New Hampshire	5	1	80	70.0	4.0
New Jersey	150	2	88	240.0	< 1.0
New Mexico	34	0	91	10.0	ND
New York	211	0	92	22.0	< 1.0
North Carolina	27	0	70	32.0	< 1.0
North Dakota	22	0	86	37.0	< 1.0
Ohio	31	0	100	7.9	ND
Oklahoma	16	2	75	94.0	< 1.0
Oregon	14	0	100	< 1.0	< 1.0
Pennsylvania	65	1	71	55.0	2.0
Rhode Island	5	0	100	8.0	3.4
South Carolina	17	0	94	11.0	< 1.0
South Dakota	22	0	68	35.0	< 1.0
Tennessee	21	2	67	390.0	< 1.0
Texas	46	0	98	11.0	ND
Utah	28	0	89	12.0	< 1.0
Vermont	3	1	0	50.0	13.0
Virginia	16	0	81	42.0	< 1.0
Washington	17	0	100	7.0	< .5
West Virginia	22	0	86	44.0	< 1.0
Wisconsin	18	0	83	26.0	2.0
Wyoming	37	0	[2]89	3.0	< 1.0
Puerto Rico	40	0	85	19.0	< 1.0
Total	1,673	13	....	......	.....
Percent of total samples	....	...	86	......	.....

[1] 50 μg/l, as established by the U.S. Public Health Service (1963).
[2] Includes four values above 10 μg/l.

detected. However, lead concentrations were below the detection limit (0.6 μg/l) in 78 percent of the stream samples analyzed.

A comprehensive investigation of the distribution of dissolved lead in Florida surface waters was carried out by the U.S. Geological Survey in cooperation with the Bureau of Geology, Florida Department of Natural Resources, and other State and local agencies (C. S. Conover, written commun., 1971). More than 180 samples were analyzed; concentrations of lead ranged from 0 to 40 μ g/l. The samples were collected during low (May 1970) and high (September 1970) streamflow conditions. The data for May 1970 indicate the following: (1) lead was found in about 60 percent of the samples in concentrations ranging from 1 to 30 μg/l; (2) 78 percent of all samples had lead concentrations equal to or less than 10 μg/l; and (3) 4 percent of all samples had concentrations of 30 μg/l. For September 1970, the following was observed: (1) lead was found in about 73 percent of the samples in concentrations ranging from 1 to 40 μg/l; (2) 75 percent of all samples had concentrations equal to or less than 10 μ g/l; and (3) 7 percent of all samples had lead concentrations equal to or greater than 30 μg/l.

Several other investigators have reported the lead content of various lake and river waters. Boswell, Brooks, and Wilson (1967) reported that the lead concentration in the bottom waters of Lakes Joyce and Hoare in Antarctica were 340 μg/l and 83–91 μg/l, respectively. The lead content of the water of the Orange River at Vioolsdrif, Cape Province, Union of South Africa, was reported by DeVilliers (1962) to range from less than 0.001 to 136 ppm (1,360 μg/l), based on 24 samples collected over a period of 1 year. Zhukhovitskaya, Zamyatkina, and Lukashev (1966) reported that lead concentrations in streams of the upper Dnieper basin ranged from 0.01 to 0.55 ppb. Lukashev, Zhukhovitskaya, and Zamyatkina (1965) found that lead concentrations in the surface waters of the Poles'e territory near Pripyat in the Belorussian S. S. R. ranged from 2 to 13.3 ppb. Krainov and Korol'kova (1964) analyzed mineral waters of the Lesser Caucasus and found a maximum lead concentration of 40 μg/l. Turekian and Kleinkopf (1956) determined lead in 439 stream and lake waters of Maine by a semiquantitative spectrographic procedure. The average concentration of lead was 0.26 ppb. Heidel and Frenier (1965) reported on the lead concentration of 156 surface waters, including some samples from the estuary of the Patuxent River basin, Maryland. The lead content ranged from 0.9 to 11 μg/l, with an average of 5 μg/l. A survey of the concentration of lead and other trace elements in the Colorado, Columbia, Ohio, Mississippi, and Missouri Rivers and in the Great Lakes was presented by Kroner and Kopp (1965). In only a few samples did the lead concentration exceed the U.S. Public Health Service drinking water standard. For most samples the concentration of lead was below the detection

TABLE 13.—*Lead concentrations in selected surface waters of the United States*

Sample locality	Date of collection	Lead Concentration (μg/l)	Reference
Alabama:			
Sipsey Fork, near Grayson	Sept. 10, 1970	1	J. R. Avrett (oral commun., 1971).
Coosa River, at Gadsden	Nov. 30, 1970	2	Do.
Cahaba River, near Centreville	Feb. 4, 1971	1	Do.
Arizona:			
Wet Bottom Creek, near Childs	Sept. 16, 1968	< 1	N. B. Carmony (written commun., 1971).
Canal (Gila River), near Arlington	Sept. 18, 1968	< 1	Do.
Arkansas:	Nov. 6, 1967	5	U.S. Geological Survey (1968a).
Bayou Meto, near Lonoke			
Bayou Bartholomew, near McGehee	Nov. 7, 1967	< 5	Do.
White River, at Clarendon	Nov. 6, 1967	4	Do.
Saline River, near Rye	Nov. 7, 1967	< 2	Do.
Ouachita River, at Arkadelphia	Nov. 8, 1967	3	Do.
Little River, near Ashdown	Nov. 9, 1967	1	Do.
Black River, at Black Rock	Nov. 16, 1967	< 4	Do.
Colorado:			
Arkansas River, at Granite	Jan. 19, 1967	30	U.S. Geological Survey (1967a).
South Platte River, near Henderson	Jan. 15, 1971	4	R. Brennan (written commun., 1971).
Connecticut:			
Naugatuck River, at Beacon Falls	Oct. 5, 1967	30	U.S. Geological Survey (1968b).
Hockanum River, near Rockville	Aug. 14, 1968	26	Do.
Florida:			
Sopchoppy River, near Sopchoppy	Mar. 10, 1970	6	R. L. Malcolm (written commun., 1971).
Iowa:			
Big Sioux River, at Akron	Apr. 4, 1967	3	U.S. Geological Survey (1967c).
Massachusetts:			
Connecticut River, at Northfield	July-Nov. 1970 (composite)	30	C. E. Knox (written commun., 1971)[1].
Hoosic River, below Williamstown	July-Dec. 1970 (composite)	3	Do.
Missouri:			
West Fork Black River, at Westfork	Oct. 24, 1967	5	U.S. Geological Survey (1968c).
Turkey Creek, near Joplin	Mar. 19, 1968	25	Do.
Spring River, near Waco	June 26, 1968	< 4	Do.
Sedalia Lake, near Sedalia	Oct. 29, 1970	1	A. Homyk (written commun., 1971).
James River, near Springfield	Feb. 16, 1971	< 4	Do.
Missouri River, near St. Louis	Mar. 12, 1971	4	Do.
Montana:			
Blackfoot River, near Lincoln	Aug. 22, 1969	< 3	U.S. Geological Survey (1969).
Nebraska:			
Dismal River, near Thedford	June 13, 1967	13	L. R. Petri (written commun., 1971).
Missouri River, at Omaha	Mar. 19, 1971	2	A. Homyk (written commun., 1971).
New Hampshire:			
Pemigewasset River, at Woodstock	July-Oct. 1970 (composite)	70	C. E. Knox (written commun., 1971)[1].
New Jersey:			
Passaic River, at Chatham	Aug. 28, 1970	9	P. W. Anderson (written commun., 1971)[1].
Whippany River, at Morristown	do	5	Do.
Rockaway River, at Boonton	Sept. 1, 1970	3	Do.
Hackensack River, at River Vale	Sept. 2, 1970	12	Do.
Millstone River, near Manville	Sept. 3, 1970	< 2	Do.
Raritan River, near Manville	do	< 2	Do.
Assunpink Creek, at Trenton	do	< 3	Do.
Delaware River, at Trenton	Sept. 29, 1970	2	Do.
New Mexico:			
Pecos River, at Artesia	Apr. 7, 1970	< 2	K. Ong (written commun., 1971)[1].
Rio Mora, at Terrero	Oct. 5, 1970	.7	Do.
Mogollon Creek, near Cliff	Oct. 14, 1970	.8	Do.
New York:			
Allegheny River, at Salamanca	Sept. 21, 1967	< 3	U.S. Geological Survey (1967b).
Oneida Lake, at Brewerton	Oct. 1, 1969	< 2	R. J. Archer (written commun., 1971)[1].
Susquehanna River, at Johnson City	Apr. 6, 1970	1	Do.
Lake Champlain, at Crown Point	June 2, 1970	7	Do.
Niagara River, at City of Niagara Falls	Nov. 16, 1970	< 5	Do.
Lake Ontario, at Oswego	Dec. 9, 1970	4	Do.
Hudson River, at Poughkeepsie	Dec. 16,1970	2	Do.
St. Lawrence River, at Alexandria Bay	Dec. 14, 1970	< 3	Do.
Black River, at Watertown	Feb. 22, 1971	1	Do.
North Carolina:			
Neuse River, at Raleigh	July 9, 1970	.7	R. Heath (written commun., 1971).
South Dakota:			
Belle Fourche River, at Wyoming-South Dakota boundary	Oct. 13, 1970	<30	F. C. Boner (written commun., 1971).
Wyoming:			
Laramie River, at Laramie	Apr. 23, 1970	< 7	Do.
Cache Creek, near Jackson	Sept. 1, 1970	< 2	Do.
North Platte River, below Casper	Jan. 13, 1971	< 8	Do.
Bighorn River, at Kane	Jan. 26, 1971	< 5	Do.

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[1] See Pt. 2, Water Quality Records, of the U.S. Geological Survey's Water Resources Data series, for the respective State and water year.

limit of the spectrographic method used to analyze the samples.

The data of Durum, Hem, and Heidel (1971) show a distinct regional pattern of dissolved-lead distribution in river water in the United States. Concentrations above the detection limit occurred in nearly all sources sampled in the States along the Atlantic Coast and in most sources in thickly populated regions around the Great Lakes. In the more thinly populated regions west of the Mississippi, a high proportion of the sources had less than 1 μg/l of lead, but relatively high concentrations appeared again along the Pacific Coast in streams of the Los Angeles, San Francisco, and Seattle areas. There were areas of higher concentrations in lead mining regions in Wisconsin, near the Ozark Mountains, and in northern Idaho and adjacent areas. The distribution pattern may be explained by considering the sources of environmental lead and by the solubility of lead carbonate and hydroxide from industrial wastes in river water.

Livingstone (1963) stated that from data then available it seemed likely that the global mean lead content for lakes and rivers ranged from 1 to 10 ppb. Data cited here suggest that this is a reasonable estimate for the dissolved fraction. In general, the presence of a few tens of micrograms per litre of lead in solution in river water appears to be most common in areas of heavy automobile traffic and extensive industrial development. In the vicinity of lead ore deposits, the content of lead in river water may also be in this range or higher.

Lead can be carried as a colloidal suspension of hydroxide in river water, and it may also be present as a coating on other mineral particles, or as ions sorbed on mineral surfaces. The available data do not clearly show the importance of suspended lead. Konovalov, Ivanova, and Kolesnikov (1968) determined lead concentrations in particulate material carried by 33 rivers in the U.S.S.R.; no data are given in their report for dissolved forms of lead. Concentrations of lead associated with sediment were as high as 152 μg/l of the original water sample, but most were below 40 μg/l. The analyses for lead in solution apparently all showed concentrations below detection, but it is not certain that the methods used give results that are comparable with those of other investigations cited here.

LEAD IN PRECIPITATION AND RUNOFF WATERS

A large amount of lead is used each year in the United States as a gasoline additive. This lead is mostly dispersed in the atmosphere, and has a readily measurable influence on the composition of rainfall—and, hence, of runoff waters—especially in the more thickly populated parts of the country. Lazrus, Lorange, and Lodge (1970) reported the average concentration of lead in rainfall to be 34 μg/l for 32 precipitation measuring stations throughout the United States during a 7-month period ending in March 1967. The concentrations of lead in rainfall in the northeastern part of the country, however, are known to exceed this average substantially. In addition, many of the dilute, relatively low pH solutions that constitute the usual river and lake waters in this region have a high capacity for retaining lead in solution at equilibrium. Many such waters could attain lead concentrations amounting to several hundred micrograms per litre before reaching chemical saturation. The potential for higher concentrations in the surface waters of industrialized and thickly settled regions does exist, although concentrations in this range have not yet become common enough to be brought to light by the rather thin distribution of sampling and analysis thus far accomplished. The amounts of lead used as gasoline additives each year in the United States are enough to give an average lead concentration near 150 μ g/l for all the runoff leaving the conterminous 48 States in the average year. This figure, of course, indicates only that lead is available in amounts that are of considerable potential hydrochemical significance. Just how much lead might be expected to accumulate in a particular stream at a given time depends on many other factors. The greatest contributions to runoff in most large streams come from areas where population is relatively sparse and lead is less abundant. A considerable fraction of the lead brought down in rain or snow can be expected to be intercepted and retained by soil and vegetation; however, the direct runoff from urbanized areas may contain substantial lead concentrations at times, and further study will probably show that such occurrences are not rare.

It is important that studies of lead in river water be continued, with special efforts to measure solubility parameters (pH and alkalinity) and to determine the particulate fraction of lead in runoff, especially in early stages of runoff events.

LEAD IN GROUND WATERS

The lead concentrations found in ground waters of many States and Puerto Rico are summarized in table 14. Again, spectrographic techniques were used for determining the lead in most of these samples. Atomic-absorption techniques were used for a few samples. Of the 353 samples anlayzed, only two contained lead concentrations exceeding the U.S. Public Health Service drinking water standards. Eighty percent of the samples contained less than 10 μg/l of lead.

The amounts of lead in ground waters used for public supplies in some of the larger cities of the United States were reported by Durfor and Becker (1964). Most of the samples represented treated water, and treatment may have influenced some of the concentrations. Results of 57 analyses, many representing mixed water from several wells, were given. Detectable concentrations of lead were present in 30 of these; the remainder had concentrations below detection. The lower limit of detection in these solutions was variable and rather high, generally above 2

TABLE 14.—*Maximum and minimum concentrations of lead found in ground waters of some States and Puerto Rico 1960 to 1971.*

[ND, sought but not found]

	Number of samples	Number of samples equaling or exceeding mandatory maximum for drinking water[1]	Percent of samples containing less than 10 µg/l	Lead concentration (µg/l)	
				Maximum	Minimum
Alabama	2	0	100	ND	ND
Arizona	9	0	56	40	ND
California	7	0	14	46	5.7
Colorado	103	0	96	30	< .5
Connecticut	1	0	100	< 8	<8
Florida	14	0	78	40	ND
Georgia	1	0	100	< 2.6	<2.6
Hawaii	3	0	100	5.8	.6
Illinois	2	0	100	7.5	ND
Indiana	3	0	67	21	ND
Kansas	3	0	[2]67	4	ND
Kentucky	5	0	100	4	< 2
Louisiana	4	0	100	4.5	ND
Missouri	43	0	95	10	< 2
Montana	8	0	50	<35	< 4
Nebraska	1	0	100	ND	ND
New Jersey	8	0	75	<22	1
New Mexico	13	0	31	30	ND
New York	19	0	89	10	ND
North Carolina	1	0	100	< 3	< 3
Ohio	26	0	54	30	< 3
Pennsylvania	27	0	74	29	< 2
Tennessee	5	0	100	3.2	< 1.7
Texas	14	0	86	38	ND
Utah	1	1	0	62	.....
Virginia	1	0	100	< 9	< 9
Washington	2	0	50	11	< 2.6
Wisconsin	1	0	100	7.4	.....
Wyoming	20	1	90	240	< 1
Puerto Rico	6	0	33	([3])	([3])
Total	353	2	....	......	.....
Percent of total samples	....	...	80	......	.....

[1] 50 µg/l, as determined by U.S. Public Health Service (1963).
[2] Includes one value above 10 µg/l.
[3] All values are reported as "less than," because of high dissolved solids.

µg/l. The highest value observed was 62 µg/l, but this was a definite anomaly; most concentrations observed were between 2 and 10 µg/l. Lead has a very low solubility in water that contains moderate concentrations of bicarbonate ions and has a pH near 8. Many ground waters display these properties, and thus are expected to be low in dissolved lead concentration.

Silvey (1967) found detectable amounts of lead in 17 percent of the samples from springs and in 15 percent of the samples from wells and oil-field brines collected at various sites in California. The average concentration of lead for the water in these samples was 17 µg/l for the springs and 2.8 µg/l for the wells and oil-field brines. However, one of the spring samples contained 143 µg/l, which strongly influenced the reported average.

The compilation of analyses of ground waters by White, Hem, and Waring (1963) contains a few values for lead concentrations, although the element was not generally determined. The highest reported concentration was about 1,400 µg/l in water from Wilbur Spring, Colusa County, Calif. Several other saline or thermal waters contained a few tens or hundreds of micrograms per litre, but most analyses for lead indicated concentrations below detection limits. In general, the ground waters that contained significant concentrations of lead were either high in chloride or low in pH, and had relatively high temperatures.

More than 100 spring-water samples were collected east of the Continental Divide in Colorado (E. C. Mallory, Jr., written commun., 1971). The dissolved-solids content of these samples ranged from less than 50 mg/l to more than 28,000 mg/l. Lead concentrations were generally low; 68 percent of the samples contained 1 µg/l or less. Only four samples contained more than 10 µg/l, and the maximum concentration was 30 µg/l. Lead concentrations in Missouri ground waters were also found to be generally low (E. C. Mallory, Jr., written commun., 1971). Of the 43 samples analyzed, 42 contained less than 10 µg/l of lead; the remaining sample contained 10 µg/l. Kosolapova (1963) reported that the lead content of subsurface waters in the Olenek River basin of Russia ranged from 5 to 90 µg/l.

Goleva, Polyakov, and Nechayeva (1970) reported 15 analyses of ground waters associated with ore deposits and 21 analyses of mineral and saline ground waters from various localities in the USSR. In the waters from ore deposits, the highest lead concentration found was 1,680 µg/l, but all the rest were below 100 µg/l; the water containing the highest concentration was strongly acid, with a pH below 1.0. The mineral and saline waters generally contained from 1.9 to 11.4 µg/l of lead.

Acid mine drainage samples in some areas contribute large quantities of iron, manganese, aluminum, and other elements to surface waters. A number of acid mine waters from Pennsylvania and Maryland and one from West Virginia have been analyzed by a U.S. Geological Survey laboratory in Denver, Colo. The concentrations of iron, aluminum, and manganese in these samples are high, showing maximum values of 190,000, 130,000, and 13,000 µg/l, respectively. On the other hand, the lead concentrations were low; 86 percent of the samples contained less than 10 µg/l lead, and 80 percent contained less than 5 µg/l.

LEAD IN THERMAL WATERS

Several investigators have made chemical studies of the lead content of hot-springs waters. The lead content of the waters at Stubic, Yugoslavia, was reported by Miholić (1945) to be 0.003 mg/kg (approximately 3 µg/l). In seven hot springs of Shikabe, Hokkaido, Japan, Uzumasa and Akaiwa (1960) determined lead concentrations ranging from 0.09 to 0.36 mg/l. Noguchi and Nishiido (1969) determined lead in Tateyama-jigokudani hot springs in Toyama Prefecture, Japan. Eighteen samples were analyzed colorimetrically with dithizone, and the concentrations of lead found ranged from 0.00 to 1.25 mg/l. Minami, Sato, and Watanuki (1957, 1958) analyzed hot-spring waters of Tamagawa, Akita Prefecture, Japan. In 10 springs along the main Tamagawa stream, the lead concentrations ranged from 0.98 to 1.8 mg/l. In 10 springs in the Yukawa River, the average lead content was 1.29 mg/l.

Goleva, Polyakov, and Nechayeva (1970) gave analyses of four thermal waters from the U.S.S.R. One, from a fumarole at Ebeko volcano, had 34.7 μg/l lead. The other three (carbonate and nitrogen-carbonate brines), obtained from the thermal area of Cheleken, had from 1,210 to 4,000 μg/l. These waters were very saline, containing more than 200 g/l of dissolved solids, and some of the other waters of this area were reported to contain up to 6 mg/l of lead.

LEAD IN SEAWATERS

Tatsumoto and Patterson (1963) determined lead concentrations in seawaters off southern California using isotope dilution techniques. The lead content ranged from 0.08 to 0.4 μg/l and averaged 0.2 μg/l. In deep waters, the concentration did not vary much and averaged 0.03 μg/l. Skurnik-Sarig, Zidon, Zak, and Cohen (1970) were unable to detect lead in Atlantic Ocean waters. However, in the Mediterranean Sea, the lead content at Ashdod and Palmachim, Israel, was 340 and 170 μg/l, respectively. In Black Sea samples, Belyaev (1966) reported that the lead content was 3.6 ppb. This value represents an average of determinations made in the course of 5 years at a number of sites. Loveridge and others (1960) stated that lead in seawater is associated with the suspended solids that are removed by filters that retain particles 1 μm in diameter or larger. The values found for dissolved lead in their study ranged from 0.6 to 1.5 μg/l.

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LEAD IN SOILS

By R. R. TIDBALL

INTRODUCTION

Investigation of the lead content of agricultural soils was first stimulated by the known toxic effects of lead on plants, animals, and man; more recently, the development of geochemical prospecting techniques has resulted in analysis of nonagricultural soils for anomalous lead concentrations related to mineralization. Lead is among the trace elements listed as harmful to various plants and animals (McMurtrey and Robinson, 1938, p. 808; Swaine, 1955, p. vi), and the toxicity of lead is of continuing concern in human health (U.S. Public Health Service, 1966; Kehoe, 1971). Early interest in the concentration of lead in soil came as a result of pollution by effluent from smelters (Holmes and others, 1915) and pesticide sprays in orchards (Jones and Hatch, 1937, 1945). Geochemical prospecting activities, which greatly expanded in the 1930's (Hawkes, 1957, p. 314), stimulated interest in background concentrations of metals in soils as an aid to identifying mineralized zones. More recent interest stems from the contamination of soils along highways by automotive exhaust (Cannon and Bowles, 1962; Singer and Hanson, 1969; Ault and others, 1970; Dedolph and others, 1970; Motto and others, 1970; Schuck and Locke, 1970; Connor and others, 1971).

The natural concentration of any trace element in soil can be viewed in at least two ways. First, the concentrations of such elements may be expressed as *total* amounts, which include all modes of occurrence ranging from water-soluble salts to relatively immobile forms locked within the crystal lattice of primary minerals. Second, the concentrations may be expressed as *extractable* amounts that are soluble in a specified solvent. Such extractable quantities will vary depending on the solvent used and the strength of that solvent. Extractable quantities are of principal interest to the agricultural worker (Brewer, 1966, p. 216) because of efforts to equate extractable with "available" quantities for given plant species.

The objective in this report is to examine the soil as a natural reservoir of lead. Therefore, total concentrations are given here because they indicate the potential ability of the soil to supply lead (Mitchell, 1964, p. 331). In contrast, the actual availability, as estimated by extractable amounts, depends on the interaction of many locally variable factors.

Average values are commonly expressed by either the arithmetic mean or the geometric mean. The familiar arithmetic mean is the sum of the values divided by the number of values. However, frequency distributions of trace-element concentrations in soils tend to be more nearly symmetrical on a logarithmic scale; therefore, a logarithmic transformation is appropriate. The best estimate of the most typical value in a log-normal distribution is given by the geometric mean, which is the antilogarithm of the arithmetic mean of the log values (Miesch, 1967, p. B1-B2). The arithmetic mean will always be greater than the geometric mean. Many authors fail to identify which kind of mean they have used; therefore, the arithmetic mean is assumed to have been used in the literature cited in this report.

CHEMISTRY OF LEAD IN SOILS

The migration and ultimate distribution of lead within the soil result from combinations of factors that include chemical processes such as oxidation and reduction reactions, adsorption of cations on the exchange complex, chelation by organic matter and by other metal oxides, and cycling by vegetation. Most of these processes are in turn influenced by the regional factors involved in soil formation—climate, biota, topography, and, especially, parent material, all operating through time (Jenny, 1941).

Entrapment is one form in which lead occurs in the soil. A study of the soils in Bulgaria, for instance, showed that most of the lead occurred as inclusions in iron and aluminum hydroxides and in calcium carbonate (Iordanov and Pavlova, 1963). A small amount of lead was also present as pyromorphite ($Pb_5Cl(PO_4)_3$).

Lead tends to associate with the soil minerals in other ways as well. Lead is presumed to be adsorbed readily onto the exchange complex of clay minerals and is replaced only with difficulty (Mitchell, 1964, p. 337). Divalent lead should be adsorbed more strongly than monovalent potassium which has a similar ionic size (Goldschmidt, 1954, p. 402). The enrichment of lead in the B horizons of some soils has been attributed in part to the presence of excess clay (Presant, 1971, p. 57). Lead also associates with amorphous iron sesquioxide and to a lesser extent with aluminum sesquioxide (Mitchell, 1964, p. 337). Although he did not specifically study lead, Jenne (1968) found that hydrous manganese and iron oxides play a predominant role in controlling the fixation of several heavy metals in the transition series. The sesquioxides and hydrous oxides may occur as surface coatings on particles of all sizes and, therefore, can exert an influence that is out of proportion to their concentration. Lead was found concentrated in that portion of the soil that was soluble in acidified hydrogen peroxide (Taylor and McKenzie, 1966). The soluble portion includes manganese minerals, organic matter, and other soluble minerals and salts. Presant (1971) found lead associated with free iron oxides in the B horizons of New Brunswick soils, but the correlation coefficient was not significant.

In general, most metals tend to be more available under acid conditions than under alkaline conditions (Hodgson, 1963, p. 141–144). In one study, plants grown in soils to which lead had been added took up more lead from acid soils than alkaline soils, but the effect was confounded somewhat by differing amounts of organic matter (MacLean and others, 1969). A summary of the composition of soils from Wisconsin, shown in table 15, suggests that greater total amounts of lead are found in the more alkaline soils; the pH-dependent stability of metal organic chelates may aid in explaining this distribution. Presant (1971) found negative correlations between total lead and pH in all soil horizons except the A_2 horizon. The effect of pH may be the indirect consequence of microbiological activity which in turn controls the oxidation and reduction of iron and manganese (Hodgson, 1963, p. 146). Studies of the distribution of the heavy metals within the soil profile based on pH alone may fail to give consistent results. Instead, the sorption-desorption exchange process should be viewed in terms of both the Eh and pH of the soil-water system, (Jenne, 1968, p. 342).

The movement of metals during the weathering process by means of organic chelating agents is another important process in the chemistry of lead in soil. The following discussion is based on a review of these processes by Pauli (1966). The creation of organic chelating agents by biologic activity serves as one of the most effective processes of metal mobilization. These agents are either plant products, microbial metabolites, or humic compounds. The humic compounds, also known as humic acids (Drozdova, 1968), are three-dimensional, interlinked, aromatic polymers that result from the reaction of heteropolycondensation. This reaction splits simpler compounds and reconstitutes them into a more complex heteropolycondensate (polymer), some units of which are possibly linked together (chelated) by heavy metal cations. As the molecular weight of the polymer is build up through additional polycondensation, a complex lattice structure with diverse interconnections is developed. Thus cations, molecules, and even mineral particles may be enmeshed within a protective "cage." Clay minerals, especially those encrusted with iron oxides and hydroxides, adsorb the polymers, and even accommodate the smaller molecules in interlayer positions.

TABLE 15.—*Lead concentrations in residual soils from Wisconsin, grouped according to pH*

[Data from computer storage of the U.S. Geological Survey; samples collected by H. T. Shacklette; spectrographic analysis by J. C. Hamilton; lower limit of detection 10 ppm. Means and deviations calculated according to methods of Miesch (1967). Detection ratio, the number of samples containing detectable concentrations versus the number of samples examined]

Soil pH	Detection ratio	Lead concentration	
		Geometric mean (ppm)	Geometric deviation
Less than 6.5	105:133	17	1.84
6.5–7.5	155:168	21	2.21
Greater than 7.5	52:57	31	2.73

Metals initially become chelated according to their susceptibility, competition from other metals present, and the nature of the complexing agent. The continued fixation of the metal ion depends on the stability of the polymer and its ability to resist the forces of degradation. The metal binding force generally diminishes with increasing acidity, as we have seen. Experiments with calcium-humate and kaolin showed that lead was held by both substances at pH 5 but was released completely at pH 1.5 (Iordanov and Pavlova, 1963). Further, the complex polymers are more resistant to microbial attack than the simpler organic compounds. Cate (1959) suggests that the metal ions might be released from the polymer by an autocatalytic decomposition process. He speculates that in the podzolization process, lead is cycled to the ground surface by vegetation, is complexed by the humic polymers, is translocated down in the profile, and finally, is released for subsequent precipitation at the lower depth. Cate's model may approximate reality but it apparently fails to account for the lack of abundant movement of lead in weathering profiles.

Finally, the amounts and types of organic matter present appear to provide an important control on the movement of heavy-metal ions in soil systems. Evidence that suggests the importance of organic matter is summarized (Jenne, 1968, p. 340) into four categories: (1) known chelating ability of both synthetic and natural organics, (2) ability of plant material extracts to leach metals from soil material, (3) positive correlation found between concentrations of metal and organic matter of the soil, and (4) release of metals during oxidation treatment of organic matter by hydrogen peroxide. The association of lead and organic matter is not always empirically consistent however. For example, the results in table 20 for tropical soils show no apparent lead-organic matter relationship.

INFLUENCE OF PARENT MATERIAL

Parent material has been recognized in some cases as a fundamental control on the concentration of lead in the soil (Swaine and Mitchell, 1960; Hodgson, 1963; Mitchell, 1964, p. 321; Fleming and others, 1968) and, among the various regional factors in soil formation, it thus deserves special attention. The lead concentration of immature soils tends to be correlated directly with its concentration in the parent material. Thus most of the averages reported for lead in soils are similar to the average concentration of 16 ppm (Goldschmidt, 1954, p. 398) of lead in the Earth's upper lithosphere. As weathering progresses to a more advanced stage, other pedogenic factors may modify the distribution of lead within the soil profile (Wells, 1960; Tiller, 1963).

DISTRIBUTION OF LEAD IN SOILS

An extensive review of the literature on the lead concentration in soils was given by Swaine (1955, p. 83–87). In most soils from nonmineralized areas, concentrations range from 2 to 200 ppm. Average concentrations in these soils are generally between 5 and 25 ppm. Vinogradov (1959, p. 155–157) reported an average of 10 ppm lead in Russian zonal soils (see table 16); these results compared well with data from the literature, which were generally in the range of 10–50 ppm. Other selected summary statistics from the literature and unpublished data of the U.S. Geological Survey are shown in table 16. Typical concentrations of lead in topsoils range from 10 to 30 ppm.

The concentration of lead in selected Scottish soils developed in a cool humid climate is shown in table 17 (Swaine and Mitchell, 1960). The higher concentrations of lead appear to be associated with granitic parent material.

Unpublished data from files of the U.S. Geological Survey, which are summarized in table 18, indicate no important differences between the concentration of lead in the parent material and that in the soil. Other data given in tables 19, 20, and 21 illustrate a range of lead concentrations in soils developed from different parent materials. The majority of values are less than 50 ppm and often less than 30 ppm. In general, the results are inconclusive in establishing soil/parent material relationships, because the natural variations in parent-material composition probably include the range of lead values observed among the soils. Further investigation in particular localities of interest to determine the magnitude of variation in both the soils and the parent material is necessary before meaningful relationships can be recognized.

The trace-element relationship between soil and parent material, if it exists, should permit prediction of the composition of the one from knowledge of the other. Oertel (1961) concluded on the basis of soils from Australia and Tasmania that such a prediction could not be satisfactorily reached; that is, a linear equation failed to describe the relationships accurately. However, a similar study of selected Belgian soils by Prabhakaran Nair and

TABLE 16.—*Lead concentrations in selected soils developed under a variety of soil-forming factors*

[Leaders (...) indicate no data]

Same description	Number of samples	Range (ppm)		Mean (ppm)[1]	Deviation	Source of data
		Minimum	Maximum			
Finland, soils from moraine, sand, silt, clay, and peat	....	....	....	16	......	Vuorinen (1958).
Tarta and Mariisk regions, U.S.S.R., soils	....	4	30	....	....	Borisova (1959).
Eastern European plain, soils, A horizon	13	<10	43	[2]10	[2]±18	Vinogradov (1959).
Kazakhstan region, U.S.S.R., desert soils, humus horizon	20	....	....	11	......	Dobrovol'skiy (1960).
Kazakhstan region, U.S.S.R., salinized soils, humus horizon	6	....	....	10	....	Do.
Westfalen-Lippe, Federal Republic of Germany, agricultural soils	....	15	68	30	....	Balks (1961).
Westfalen-Lippe, Federal Republic of Germany, grassland soils	....	12	79	34	....	Do.
Dahomey, (Africa), tropical topsoils	5	3	23	....	....	Pinta and Ollat (1961).
People's Republic of China, soils	111	....	....	26	....	Fang, Sung, and Bing (1963).
Novosibirsk region, U.S.S.R., soils	43	10	30	....	....	Viller and Khrapov (1963).
U.S.S.R., gray forest soils	25	10	45	....	....	Akhtyrtsev (1965).
New Brunswick, Canada, podzol soils, A horizon	53	....	....	13	....	Presant and Tupper (1965).
Kox'vinskii (Kamen region, U.S.S.R., alpine soils, humus horizons	....	....	....	100	....	Mikhailova and Mikhailov (1967).
Silesia, Poland, topsoils	94	....	....	[3]28	....	Roszyk (1968).
Missouri, U.S.A., subsoils under cedar trees, off road	16	....	....	[3]15	....	Connor and others (1971).
Wisconsin, U.S.A., soils	422	<10	>1000	[3]24	[3]×÷2.60	H. T. Shacklette (unpub. data, 1972).
Kentucky, U.S.A., red-yellow podzolic soils, A horizons	96	< 7	96	[3]14	[3]×÷1.51	Connor and others (1976).

[1] Arithmetic mean assumed unless otherwise noted.
[2] Arithmetic mean and standard deviation estimated by methods described by Miesch (1967).
[3] Geometric mean and geometric deviation estimated by methods described by Miesch (1967).

Cottenie (1971) reached just the opposite conclusion. The accuracy of prediction improved by grouping the soils within taxonomic classes.

TABLE 17.—*Lead concentrations (in ppm) in selected Scottish soils developed from different parent materials*

[Data from Swaine and Mitchell (1960). Soil profile averages calculated by weighting each horizon according to thickness]

Parent material	Soil Pb
Igneous:	
Serpentine till	12
Olivine gabbro	13
Andesitic moraine	18
Granitic till	25
Metamorphic:	
Granitic gneiss	42
Quartz-mica schist till	54
Slate	18
Sedimentary:	
Sandstone till	12

TABLE 18.—*Mean concentrations of lead in selected parent material types and derivative soils*

[Unpublished data of the U.S. Geological Survey. Statistics calculated according to Miesch (1967). Leaders (...) indicate insufficient data for calculation. Detection ratio, the number of samples containing detectable concentrations versus the number of samples examined]

Sample material	Detection ratio	Range (ppm)		Geometric mean (ppm)	Geometric deviation
		Minimum	Maximum		
Cambrian and Lower Ordovician rock, western craton, western United States[1]					
Sandstone:					
Soil	33:80	< 20	130	16	$\overset{\times}{\div}2.23$
Parent material	3:80	< 20	36	<20	......
Shale:					
Soil	28:72	<20	870	12	$\overset{\times}{\div}3.45$
Parent material	28:72	<20	1,300	12	$\overset{\times}{\div}3.33$
Carbonate:					
Soil	25:76	<20	350	11	$\overset{\times}{\div}4.07$
Parent material	12:76	<20	120	<20	......
Nonmineralized areas of Kentucky, Missouri, and Wisconsin[2]					
Sandstone, siltstone, and quartzite:					
Soil	38:52	<10	30	11	$\overset{\times}{\div}1.62$
Parent material	6:11	<10	50	9	$\overset{\times}{\div}2.45$
Dolomite:					
Soil	37:38	<10	70	15	$\overset{\times}{\div}1.90$
Parent material	11:16	<10	70	13	$\overset{\times}{\div}2.33$
Limestone:					
Soil	27:27	15	50	23	$\overset{\times}{\div}1.43$
Parent material	5:8	<10	20	9	$\overset{\times}{\div}1.56$
Granite, rhyolite:					
Soil	12:12	10	70	18	$\overset{\times}{\div}2.25$
Parent material	6:6	15	50	25	$\overset{\times}{\div}1.75$

[1] Collected by A. T. Miesch and J. J. Connor; analyzed on direct reader spectrograph by R. G. Havens; lower limit of detection, 20 ppm. Soil samples from surface horizon.

[2] Collected by H. T. Shacklette; semiquantitative spectrographic analysis by J. C. Hamilton; lower limit of detection, 10 ppm. Soil values based on averages of samples from all horizons.

TABLE 19 —*Lead concentrations in tropical soils developed on different parent materials*

[Data from Nalovic and Pinta (1969). Leaders (...) indicate no data]

Parent material	Soil type	Pb (ppm)
Igneous:		
Basic rocks	Ferruginous	88.0
Basalt	Ferrallitic	17.5
Granite	do......................	40.0
Acid rocks	do......................	14.0
Volcanic ash	do......................	9.0
Metamorphic:		
Marble	do......................	19.0
Gneiss	do......................	40.0
Schist	Ferruginous	22.0
Sedimentary:		
Limestone	Ferrallitic	41.0
	Ferruginous	21.0
Sandstone	do......................	20.0

TABLE 20.—*Distribution of lead concentration and organic matter in soil profiles from the tropical climatic zone*

Parent material and soil type	Soil depth (cm)	Organic matter (percent)	Soil Pb (ppm)
Dahomey, Africa (Pinta and Ollat, 1961)			
Clay	0–10	3.0	23
(ferrallitic soil)	40–60	.8	20
	180–190	.3	27
Unknown	0–20	1.0	9
(ferruginous soil)	40–60	.6	11
	80–100	.6	14
Tertiary sediments	0–15	2.3	15
(ferrallitic soil)	20–30	.6	20
	80–90	.4	22
	375–385	.2	20
Madagascar (Nalovic and Pinta, 1969)			
Marble (red-brown	0–18	8.2	21
(ferrallitic soil)	18–40	4.3	17
	40–85	.2	23
	85–130	.2	18
	130–280	.1	14
Calcareous material	0–15	1.1	24
(ferruginous soil)	15–200	.3	20
	200–240	.3	24
	>240	.1	18
Alluvium	0–40	1.2	19
	40–110	.2	19
	110–320	.2	22
	320–350	.2	19
	>350	.2	23

GEOGRAPHIC DISTRIBUTION OF LEAD IN SOILS OF THE UNITED STATES

The distribution of lead concentration in soils and other surficial materials at 964 sites throughout the United States is shown in figure 8. The symbols on the map represent concentrations within selected frequency classes as shown in the accompanying histogram. The distribution map is modified from Shaklette, Hamilton,

TABLE 21.—*Distribution of lead concentration in soil profiles from the temperate climatic zone*

Parent material	Soil depth or horizon	Soil Pb (ppm)
Wales (Archer, 1963)		
	Depth (cm)	
Dolerite	0-5	150
	5-18	100
	18-46	100
Pumice tuff	0-5	80
	5-15	20
	15-23	8
	23-30	25
Rhyolite	0-10	180
	10-25	60
Mixed glacial drift	0-5	200
	5-41	100
Ireland (Fleming and others, 1968)		
	Horizon	
Granite (Brown podzolic soil)	Ap	25
	B_1	20
	B_2	20
	C	25
Shale (Brown podzolic soil)	A_1	25
	B_2	10
	C	15
Limestone (Gray-brown podzolic soil)	A_1	45
	A_2	60
	$B_{2}t$	50
	C	50
	Depth (cm)	
Peat over granite	0-8	120
	8-20	30
	20-41	3
	41-46	11
	Bedrock	20
New Brunswick, Canada (Presant and Tupper, 1965)[1]		
	Horizon	
Mixed parent materials (nonmineralized terrain)	L-H	73
	Ae	13
	B_1	36
	B_2	28
	C	65
Wisconsin (unpub. data, U.S. Geological Survey[2]		
	Horizon	
Mixed parent materials (nonmineralized terrain)	A	24
	B	14
	C	22

[1] Average (arithmetic?) lead in each horizon computed from 53 podzol profiles.

[2] Samples collected by H. T. Shacklette; analyses by J. C. Hamilton. Geometric means are estimated from a number of soil samples, as follows: A, 146 samples (no lead detected in 11 samples); B, 70 samples (no lead detected in 17 samples); C, 97 samples (no lead detected in 20 samples).

Boerngen, and Bowles (1971) with 101 additional sample values added. The sampling sites were located at approximately 50-mile intervals, and samples were collected either along highways or within various geologic study areas. There is some risk that the distribution shown has been modified by lead fallout along the highways. However, collectors were asked to select quiet rural roads if possible, to avoid roadcuts or fills, to move away from the roadside, and to sample at a depth of about 8 inches (20 cm). Studies in the vicinity of highways show that the amount of lead decreases very sharply within the first 6 inches (15 cm) depth of soil (Lagerwerff and Specht, 1970; Motto and others, 1970). Thus, the risk of modification by fallout is believed to be minimal. The reader should avoid inferences about any single value, but rather examine only patterns of larger regions.

The largest regional patterns examined by Shacklette and others (1971) were "eastern" soils versus "western" soils. This division between east and west was established along the 97th meridian because that was the approximate boundary between Marbut's (1935) pedocals of the west and pedalfers of the east.[1] It also corresponds approximately to the division between moist soils of the east and dry soils of the west (U.S. Geological Survey, 1970, p. 86). The mean lead concentration in eastern soil samples is 14 ppm as compared with 18 ppm for western soil samples. Although the difference is small, it appears to reflect a real difference in the background lead content of soils of the two regions (statistically significant at the 95 percent confidence level).

The histogram in figure 8 shows that about 94 percent of the samples have lead concentrations that are equal to or less than 30 ppm. About 58 percent of the samples have concentrations equal to or less than the mean of 16 ppm. Thus, most of the sample sites across the country are typified by concentrations of 15–30 ppm, with few distinctive local geographic variations. Regions having many sites with lead concentrations below average include the Atlantic Coastal Plain and Gulf Coastal Plain from North Carolina to Texas, the High Plains of west Texas and southeastern New Mexico, the Lake States of Michigan, Wisconsin, and Minnesota, and parts of the northern Great Plains, particularly the Sand Hills of Nebraska. There were even fewer regional instances of above-average concentrations, although most of the sites in Colorado exhibit above-average lead concentrations: four samples with concentrations of 100 ppm were collected in the western half of Colorado. Otherwise, high concentrations in the range of 100–700 ppm are found only at widely scattered and isolated sites in the United States.

The distribution of lead in soil has been studied in detail in Missouri, which has large lead deposits and a well-established lead mining industry. Samples of agricultural soils were collected extensively throughout the State from the surface horizon (0–6 in. (0–15 cm) depth), through the

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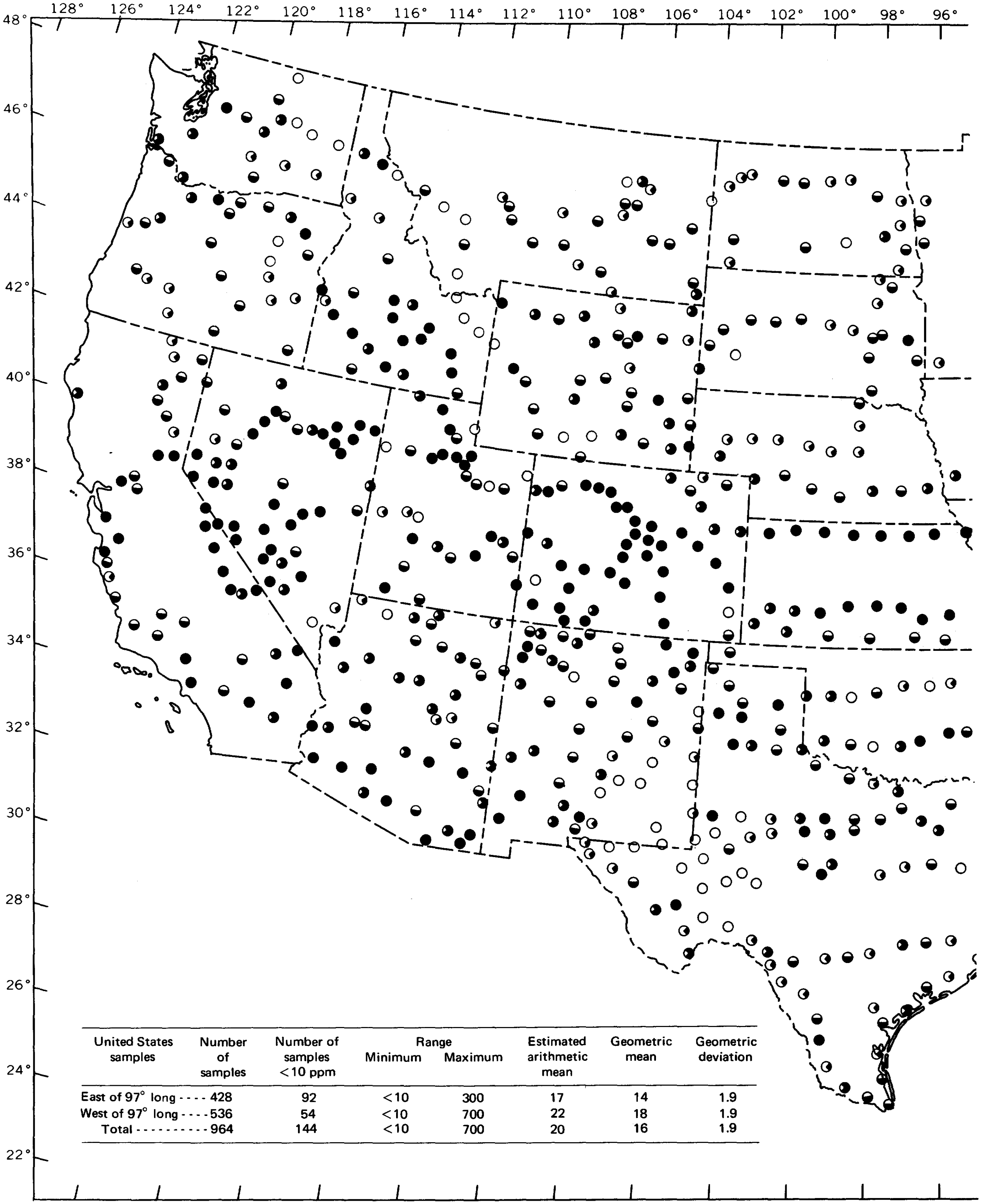
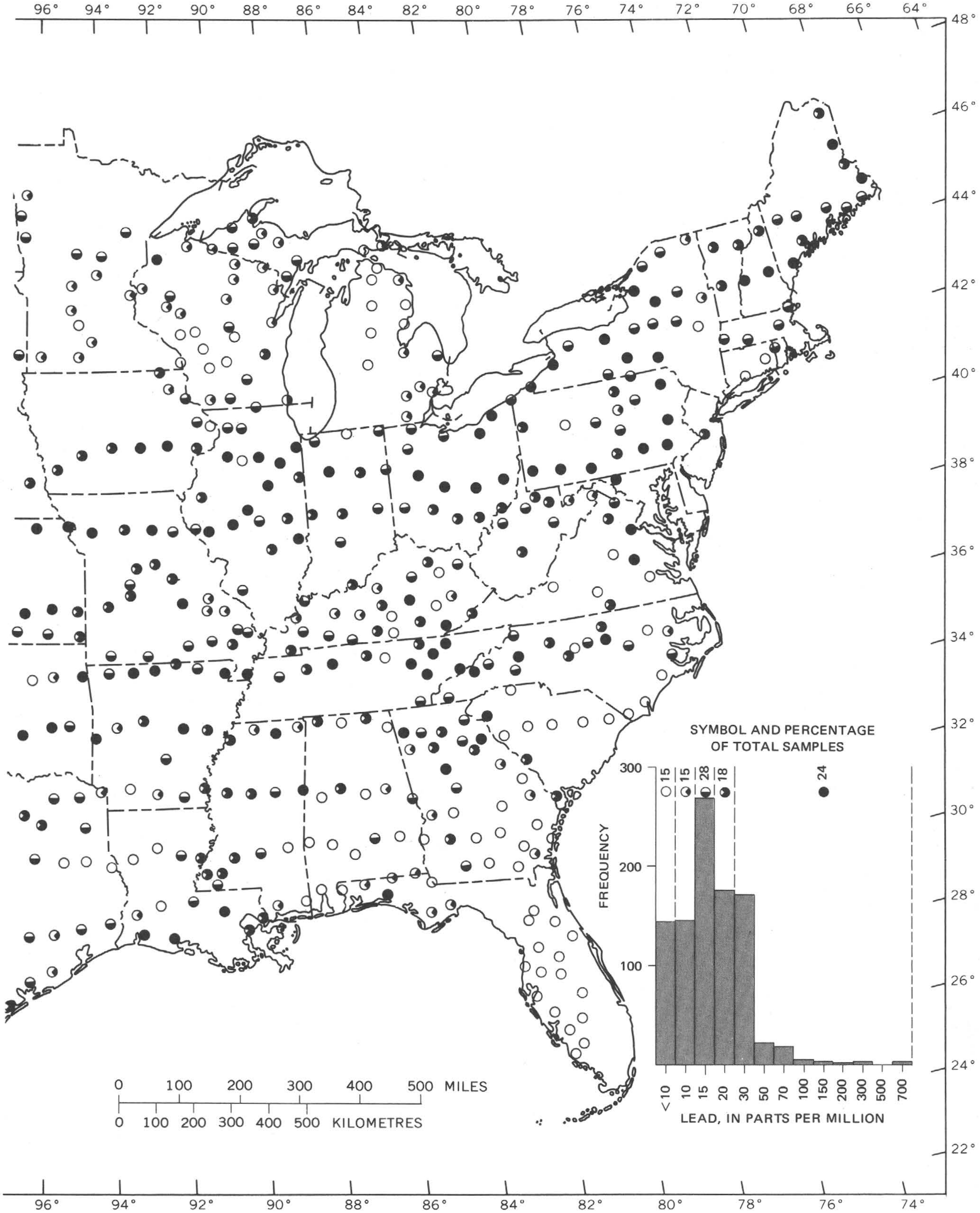
[1] Pedocal and pedalfer are Marbut's terms for mature soils with and without a lime horizon, respectively.



United States samples	Number of samples	Number of samples <10 ppm	Range		Estimated arithmetic mean	Geometric mean	Geometric deviation
			Minimum	Maximum			
East of 97° long - - - - 428		92	<10	300	17	14	1.9
West of 97° long - - - - 536		54	<10	700	22	18	1.9
Total - - - - - - - - - - 964		144	<10	700	20	16	1.9

FIGURE 8.—Distribution of lead in soils and other surficial materials at 964 sites throughout the United States. Symbols correspond Map adapted from Shacklette, Hamilton, Boerngen, and Bowles (1971), supplemented with an additional 101 sites, data courtesy Neiman.



to classes of lead concentration as shown on histogram. Location of the symbol is approximately at the point of sample collection. of H. T. Shacklette. Semiquantitative spectrographic analysis in U.S. Geological Survey laboratories by J. C. Hamilton and H.G.

cooperation of Missouri farmers and the Extension Division of the University of Missouri. Ten samples were collected in each of the 114 counties of the State. The samples were analyzed semiquantitatively for 45 elements by emission spectrograph (Myers and others, 1961). The lower limit of determination for lead by this method is 10 ppm.

The distribution of lead revealed by the analyses is generalized in figure 9, and is adapted from a more detailed distribution map by Tidball (1972, p. 39). The inclusion of a few high lead values from the lead mining districts results in an estimate of the mean of Missouri soils of 20 ppm as compared to the mean for eastern United States soils of 14 ppm (fig. 8).

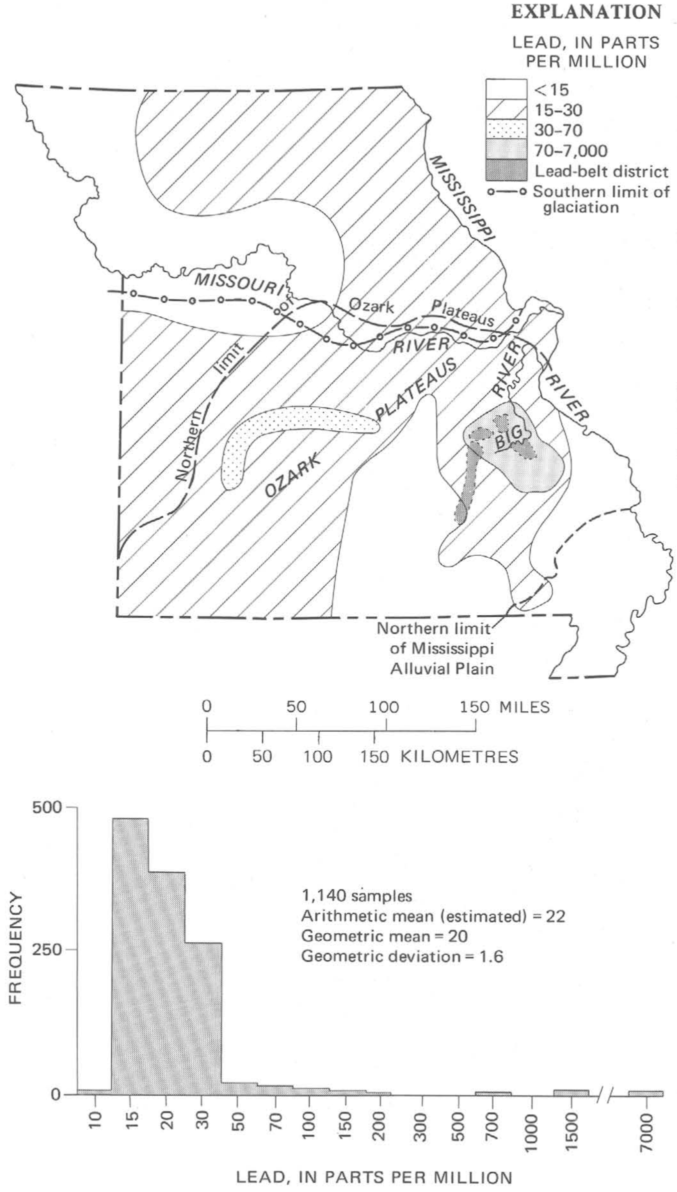


FIGURE 9.—Histogram showing lead concentrations in Missouri soil samples and map showing general distribution throughout the State. Physical divisions from Fenneman (1946); mining district from Kiilsgaard, Hayes, and Heyl (1967); statistics calculated according to Miesch (1967).

The highest lead concentrations were found in soils in the southeast Missouri lead belt. These values may represent either natural occurrences of lead in the soil or aritifical occurrences resulting from mining activity. Some highly anomalous samples, ranging in concentration from 700 to 7,000 ppm and collected from agricultural fields on the flood plain of Big River, are believed to reflect the mineralized zone. Upstream from the sample sites Big River flows through the center of the mining district that has produced more than 90 percent of the lead ores mined in southeast Missouri since the deposits were discovered in the area in 1701 (Kiilsgaard and others, 1967, p. 50). Other samples with lead concentrations ranging from 50 to 150 ppm were obtained from uplands within the lead-belt areas and may reflect conditions less influenced by mining activity.

The Big River flood-plain samples also contain anomalous concentrations of barium which are believed to originate from important near-surface barite deposits that are located just northwest of the lead belt. Numerous small barite deposits also occur along the northern flank of the Ozark Plateaus. These deposits have accessory galena (lead sulfide) which may explain the band of above-average lead values occurring in the soils of this area. Other mining districts in southwest Missouri have not been clearly delineated by the soil samples.

Below-average concentrations of lead were found in two large areas of the State, as shown in figure 9. One of the areas in northwest Missouri is associated with prominent surfical deposits of glacial material that at one time probably covered the entire landscape, but subsequent erosion has exposed the underlying rock in many places. From 67 to 100 percent of the land is covered with loess in deposits ranging in depth from 4 feet (1 m) to more than 32 feet (10 m) (National Research Council, 1952). The average (geometric mean) concentration of lead in loess in the bluffs along the Missouri River in this area in northwest Missouri was estimated to be 15 ppm (Connor and Ebens, 1972, p. 12; R. J. Ebens, oral commun., 1971).

The second area of low-lead soils is in southeast Missouri and comprises the Mississippi Alluvial Plain and the central part of the Ozark Plateaus. Soils on the alluvial plain area are developed on alluvial materials of both Tertiary and Quaternary ages. Soils of the Ozark Plateaus area are on a very old landscape being developed from highly weathered residuum of carbonate rocks of Cambrian and Ordovician ages. These soils tend to have below-average concentrations of numerous trace elements in additon to lead.

The remainder of the soils sampled throughout a wide part of the State are characterized by near-average concentrations of lead that range from about 15 to 30 ppm. Most of this area exhibits considerable local variation within this midrange of lead concentration.

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LEAD IN VEGETATION

By H. L. Cannon

Lead occurs naturally in small amounts in all plants, but the average concentration of lead in vegetation in highly populated countries has risen in the last several decades owing to man's activities. Because of this contamination from artificial lead, it is important that information on lead concentrations in plants be documented as to both date of collection and location with respect to sources of manmade lead. Information from primitive areas on lead in vegetation is therefore of prime value and should be collated and preserved. Only by comparison with such information can the effects of present-day contamination be properly assessed. Finally, averages for lead contents in vegetation are affected by natural variation in and among plants owing to differences in seasonal uptake, species, parts of the plant, and lead concentrations in the substrate.

THE BIOGEOCHEMICAL CYCLING OF LEAD

Bormann and Likens (1967) have pointed out that in the biological community the vertical extensions of the terrestrial ecosystem will be delimited by the top of the vegetation and by the depth to which roots penetrate into the regolith, and that the terrestrial ecosystem participates in the various larger biogeochemical cycles of the earth through a system of inputs and outputs. Thus, if we consider the geologic input, the weathering of the rocks will provide to the soil both elements incorporated in primary and secondary minerals and soluble ions that may be dissolved in the soil solution or adsorbed on the clay-humus complex. The degree of accumulation or loss in the ecosystem will vary with the response of a particular element to erosion and weathering. MacLean, Halstead, and Finn (1969) studied the uptake of lead by oats and alfalfa in soils with different levels of lead chloride, organic matter, and pH. They found that low humus content and high acidity of the soil increase lead uptake.

Lead, although not readily soluble, is absorbed by plants and stored in woody tissue to a considerable degree. An unpublished study of the uptake of lead by native plants and vegetables growing on various rock types in Hagerstown valley, Maryland, made by the author in 1958–59, suggests that there is a buildup of lead in the terrestrial ecosystem, inasmuch as median values increase from 11 ppm in rocks to 33 ppm in residual soils to 93 ppm in the ash of native vegetation in this particular area. Unfortunately at that time no consideration was given to the possibility of atmospheric lead, and the higher values in soils and vegetation probably reflect contamination from car exhaust. A similar progressive increase from rocks to vegetation was found by Lounamaa (1956), who studied native vegetation on various rock types in Finland and found lead to be concentrated in twigs and roots. Elsewhere, native vegetation and soils, largely on sandstone from the Navajo Reservation in New Mexico, were collected by the author in 1961 and 1962 using the same collection methods as those used in Maryland, but at sites considerably more remote from roads. Analyses showed a mean concentration of 20 ppm lead and a range of 5–700 ppm in the ash of 101 native plants that were rooted in soils having a mean of 18 ppm lead and a range of only 10–20 ppm. In both Maryland and New Mexico, the leaves of deciduous trees and the two most recent years of twig growth and needles of conifers were collected. The vastly different means of lead in plant ash from New Mexico (20 ppm) and from Maryland (93 ppm) are further interpreted to suggest the possibility of atmospheric contamination in the relatively more populated area of Maryland. A comparison of the cycling of lead from soil to tree leaves to humus for uncontaminated and contaminated areas is given in table 22.

The data suggest that lead is not concentrated in the humus under ordinary conditions, but that in areas of mining and smelting lead contamination of the humus and soil is largely unavailable to the vegetation or is held in the root and is not translocated to the upper portions of the plant to any appreciable degree.

Bolter and others (1972) made a more recent study of the cycling of lead in the so-called Viburnum Trend, or New Lead Belt, in southeastern Missouri. Several hundred soil and vegetation samples were collected and analyzed to delineate areas of anomalous high concentrations caused by the mining and smelting activity. Elevated heavy metal

TABLE 22.—*Cycling of lead in different environments*

[Leaders (...) indicate no data]

Source	Pb (ppm)				
	Leaves (in ash)	Roots (in ash)	Humus	Soil horizons	
				A	B
Uncontaminated ground					
Jefferson County, Colo. (on schist; ½ mi (1 km) from road):					
Populus tremuloides (aspen)	65	35	50	70	20
Acer glabrum (maple)	50	100	30	30	30
Pinus ponderosa (pine)	200	150	50	30	20
Pseudotsuga taxifolia (Douglas-fir)	200	60	50	30	20
Washington County, Md. (on Limestone; 200 ft (60 m) from road):					
Carya cordiformis (hickory)	100	......	20	30	...
Carya ovata (hickory)	200	......	30	20	...
Fraxinus americana (ash)	150	......	15	15	...
Cedar County, Mo. (on limestone):					
Juniperus virginiana (cedar)	140	......	80	30	...
Quercus stellata (oak)	40	......	83	......	...
Contaminated ground					
Joplin, Mo. (contamination by drainage from mines):					
Betula nigra (birch)	340	1,600	1,700	2,000	...
Quercus muhlenbergia (oak)	150	......	3,200	1,290	...
Bartlesville, Okla. (contamination from smelter):					
Populus deltoides (poplar)	120	......	2,500	2,500	...
Allium porrum (onions)	....	200	1,000	125	...
Asparagus officinalis (asparagus)	25	......	1,000	125	...

concentrations in soils were found to be mainly restricted to the humus and to the A horizons. A large part of the lead found in samples of leaves of vegetation was thought to be lead present on the surface of the leaves.

BACKGROUND LEAD CONCENTRATIONS IN VEGETATION

Before manmade contamination can be evaluated or the effect of mineralized ground appraised, the normal concentrations of lead that might be expected in various types of vegetation must be determined in samples from primitive areas with no manmade contamination and from results of sampling many years ago before manmade contamination had occurred. Warren and Delavault (1962) proposed, on the basis of analyses of uncontaminated Canadian plants, that the normal lead content of the twigs of trees be considered as 2.5 ppm in the dry weight and 50 ppm in the ash. They also suggested that the normal lead content of vegetables and cereal grains, which absorb less lead than trees, be taken as ranging from 0.1 to 1.0 ppm in the dry weight and from 2 to 20 ppm in the ash. Mitchell (1963) reported that in spring and summer pasture herbage normally contains less than 1 ppm lead in the dry weight, but that in autumn and winter it may contain several times this level.

However, unless the samples are collected from ground known to be unmineralized and are carefully screened to exclude any possibility of manmade contamination, a few very high values will unduly raise the arithmetic mean. For this reason, a better measure of the expected "normal" value is the median concentration, as has been calculated for various classes of natural vegetation and given in table 23.

The lead medians for 193 deciduous tree tips (all from paloverde trees) and 131 leaves and stems (mostly from creosotebush) are considerably higher than values for other plants and may represent greater absorption of lead by these species. Large concentrations of lead are found in lichens and mosses, which are very slow growing. The normal levels of lead in garden vegetables are more difficult to establish, inasmuch as they are generally grown only in populated areas that are subject to airborne pollution and contamination from sprays. The results of analyses for lead in vegetables have been studied most intensively by H. V. Warren of British Columbia (Warren, 1972; Warren and Delavault, 1971). Median values from his data and those from Kehoe (1961) are given in table 24. A concentrated effort has recently been made by Warren (1972) to determine the "normal" (presumably median) concentrations of lead and other metals in vegetables. He concluded that variations in trace-element content of vegetables of both urban and rural areas are greater than have been generally realized and suggested a normal range for lead of 16–40 ppm in the ash or 1.6–2.0 ppm in the dry weight. These values are twice those he suggested earlier (Warren, 1961).

Median values for lead in vegetables that I collected in 1961–63 in New York, Maryland, and New Mexico are also shown in table 24. In many of the samples the amounts of lead were below the limit of detection by the spectrographic method used. All the samples of beet tops and onions and most of the cabbage samples had 10 ppm or more lead in the ash. The median lead in the dry weight of 111 vegetables was <1.3 ppm and that of 16 fruits about 0.25 ppm. One hundred vegetables collected by H. T. Shacklette in 1961 (written commun., 1961) from driftless and drift-covered areas in Wisconsin, Iowa, and Minnesota were analyzed colorimetrically by a method having a lower limit of detection of 25 ppm for lead in the ash. These vegetables were found to contain about 25 ppm lead in the ash or 1.3 ppm lead in the dry weight (table 24). A few of his samples were undoubtedly collected from mineralized ground. Both sets of values are lower than those reported by Warren (1972), but correspond rather well with those reported by Kehoe (1961) and suggested by Warren and Delavault (1962). The possibility must be kept in mind that many of Warren's (1972) samples from Great Britain were collected from Wales, where background lead in the soils and vegetation is considerably higher than normal, because of long-continued lead mining activities that have contaminated the valley alluvium and port-city soils with lead.

TABLE 23.—*Normal lead concentrations in various classes of vegetation*
[Leaders (...) indicate no data]

Locality	Number of samples	Part of plant	Median (ppm) Ash	Median (ppm) Dry weight	Range (ppm) Ash	Range (ppm) Dry weight	References
Conifer trees							
Western United States (wilderness areas).	20	Tips	50	1.8	30- 300	1 -10	H. L. Cannon (this paper).
Canada	17	2d-year twigs	25	....	8- 74	....	Warren and Delavault (1960).
Finland	83	Needles	30	....	<10-1,000	....	Lounamaa (1956).
Deciduous trees							
Western United States (wilderness areas).	193	Tips	36	2.5	5- 150	0.27- 13.0	M. A. Chaffee and H. L. Cannon (this paper).
	168	Stems	12	1.0	2- 50	.16- 4.0	Do.
	178	Leaves	14.4	1.7	5- 70	<.61- 9.1	Do.
British Columbia	15	2d-year twigs	31	....	11- 53	....	Warren and Delavault (1960).
Finland	97	Leaves	30	....	<10-1,000	....	Lounamaa (1956).
Sussex, England	4	....	30	1.0	7- 50	.4- 2.0	Warren (1972).
Shrubs							
Western United States (wilderness areas).	131	Leaves	60	4.9	7- 100	0.57- 8.2	M. A. Chaffee and H. L. Cannon (this paper).
	56	Tips	21	1.8	7- 70	.57- 4.3	Do.
	110	Stems	41	2.1	7- 100	.57- 8.2	Do.
Canada	29	2d-year twigs	17	....	7- 46	....	Warren and Delavault (1960).
Finland	48	Tips	30	....	<10- 300	....	Lounamaa (1956).
Herbs							
Finland	50	....	......	1.8	....	<1.2- 3.0	Fletcher and Brink (1969).
	205	Leaves	10	......	<10- 100	....	Lounamaa (1956).
Grasses							
British Columbia	20	....	......	1.8	....	<1.2- 3.6	Fletcher and Brink (1969).
Western United States	226	Above ground.	27	....	<20- 480	....	A. T. Miesch (written commun., 1970).
Western United States (wilderness areas).	15	do	20	1.6	<10- 70	< .8- 5.6	H. L. Cannon (this paper).
Finland	26	do	30	....	<10- 300	....	Lounamaa (1956).
Lichens							
Finland	59	Entire	1,000	....	30-6,000	....	Lounamaa (1956).
Colorado	10	do	1,000	81	300-1,500	12.3-150.0	LeRoy and Koksoy (1962).
Mosses							
Finland	16	Entire	100	....	<10-6,000	....	Lounamaa (1956).
Ferns							
Finland	93	Fronds	30	....	<10- 600	....	Lounamaa (1956).

SEASONAL VARIATIONS IN LEAD CONCENTRATIONS

The seasonal variation in the chemical composition of plants has been reported by many workers, but few studies have included the element lead. Guha and Mitchell (1966), however, studied seasonal variations of lead in three deciduous trees. They reported that concentrations in the dry weight of leaves decreased from May to June, owing to dilution from rapid growth, reached a maximum in mid-September, then decreased slightly in October, a pattern which suggests a back translocation of lead into the twig. Concentrations in the petiole, blade, and inflorescence of sycamore are shown in table 25. Current studies in greater detail (R. L. Mitchell, oral commun., 1972) show a sharp peak in metal content in the early spring before the dilution drop.

The differences in concentrations of elements resulting from variation in uptake by species, parts of the plants, and season of collection were determined using four trees growing on unmineralized schist in a remote area of

Colorado more than half a mile (0.8 km) from the nearest road. The leaves, twigs, wood, roots, and, in some cases, fruit of two coniferous trees, ***Pinus ponderosa*** (Ponderosa pine) and ***Pseudotsuga taxifolia*** (Douglas-fir), and two deciduous trees, ***Populus tremuloides*** (aspen) and ***Acer glabrum*** (mountain maple), were sampled in spring, summer, and fall and analyzed for lead (table 25). Each value represents an average of several analyses. A drop in lead occurs as expected in the summer collections of pine, Douglas-fir, and aspen leaves, but not in maple. A drop is apparent in young twigs—again as expected—but also occurs in either the older twigs or older needles. As might be expected, the seasonal differences in older twigs are not so great nor so consistent as in young twigs in any species. However, the fact that seasonal differences of as much as four to nine times can occur in the young twigs and leaves of trees argues in favor of making all the collections for any project during the same month.

For prospecting purposes, Warren (1966) advised collecting older growth, preferably second year, which varies less seasonally in lead content and more consistently reflects anomalous lead contents in the soil than do other accessible parts of the tree.

TABLE 24.—*Lead in garden produce*

[Leaders (...) indicate no data]

Type of produce	Number of samples	Lead in ash (ppm) Median	Lead in ash (ppm) Range	Lead in dry weight (ppm) Median	Lead in dry weight (ppm) Range
Great Britain and British Columbia					
Leafy vegetables[1]	30	14	2–260	2.3	0.2 -56
Do[2]	8	....	......	.17	.03- .94
Other vegetables[1]	20	25	4–160	1	.2–11
Do[3]	415	31	4–620	2.1	.19–29
Fruit[2]	5	....	......	.08	.04- .18
New York, Maryland, and New Mexico					
Fruits:					
Apples	8	10	<10- 20	0.2	<0.2 - 0.59
Peaches	2	10	<10- 10	.3	< .4 - .53
Pears	2	20	......	.5	....
Total fruit	12	10	<10- 20	0.25	<0.2 - .59
Nonleafy vegetables:					
Asparagus	3	<10	<10- 50	<1	<0.9 - 3.75
Beans (green)	5	10	<10- 70	.63	< .58- 8.4
Beans (shelled)	4	12	<10- 20	.93	< .65- 2.2
Beets	7	<10	<10- 50	<1.8	<1 -12.5
Carrots	8	<10	<10- 50	<1.5	< .99- 9
Corn	15	<10	<10- 70	< .25	< .2 - 1.05
Cucumbers	4	<10	......	<2	....
Green peppers	7	<10	<10- 20	<1.3	< .9 - 2.1
Onions	5	20	10- 20	1.3	.7 - 1.84
Potatoes	9	<10	<10- 30	< .48	< .44- 1.65
Rhubarb	4	10	......	1	....
Salsify	2	12	<10- 20	1.4	<1.2 - 1.7
Squash	8	<10	......	<1.4	....
Tomatoes	10	10	<10–100	1	< .96- 6.8
Turnips	2	<20	......	<2.7	....
Leafy vegetables:					
Cabbage	9	10	<10- 30	2.3	<1.8 - 4.2
Beet tops	3	33	20- 50	8	4.2 -12.5
Kale	4	<20	<10- 20	<2.5	<1.9 - 2.4
Lettuce	6	<10	<10- 70	3.3	<2 -14
Total vegetables	116	<10	<10–100	<1.3	<0.2 -14
Wisconsin, Iowa, and Minnesota[4]					
Fruit:					
Apple	3	25	<25- 50	0.5	<0.5 - 1.0
Vegetables:					
Asparagus	5	150	25–300	12.0	2.3 -30
Bean, pinto (seed)	1	<25	......	<1.5	....
Bean, green (pod)	3	<25	......	<1.5	....
Beet (root)	4	25	<25- 25	2.6	<1.4 - 3.6
Cabbage	11	25	<25- 25	2.2	<1.4 - 3.5
Carrot	8	<25	<25- 25	<2.4	<2.2 - 3.8
Cauliflower	2	<25	<25- 25	<2.0	<2.0 - 2.1
Corn (field)	25	25	<25–150	.4	< .3 - 2.2
Corn (sweet)	4	25	<25- 50	.5	< .5 - 1.0
Cucumber	4	25	<25–150	2.9	<2.4 -18.7
Onion	7	<25	<25- 25	<1.2	<1.1 - 1.1
Parsnip	1	<25	......	<1.2	....
Pepper (sweet)	4	<25	......	<1.7	....
Potato (white)	10	25	<25- 50	1.2	< .95- 2.1
Pumpkin	1	<25	......	<3.0	....
Radish (white)	1	<25	......	<4.1	....
Rhubarb	1	<25	......	<4.0	....
Rutabaga	2	<25	......	<2.3	....
Squash, hubbard	1	25	......	1.2	....
Swiss chard	1	25	......	4.8	....
Turnip	1	25	......	5.9	....
Total	100	25	<25–300	1.3	<0.3 -30

[1] Warren and Delavault (1971).
[2] Kehoe (1961).
[3] Warren (1972).
[4] H. T. Shacklette (written commun., 1970).

TABLE 25.—*Seasonal variations of lead in trees and soils*

Material analyzed	Season or date						
Sycamores from Craigiebuckler, Scotland (Guha and Mitchell, 1966) (ppm, dry weight)							
	May 13	June 15	July 3	July 30	Aug. 24	Sept. 23	Oct. 26
Petiole	0.9	0.6	1.1	0.8	1.0	1.3	1.4
Leaf blade	3	.9	1.8	1.8	1.3	3.1	2
Inflorescence	2.3	1.1	.9	.5	.4	1	no data

Colorado trees and soil (H. L. Cannon, this report) (ppm, average of three sample splits; soil collected under respective trees)

	Spring		Summer		Fall		Other[1]	
	Ash	Dry wt	Ash	Dry wt	Ash	Dry wt	Ash	Dry wt
Aspen:								
Young leaves	65	4.6	20	1.1	45	3.9	....	....
First-year twigs	40	2.9	20	1.1	50	3.4	....	....
Older twigs	60	4.1	50	3.4	80	6.3	....	....
Wood							40	1.2
Roots							35	1.4
Soil:								
Humus								50
A zone								70
B zone								20
Maple:								
Young leaves	50	2.9	70	4.8	85	7.0	....	....
First-year twigs	200	8	20	1.1	50	2	....	....
Older twigs	500	15	200	8.8	180	7.5	....	....
Seeds							30	.90
Wood							300	6.9
Roots							100	8.3
Soil:								
Humus								30
A zone								30
B zone								30
Pine:								
Young needles	200	4	30	.96	50	1.25	....	....
Older needles	200	4.89	300	6	300	8.1	....	....
First-year twigs	300	9	100	2.5	370	8.3	....	....
Older twigs	1,000	29	850	19	700	16	....	....
Seeds or cones							400	16
Wood							700	16
Roots							150	3.6
Soil:								
Humus								50
A zone								30
B zone								20
Douglas-fir:								
Young needles	200	5.6	70	2.1	200	6.6	....	....
Older needles	200	8.2	200	8.3	320	9.4	....	....
First-year twigs	600	18	70	2.1	500	14	....	....
Older twigs	1,750	44	1,750	35	1,500	32	....	....
Seeds or cones							1,000	32
Wood							700	14
Roots							60	1.7
							[2]45	1.7
Soil:								
Humus								50
A zone								30
B zone								20

[1] Season not specified.
[2] In root bark.

VARIATION IN LEAD CONTENTS WITH PARTS OF PLANT

Lead contents vary greatly in different parts of the plant. Jones (1959) reported higher concentrations of lead in leaves than in stems of kale and rape. John and Van Laerhoven (1972) found that the leaves of lettuce and spinach and the tuberous portions of radish and carrot plants accumulated markedly higher lead concentrations than did the heads—the edible portions—of cauliflower, broccoli, or oats. Guha and Mitchell (1966) found more lead in leaves than in stems of four deciduous trees. The data for aspen, maple, pine, and fir in Colorado (table 25) indicate considerable variation in different parts of a tree, as well as variation depending on season. Certainly in the conifers (pine and Douglas-fir), large concentrations of lead are stored in older twigs and cones. In the spring collection, Douglas-fir contained 5.6 ppm lead in the dry weight of leaves, 18 ppm in the first-year twigs, 44 ppm in older twigs, 32 ppm in cones, 14 ppm in wood, and only 1–7 ppm in roots. Lounamaa (1956) demonstrated a definite increase in concentration of lead in roots. This increase is not apparent in the data from Colorado, but large concentrations have been observed in roots of plants growing in highly mineralized ground.

Zimdahl and Arvick (1972) have measured lead uptake by sugar beets, corn, beans, and wheat grown in hydroponic solutions and in soil containing various levels of lead nitrate. Lead uptake by and distribution within the plants were directly related to the concentration of lead in the solution. Lead was concentrated in the root with limited translocation to the shoot. Similarly, the primary leaf of pinto beans contained less lead than did the stem but always more than the trifoliate leaf. The following table shows that massive amounts of lead can be absorbed by a plant when the metal is present in an available form. Translocation of lead is increased with increasing concentration from 100 to 1,000 ppm in the $Pb(NO_3)_2$ medium.

In vegetables fed lead in a nutrient solution, Motto, Daines, Chilko, and Motto (1970) reported as much as an eightfold increase in lead content of leaves, with a corresponding increase of as much as fortyfold (to a maximum of 764 μg/g in dry weight) in the roots. Shacklette (1963) found an average of 3.32 ppm lead in leaves and 3.84 ppm in branches of 22 samples of American elm collected in Wisconsin in nonmineralized soil.

Plant and part	100 ppm Pb: Pb absorbed (μg/g dry weight)	100 ppm Pb: Root/shoot ratio	1,000 ppm Pb: Pb absorbed (μg/g dry weight)	1,000 ppm Pb: Root/shoot ratio
Pinto bean:				
Root	32,400	231.4	54,400	4.1
Shoot	140		13,300	
Sugar beet:				
Root[1]	54,300	......	84,800	....
Wheat:				
Root	9,300	35.8	16,000	2.8
Shoot	260		5,800	
Corn:				
Root	10,600	27.2	22,700	2.5
Shoot	390		9,160	

[1] Shoot not analyzed.

Samples of cedar and oak that I collected for background material in Missouri had the following concentrations of lead, in parts per million:

	Cedar	*Oak*
First-year twigs with leaf scales	6	.....
Leaves	......	1.6
First-year twigs	......	3.8
Wood	.54	1.5
Bark	5.5	12.5

The analyses show that, as compared to the bark, wood has a low lead content. Similar data are shown later in the discussion of lead contents in trees on contaminated ground.

Kennedy (1960) sampled needles, twigs, and cones of seven coniferous species in the Coeur d'Alene, Idaho, lead-zinc district and found marked accumulations in the twigs, with a maximum of 130 ppm in the dry weight for Douglas-fir twigs; concentrations in roots and humus were not measured.

The concentrations of lead in peeled and unpeeled vegetables and fruits were compared in a study of produce from Washington County, Md. (table 26).

Although these analyses include the entire vegetable and do not give a separate value for the skins, the difference between peeled and unpeeled produce is striking. Similarly, the contrast between the relatively high concentrations in the root crops and the relatively low ones in fruits reflects a true difference in distribution of lead. However, the values in the leafy vegetables, even though washed, may have been raised by vehicular exhaust lead, as many of the gardens were in contaminated areas.

TABLE 26.—*Concentrations of lead in unpeeled and peeled garden produce from Maryland*

[Analysts: Uteana Oda, E. F. Cooley, D. J. Fennelly, and H. G. Neiman, U.S. Geological Survey. Numbers in parentheses indicate number of samples collected]

	Unpeeled	Peeled
Root vegetables (26):		
Salsify	1.7	<2.2
Onions	1.84	1.3
Beets	16.5	<1.4
Potatoes	2.6	< .62
Carrots	2.1	<1
Fruits (8):		
Peaches	< .6	.53
Apples	.37	< .22
Leafy vegetables (22)	5.24	.....

PHYSIOLOGICAL EFFECTS OF LEAD ON PLANT GROWTH

Lead is not considered to be an element essential to plant growth, although Stoklasa (1913) reported that lead nitrate in small amounts increased the growth of plants; in large amounts, however, it proved toxic. Tsetsura (1948), also using solutions of lead nitrate, reported an increase in the germination of seeds at low lead concentrations and a retardation at high levels. One questions whether the stimulation in both experiments may not have been caused by the nitrate ion. Using lead acetate, Bonnet (1922) found that lead was readily taken into the root but that little was translocated to the leaves. Transpiration was greatly diminished, and the roots were short and thin. Seeds of many plants were found to be sensitive to lead, but corn was very tolerant and germinated after being soaked in lead acetate for 19 days. Hevesy (1923) used a radioisotope of lead to trace the localization of lead in different parts of the plant *Vicia faba* (horsebean). Only 0.3 percent of the lead was taken into the root from a 10^{-1} N solution in 24 hours but 60 percent of the lead from a 10^{-6} N solution was taken up in the same length of time. The percentage of lead that is translocated to the tops is greater in concentrated solutions because the roots are capable of binding nearly all of the lead in dilute solution. When the plants were moved to different solutions, Hevesy found that the tagged lead could be readily interchanged with other lead atoms or with copper atoms but not as readily with cadmium, zinc, chromium, barium, or sodium atoms. He also found that lead uptake by plants is not dependent on the absorption of water.

Hammet (1928) studied the effects of lead at the cellular level and found that lead retarded cell proliferation, while it allowed the cells to increase in size. Lead is most concentrated in areas of greatest mitotic activity (the area of rapid elongation), where a reaction takes place between the lead and an organic sulfhydryl.

Culture experiments by Scharrer and Schropp (1936) showed that corn and rye were particularly resistant to lead toxicity but that barley, oats, and especially wheat were sensitive to lead poisoning. Recent sand culture studies with corn by Miller and Koeppe (1971) have clarified in several respects the effects of lead on plants in relation to other substances, particularly phosphorus. No effects on growth were noted when lead was absorbed under phosphorus-sufficient conditions, but under phsophorus-deficient conditions growth was retarded and corn died at a level of 6,000 μmol lead. The age of the plant at the time of lead treatment was also found to be important, as the effects of lead were much more pronounced on the younger plants. Corn leaves accumulated large amounts of lead depending on the amount of lead applied and the phosphate condition of the plant; phosphate-deficient plants accumulated 5–10 times as much lead as the phosphate-sufficient plants.

Mitochondria studies (Miller and Koeppe, 1971) show that lead affects mitochondrial respiration, which is related to the phosphate status. Diaphorase experiments suggest that the sites of lead action are the specific flavoproteins for the oxidation of NADH and succinate. The lack of a lead effect on the oxidation of malate indicates that not all flavoproteins are sensitive to lead.

Malyuga (1964) reported that an unusual double-petaled form of the large poppy, *Papaver macrostomum,* grows in high-lead soil at Kadzharan. The double-petal form is created by a deeper incision of the petals, often to the base, which gives the impression of eight petals instead of four.

Other effects of lead on plants can be seen in the results of a study carried out by the author and L. W. Reichen in 1947. We grew sweetpeas, tomatoes, bluegrass, and violets in vermiculite at pH values of 7.6 and 5.8 and fed the plants increasing dosages of lead, copper, and zinc, both separately and in combination in Hoagland nutrient solution. The nutrient solution also contained small amounts of minor metals that had proved sufficient to maintain the control plants in healthy condition. The objectives of this experiment were to determine (1) the ultimate toxic limits for these three metals in representatives of several plant families, (2) the amounts of these metals that can be absorbed by these plants before toxic limits are reached, (3) the effects of each metal on uptake of other metals, and (4) the observable physiologic effects of these metals on plants. The experiment was originally conceived in connection with studies of a muck area in New York State that contained large quantities of zinc and lead (Cannon, 1955). That experiment was performed to determine whether the vegetation of the bogs could have extracted the metals from ground waters draining dolomites rich in zinc and whether observable physiological effects could be used as indicators of mineralized substrate.

In the 1947 study, the plants were fed the following solution, which was prepared in the laboratory and had a pH of 7.6:

10 cm^3 $MgSO_4 \cdot 7H_2O$
20 cm^3 $Ca(NO_3)_2 \cdot 4H_2O$
5 cm^3 KH_2PO_4
12 cm^3 minor elements in 0.5 l H_2O:
    0.50 g $MnSO_4$
    .25 g $ZnSO_4$
    .25 g $CuSO_4$
    .75 g boric acid

Iron solution (0.5 percent $FeSO_4$+0.4 percent tartaric acid) was added three times a week as 0.6 cm^3/l of solution. To lower the pH of the nutrient solution from 7.6 to 5.8, 10 cm^3 of $(NH_4)_2SO_4$ was substituted for 10 cm^3 of $Ca(NO_3)_2 \cdot 4H_2O$. After the plants had become well established, increasing amounts of copper sulfate, lead acetate, and zinc acetate were added to the solution in milliequivalents for 1 month until the tolerance limits of the plants were reached. The plants were then harvested and analyzed by dithizone methods for copper, lead, and zinc contents. The results involving lead and its enteractions with zinc and copper are summarized in table 27.

The uptake by plants under acid and alkaline conditions varied greatly among species. Sweetpeas and violets were unable to take up lead from the acid solutions, but at a pH of 7.6 the vines and leaves of sweetpeas contained as

TABLE 27.—*Effects of lead and other metals on growth of plants from four plant families*

[The original vermiculite contained 25 ppm lead. Control plants were germinated and grown in a nutrient solution at pH 7.6; their lead contents in the dry weight at harvest were as follows: sweetpea, 18 ppm; tomato, 18 ppm; bluegrass, 33 ppm; violet, 13 ppm. Leaders (...) indicate no data]

Plant	Solution pH	Metal contents at harvest (ppm, dry weight)			Height at harvest		Effects of metals on growth
					(in.)	(cm)	
Plants grown in lead solution[1]							
		Lead					
Sweetpea	7.6	8,200			60	152	Thin vines; no chlorosis; brittle roots.
	5.8	11			41	104	Healthy; slightly chlorotic.
Tomato	7.6	1,500			31	79	Healthy; buds still developing.
	5.8	130			14	36	Healthy; white tips on leaves.
Bluegrass	7.6	2,400			14–24	36–60	80 percent alive; still growing dark-blue-green smooth leaves.
	5.8	2,400			10–15	25–38	95 percent alive; still growing dark-blue-green rough leaves.
Violet	7.6	430			7.5	19	Dark green, glossy; healthier than control plant; seed pods developed.
	5.8	12			6	15	Dark-green dull leaves.
Plants grown in lead-copper-zinc solution[1]							
		Lead	Copper	Zinc			
Sweetpea	7.6	190	1,700	4,300	60	152	Very thin vines.
	5.8	14	140	450	36	91	Tip dead; leaves crinkled.
Tomato	7.6	260	190	260	27	68	Slight chlorosis; a few buds.
	5.8	850	80	620	16	4	All leaves chlorotic.
Bluegrass	7.6	150	290	880	9–14	23–36	75 percent alive; smooth leaves.
	5.8	430	58	1,100	8–13	20–33	95 percent alive; rough leaves.
Violet	7.6	550	......	5,000	5	13	Advanced chlorosis; brittle roots.
	5.8	......	......	......	3.5	10	Dark glossy curled leaves.

[1] Transpiration of water was much less from plants fed solutions containing lead.

much as 8,200 ppm lead dry weight. Bluegrass contained 2,400 ppm lead at pH's of both 7.6 and 5.8. Tomatoes concentrated more lead in an acid solution in the presence of excess copper and zinc. The symptoms of lead toxicity include thin weak stems, white leaf tips, brittle roots, and, in the more tolerant species, dark-blue-green foliage. Bluegrass and violets were extremely tolerant of lead and were, at the time of harvest, as healthy as the controls. Certainly, plants can extract lead from nutrient solution and do not appear in general to be as affected by lead as by zinc and copper.

ANOMALOUS LEAD CONCENTRATIONS IN PLANTS

Plants absorb lead in anomalous quantities from agricultural activity, from the air, from mineralized ground, and from contaiminated alluvium along streams that drain areas of mining processing activity. Let us consider first the accumulation of lead by plants in mineralized ground and the species of plants that can grow there.

Plants rooted in soils naturally enriched in metals or in soils in which the metal occurs in an unusually available form have been subject to lead accumulation since plants first appeared on the Earth. Although plants growing in mineralized areas may contain lead at levels deleterious to the health of animals, including man, the areas of undisturbed mineralized ground are relatively small and are mostly in forested or uncultivated regions. Therefore, the greatest effect of lead from plants growing in a naturally mineralized substrate may be on animals rather than on man. One exception may be vegetables raised commercially on peats enriched in lead.

The first analyses for lead in plants from a mineralized area were made in Sweden by Hedstrom and Nordstrom (1945), who developed a method of sampling trees along transects in favorable areas as a prospecting tool. At about the same time Hans Lundberg (written commun., 1947), in tracing the source of toxic lead in maple syrup from Pakenham, Ontario, found that the lead had originated in sap of trees growing in an area with a high soil-lead anomaly. Further studies showed high lead in maple at the Frontenac lead mine in Ontario and in ***Ledum palustre*** (crystaltea ledum) and ***Betula*** sp. (birch) at the Buchans mine in Newfoundland. In Missouri, Harbaugh (1950) also found lead levels in plants to be higher in mineralized ground than in barren ground, but not as consistently high as zinc levels were. Webb and Millman (1951) tested plants as a method of prospecting in Nigeria. They found that the concentrations of lead in twigs and leaves of savanna trees in the lead-zinc belt increase near mineralized ground and that the lead values gave pronounced geochemical anomalies many times wider than the lodes. The normal lead content in the ash of twigs of several species of trees averaged 1 ppm in unmineralized areas and ranged from 7 to 270 ppm in mineralized areas. Comparable anomalies were found in the leaves. Hawkes (1954) later compared lead content of soils along the same traverse (fig. 10).

Malyuga (1964) similarly compared lead contents of soil and ash of plant leaves and roots, that of roots being considerably higher than that of soil or leaves.

J. B. Cathrall and G. B. Gott (written commun., 1975) collected twigs and needles from eight species of conifers, from more than 600 trees in the highly mineralized Coeur d'Alene district, Idaho. Mull was collected from the same localities. The concentration of lead in the soils in which the trees grew ranged from 10 ppm to 1,500 ppm, with a median value of 28 ppm.

The plant ash was analyzed by an arc emission spectrographic method that permitted the determination of concentrations of as much as 5,000 ppm lead. The arithmetic means of lead in the ash of these samples was 3,088 ppm for twigs, 1,039 ppm for needles, and 1,611 ppm for mull (see table 28). The lead content of these samples, from all species, was consistently about three times higher in twigs than in needles and about two times higher in twigs than in mull. The mean value of lead in twigs, relative to lead in needles and mull, must be even greater, because 91 twig samples contain more than 5,000 ppm lead.

Worthington (1955) made a biogeochemical survey of the Showangunk lead-zinc-copper mine in New York State using white birch twigs and soil. The lead values and copper-zinc ratio were more useful than the copper or zinc values in outlining the orebody. In Finland, Salmi (1959) became interested in sampling peat as a method of prospecting glaciated country. At the copper-zinc-lead area in Vihanti Parish, he sampled leaves and twigs of ***Ledum palustre*** (crystaltea ledum) and peat at the same traverse stations to test the method in an area where the ore had already been outlined. Anomalous metal in the plants in an area not known to be mineralized was later explained by the discovery of a new ore body. Similar tests were made by Talipov (1964) in Uzbekistan where he reported concentrations of lead in soils to be 10–20 times above average and to accumulate in the humus layer; and Polikarpochkina, Polikarpochkina, and Abramov (1965) showed that dispersion halos of the metals in plants repeat the zonal structure of metal ores in the eastern Transbaikal province.

High lead contents were found by Poskotin, Yushkov, Yurinskii, and Snegirev (1969) in birch, aspen, and pine in areas of mineral deposits. They concluded that the amount of lead depended on the depth to ore, plant species, age,

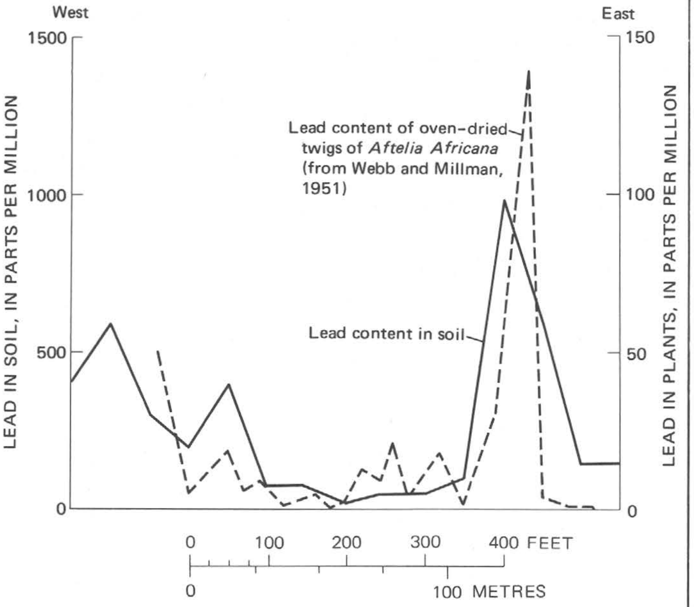

FIGURE 10.—Comparative lead content of soils and plants near Ameka lode, Nigeria (from Hawkes, 1954).

TABLE 28.—*Lead in conifer twigs, needles, and subjacent mull, Coeur d'Alene district, Idaho*

Lead concentrations (ppm in ash)

	Total samples	Minimum	Maximum	Arithmetic mean	Geometric mean
Douglas-fir					
Twigs	396	200	>5,000	3,288	2,775
Needles	425	100	>5,000	927	712
Mull	437	70	>5,000	1,564	1,105
Western white pine					
Twigs	37	200	>5,000	3,354	2,394
Needles	37	100	>5,000	2,777	1,538
Mull	37	100	>5,000	3,030	2,094
Grand fir					
Twigs	42	1,000	>5,000	2,938	2,739
Needles	42	200	>5,000	779	634
Mull	42	300	>5,000	1,940	1,591
Western hemlock					
Twigs	4	2,000	>5,000	4,250	3,942
Needles	4	500	>5,000	925	851
Mull	4	1,000	>5,000	2,250	2,060
Sub alpine fir					
Twigs	40	200	>5,000	2,280	1,710
Needles	52	100	>5,000	734	642
Mull	52	100	>5,000	1,219	953
Lodgepole pine					
Twigs	39	200	>5,000	1,851	1,342
Needles	39	150	>5,000	1,419	876
Mull	37	150	>5,000	1,048	651
Ponderosa pine					
Twigs	5	150	1,500	710	412
Needles	5	150	500	270	246
Mull	5	100	1,000	400	306
All species					
Twigs	549	150	>5,000	3,080	2,478
Needles	605	100	>5,000	1,039	735
Mull	616	70	>5,000	1,611	1,117

Lead frequency (number of occurrences in all species studied)

Lead (ppm)	Twigs	Needles	Mull
0	0	0	0
70	0	0	1
100	0	4	9
150	1	9	1
200	11	41	27
300	9	69	55
500	7	89	83
700	24	151	15
1,000	32	118	120
1,500	46	46	67
2,000	104	36	119
3,000	109	13	68
5,000	115	14	29
>5,000	91	15	22

development of the root system, and mobility of lead in the particular geochemical environment. Brown and Meyer (1956) have also tested plants as a prospecting tool in the Edwards-Balmat district in New York and obtained positive results over known orebodies, although there was a wide variation in absorption by species.

A very thorough pilot study by Hornbrook (1969) of the Silvermine lead deposit, Cape Breton Island, Nova Scotia, indicates the scope and limits of geobotanical and biogeochemical prospecting methods. The data included 4,050 spectrographic determinations for lead in organic soil and plant material. The lead deposits are overlain by till that showed anomalous concentrations of lead, although the extent of the anomaly had been modified by glacial action. The pattern of lead anomalies in plant organs of different ages was compared, and anomalous concentrations in bark and twigs were sufficient to outline the extent of the ore. Although twigs contained more lead than bark, bark provided a more reliable basis for interpretation. The differences in lead concentration for different ages of twigs were not significant for prospecting purposes.

Several studies of lead uptake by plants in mineralized areas have been made by U.S. Geological Survey scientists. Shacklette (1960) made a study of vegetation and soils at the Mahoney Creek lead-zinc deposit in southeastern Alaska. The results given in table 29 show that mean lead concentrations increase from 90 ppm in the ash of plants from unmineralized ground to 160 ppm in the ash of plants rooted in soil over the vein. Shacklette suggested that the significance of differences between background, halo, and vein values of a species may be judged by the standard error. If a difference between two values is as great as or greater than twice the standard error, it can be considered a significant difference, not a sampling error.

Keith (1969) reported on similar studies of three deciduous tree species in the Upper Mississippi Valley lead-zinc district, where he collected 152 soils and 256 plants in mineralized areas and 306 soil and 368 plant samples in nonmineralized areas (table 29). It is apparent that, as expected, stems contain at least twice as much lead as leaves, but, contrary to expectations, lead is not noticeably concentrated in the trees growing on mineralized ground and is actually higher in nonmineralized areas. On the other hand, zinc (not shown here) was significantly concentrated in trees on mineralized ground. Keith believed the anomalously low concentrations of lead to be due to a higher pH in mineralized limestones in contrast to the surrounding areas of sandstone and glacial drift.

A study of lead in vegetation of the Ruby Hill lead-silver mining district in Arizona by Maurice Chaffee (written commun., 1970) shows the increase in lead uptake in an acid sulfide environment (table 29). The data show a remarkable concentration of lead in the older wood of sage and, in other vegetation, about a tenfold increase in lead over the levels in vegetation of the Upper Mississippi Valley limestone district.

Studies by Wallace (1971) show no effect of calcium on lead uptake by bushbeans, but a large increase in root absorption of lead when iron is added and a decrease with increments of $NaHCO_3$.

Lead accompanied by zinc and cadmium may also accumulate in spring-fed peat bogs that drain dolomites of relatively high, but noneconomic, lead concentrations. When these peats are drained for "muck" farming of commercial vegetable crops, the metals become oxidized and are thus available to the vegetation to such an extent that vegetables cannot be grown in certain areas of highly mineralized peat. Such a situation developed on the "Manning muck" in Orleans County, N.Y., in 1938, but, during the last 30 years, the oxidized metals have been leached from the muck by ground and surface waters and neither wild plants nor vegetables now contain anomalous amounts of lead (Cannon, 1955, 1970). Some of the actual lead and zinc contents for the years 1946 and 1967–68 are given in table 30.

It is unfortunate that vegetables grown on the "Manning muck" were not analyzed for lead by Staker (1942) in 1938, as the median zinc content he recorded at that time was 140 ppm, and by 1946 the zinc content of native vegetation had dropped to one-third that level. Presumably, lead levels would have shown the same sharp decrease. In the 1946 collections, native vegetation (37 samples) had a median of 10 ppm and a range of 2–58 ppm lead in the dry weight; in the 1967–68 collections, native vegetation (7 samples) had a median of 4.7 ppm and a range of <0.5–10.2, and the vegetables (15 samples) had a median of <0.5 ppm and a range of <0.5–6.

LEAD INDICATOR AND ACCUMULATOR PLANTS

Certain species of plants that are tolerant of high-lead soils have been used as indicators in prospecting. These species may have adapted to living exclusively on rocks or soils that supply unusual amounts of a particular element, or they may have acquired an immunity to large amounts of an element by being able to reject the metal at the root site. Some indicator plants that have been found universally associated with a particular mineral assemblage absorb and concentrate large amounts of one or more metals in their storage tissues; others that do not concentrate large amounts of the metals in question may be species of wide distribution that favor mineralized ground under certain local conditions, because of a reduction in competition or a change in acidity, water conditions, or availability of major plant nutrients (Cannon, 1971).

Inasmuch as lead and zinc commonly occur together in ore deposits, it is difficult to establish positively that a particular plant is an indicator of lead. Plants that have

TABLE 29.—*Lead content of vegetation and soils from several mining districts*

[Number of samples, where specified, shown in parentheses]

Mahoney Creek Lead-zinc deposit, Alaska[1]

Material analyzed	Plant part	Mean lead contents (ppm) Background (± standard error)	Halo	Vein
Menziesia ferruginosa (rusty menziesia).	8-in. older stems	140±10 (20)	160±20 (10)	350±60 (5)
Do	Leaves and young stems	40±10 (20)	60±20 (10)	110±30 (5)
Vaccinium ovalifolium (whortleberry).	8-in. stems and leaves	40±10 (20)	60±20 (10)	100±30 (5)
Tsuga heterophylla (hemlock).	10-in. stems and needles	160±10 (18)	160±20 (9)	140±40 (5)
Gaultheria shallon (wintergreen).	10-in. stems and leaves	50±10 (15)	170±120 (8)	110±40 (4)
Vaccinium parvifolium (whortleberry).	8-in. stems and leaves	50±10 (4)	40±10 (4)	180±100 (2)
Picea sitchensis (spruce).	8-in. stems and needles	50 (1)	50 (1)	150 (2)
Mean of all plants		90±10	110±20	160±20
Soil samples		20±10	110±40	1,300±690

Upper Mississippi Valley district[2]

Material analyzed	Plant part	Nonmineralized areas In ash of plants	In dry wt of plants	In dry wt of soils	Mineralized areas In ash of plants	In dry wt of plants	In dry wt of soils
		(368)	(368)	(306)	(256)	(256)	(152)
Ulmus sp. (elm)	Stems	102	4.9	....	78	3.7	....
	Leaves	29	3	....	26	2.7	....
Acer sp. (maple)	Stems	119	4.7	....	135	6.5	....
	Leaves	44	4.5	....	62	6.3	....
Quercus sp. (oak)	Stems	150	6.8	....	99	4.5	....
	Leaves	61	2.8	....	57	2.6	....
Soils:							
A Horizon				18			124
B Horizon				13			67
C Horizon				13			117

Ruby Hill mining district, Arizona[3]

Material analyzed	Plant part	In ash	In dry wt
Pinus edulis (pinyon)	Needles	500	12.0
	1- to 2-year twigs	500	13
	Needles	500	11
	1- to 2-year twigs	500	13
	Needles	700	14
	1- to 2-year twigs	700	16.8
Artemisia tridentata (sage)	1-year growth	700	42
	Older wood and leaves	5,000	270
	1-year growth	1,500	90
	Older wood and leaves	>5,000	>220
Juniper sp. (juniper)	1-year growth	200	7.2
	do	100	3.8
	do	200	8.4
Cercocarpos ledifolius (mountain mahagony).	do	700	36
	do	700	36
	do	2,000	88
Median		700	15.4
Range		100->5,000	3.8->220

[1] Collected by H. T. Shacklette; analyzed by D. R. Marx.

[2] Analyzed by Maurice DeValliere and J. C. Hamilton.

[3] Analyzed by E. L. Mosier.

TABLE 30.—*Maximum lead and zinc contents, in parts per million dry weight, of plants and drained peat, Orleans County, N.Y.*

[N, not detected. Analysts: H. W. Lakin, F. N. Ward, Laura Reichen, H. Almond, F. Grimaldi, H. Bloom, T. H. Harms, C. S. E. Papp. From Cannon (1970)]

	Year of collection	Lead		Zinc	
		Plant	Soil	Plant	Soil
Portulaca oleracea (purslane)	1946	42	67	10,000	26,000
Ambrosia elatior (ragweed)	1946	50	250	4,800	88,000
Amaranthus retroflexus (pigweed)	1946	6	250	2,000	88,000
Urtica diocia (nettle)	1946	2	250	1,000	88,000
Sedge	1946	55	250	600	88,000
Arctium minus (burdock)	1946	58	110	390	4,200
Salix sp. (willow)	1946	4	28	860	5,100
Populus tremuloides (aspen)	1946	4	110	860	4,200
Solanum nigrum (nightshade)	1946	10	67	10,000	26,000
Solanum tuberosum (potato)	1967–68	2.4	105	104	9,900
Daucus carrota (carrots)	1967–68	2.0	38	156	5,200
Allium cepa (onions)	1967–68	N	16.5	44	600
Brassica oleracea (cabbage)	1967–68	N	16.5	150	2,800
Cucurbita moschata (squash)	1967–68	N	16.5	225	2,800
Urtica diocia (nettle)	1967–68	4.7	23	487	6,200
Pilea pumila (clearweed)	1967–68	3.0	38	450	31,000
Rubus occidentalis (wild raspberry)	1967–68	7.5	38	487	6,200
Salix sp. (willow)	1967–68	10.2	23	490	1,100

been reported as indicators or accumulators of lead are given in table 31. Plants that have been mentioned in the literature as being indicators of lead deposits in the Mississippi Valley lead-zinc district include white birch, cottonwood, and wild indigo. The association of *Amorpha canescens* (leadplant) with lead that has been mentioned in the early literature has not been verified. In northern Australia, zone of copper-lead-zinc minerals permits a more careful study of the tolerance of the various species that grow there (Cole, Provan, and Tooms, 1968). *Gomphrena canescens* R. B. (globe amaranth) and *Polycarpea synandra* F. Muell. var. *gracilis* (a pink), two of the indicator species, were found to tolerate 50,000 ppm zinc and 5,000 ppm lead in the soil. At another deposit, *Polycarpea glabra* (a pink), *Bulbostylis barbata* (bulletwood), and *Eriachne mucronata* indicated lead-zinc ores, the last concentrating as much as 50 ppm lead in the dry weight.

Although no trees were considered to be indicators of lead ores in studies that have been made by H. V. Warren in Canada and H. T. Shacklette in Alaska, very high contents of lead have been found in Douglas-fir, mountain hemlock, alder, birch, and heather. Shacklette (1965) described the distribution of a liverwort (*Cephalozia bicuspidata)* as entirely covering the surface of the ore, to the exclusion of all other species, at the Mahoney Creek lead-zinc mine in Alaska. The exposed ore contained 12.9 percent lead. The concentrations of lead in Canadian hemlock, arborvitae, and several common adventive weeds from mineralized, drained peat in New York were also high, the lead content in the dry weight of coniferous species exceeding that of the peat. *Ledum palustre* in Finland was found by Salmi (1959) to accumulate high lead contents compared to other species. Thyssen (1942) has reported a grass, *Molina altissima,* growing at Innerstetal, Germany, to contain 35,600 ppm lead in the ash. The grass species, *Agrostis tenuis,* appears to have adapted specifically to high-lead soils, and seed from selected heavy-metal-tolerant races of this species is being used as cover on mine dumps and tailings in Wales (Jowett, 1964; Wild and Wiltshire, 1971).

Some naturally lead poisoned areas have been studied and described in detail by Låg and Bølviken (1974). Occurrences of naturally lead poisoned soil and vegetation have been found in 5 different areas in Norway where deposits of galena occur in the bedrock. In the initial stages of poisoning, the forest trees and *Vaccinium* spp. (blueberry) are replaced by *Deschampsia flexuosa* (hairgrass), which grows profusely but without seed. Where lead poisoning is more advanced, the vegetation is abnormal or dying, and in highly mineralized soils, the ground is barren. *D. flexuosa* responds to increasing contents of lead in the soil with a corresponding decrease in the plant-Pb/soil-Pb ratio. After a low ratio of 0.6 percent is reached, at level of 1 percent lead in the soil, the ratio remains constant with increasing soil lead until the plant is killed. This defense mechanism of *D. flexuosa,* combined with a restricted availability of lead in the soil, effectively counteracts poisoning of the plant. Because plant growth is retarded, podzolization of the soil in these poisoned areas is lacking and erosion of morainic soils is increased, resulting in a stony soil surface. Låg and Bølviken believe the search for areas showing signs of natural heavy-metal poisoning to be a valuable method of geochemical prospecting.

ANOMALOUS LEAD CONCENTRATIONS IN PLANTS RESULTING FROM MAN'S ACTIVITY

LEAD ACCUMULATION RELATED TO MINING AND SMELTING ACTIVITY

The activities of man in the mining, milling, and smelting of ores have released considerable lead into the environment. These accumulations, because they occur as the result of activities in populated areas and because they may be released in a more available form than the original sulfide ores, may have a greater effect on health and disease than the lead in vegetation rooted in mineralized ground. Extensive studies are being conducted in Great Britain and Japan, where health problems have arisen in populations living in contaminated areas.

In Japan, lead analyses have been made of agricultural products grown near a large zinc refinery in Annaka City, where a chronic disease, itai itai, has been shown to be caused by contamination of water and rice crops by cadmium from the refinery (Kobayashi, 1972). Mulberry

TABLE 31.—*Lead indicator and accumulator plants rooted in mineralized ground*

Plant species	Indicator (I) or accumulator (A)	Locality	Maximum lead content (in ppm) reported			Reference
			In plants		In soil	
			(ash)	(dry weight)	(dry weight)	
			Conifers			
Pseudotsuga menziesia (Douglas-fir twigs).	A	British Columbia	2,200	....	....	Warren and Delavault (1960).
Pseudotsuga taxifolia (Douglas-fir tips).	A	Coeur d'Alene, Idaho	....	130	20,000	Kennedy (1960).
Larix occidentalis (larch tips).	A	do	....	100	1,000	Do.
Pinus monticola (white pine tips).	A	do	....	100	20,000	Do.
Tsuga mertensiana (mountain hemlock twigs).	A	Alaska	4,000	....	....	H. T. Shacklette (written commun., 1960).
Tsuga canadensis (Canada hemlock tips).	A	New York (peats)	....	40	10	Cannon (1955).
Tsuga heterophylla (Pacific hemlock stems).	A	British Columbia	1,100	....	....	Warren and Delavault (1960).
Thuja occidentalis (eastern arborvitae tips).	A	do	....	19	13	Do.
Thuja plicata (giant arborvitae stems).	A	British Columbia	3,100	....	....	Do.
Picea sp. (spruce wood).	A	Wisconsin	1,300	....	....	Thyssen (1942).
Equisetum arvense (horsetail stalks).	A	Warren, N.H. (ore)	420	140	....	Cannon, Shacklette, and Bastron (1968).
Do	A	Warren, N.H. (tailings)	344	86	21,000	Do.
			Deciduous trees			
Alnus crispus (American green alder).	A	Alaska	5,000	....	....	H. T. Shacklette (written commun., 1960).
Alnus sinuata (Sitka alder)	A	do	4,000	....	....	Do.
Populus sp. (cottonwood twigs).	I	Wisconsin	....	....	....	A. V. Heyl (oral commun., 1948).
Do	A	Missouri	400	45	5,000	Cannon and Anderson (1971).
Betula populifolia (gray birch).	A	Alaska	5,000	....	....	H. T. Shacklette (written commun., 1960).
Do	I	Wisconsin	....	....	....	A. V. Heyl (oral commun., 1948).
Betula glandulosa (birch stems).	A	British Columbia	25,000	....	....	Warren and Delavault (1960).
Salix sp. (willow root).	A	Harz Mountains, Germany	17,300	....	....	Thyssen (1942).
Betula lutea (yellow birch twigs).	A	Joplin, Mo	4,600	175	2,000	Cannon (1971).
			Shrubs			
Calluna sp. (Alaskan heather).	A	Alaska	3,000	....	....	H. T. Shacklette (written commun., 1960).
Vaccinium canadense (dewberry fruit).	A	Warren, N.H.	238	81	21,000	Cannon, Shacklette, and Bastron (1968).
Holodiscus discolor (rockspirea leaves).	A	Coeur d'Alene, Idaho	....	77	20,000	Kennedy (1960).
Ledum palustre (Labrador tea, twigs).	A	Finland	600	....	[1]600	Salmi (1959).
			Herbs			
Arenaria (Minuartia) verne (leadwort).	A	North Wales	47,000	....	....	H. V. Warren (written commun., 1972).
Portulaca oleracea (common purslane).	A	New York (peat)	....	42	[1]67	Cannon, Shacklette, and Baston (1968).
Ambrosia elatior (common ragweed).	A	do	....	50	[1]250	Do.
Arctium minus (small burdock).	A	do	....	58	[1]110	Do.
Polycarpea glabra (pink).	IA	Australia	....	....	....	Nicolls. Provan, Cole and Tooms (1964–65).
Tusilago farfara (coltsfoot).	I	Siegerland, Germany	....	....	....	Linstow (1929); Dorn (1937).
Baptisia bracteata (wild indigo).	I	Wisconsin	....	....	....	H. L. Cannon (unpub. data, 1948).

TABLE 31.—*Lead indicator and accumulator plants rooted in mineralized ground*—Continued

Plant species	Indicator (I) or accumulator (A)	Locality	Maximum lead content (in ppm) reported			Reference
			In plants (ash)	In plants (dry weight)	In soil (dry weight)	
Herbs—Continued						
Polycarpea synandra v. gracilis (pink).	IA	Australia	....	....	5,000	Cole (1965).
Gomphrena canescens						
(globe amaranth leaves)	IA	do	....	49	5,000	H. E. King (written commun., undated).
(globe amaranth flowers)	IA	do	....	114	5,000	Do.
(globe amaranth stems)	IA	do	....	51	5,000	Do.
Bulbostylis barbata (bulletwood).	IA	do	....	....	....	Nicolls, Provan, Cole, and Tooms (1964–65).
Eriachne mucronata	IA	do	....	50	....	Do.
Campanula alpina (alpine bellflower).	IA	Caucasus	1,000	....	....	Starikov, Konovalov, and Brushtein (1964).
Grasses						
Molinia altissima (Indian grass).	IA	Innerstetal, Germany	35,600	....	....	Thyssen (1942).
Deschampsia flexuosa	I	Norway	2,000	99	17,200	Låg and Bølviken (1974).
Agrostis tenuis (subsp.)	I	North Wales	....	....	....	Jowett (1964).
Calamagrostis epigeios (reed grass).	A	Poland	>100	....	....	Sarosiek (1959).
Ferns						
Dryopteris cristata (woodfern).	A	Wisconsin	....	30	71	Cannon, Shacklette, and Bastron (1968).
Dryopteris spp.	A	Norway	4,100	410	23,300	Låg and Bølviken (1974).
Pryopteris spirulosa	A	New Brunswick	....	....	....	Schmidt (1955).
Liverwort						
Cephalozia bicuspidata	I	Alaska	....	....	129,000	Shacklette (1965).
Algae						
Spirogyra type	A	Warren, N.H.	9,420	6,600	(2)	Cannon, Shacklette, and Bastron (1968).

[1] Peat.

[2] Water in which algae were growing contained 16 ppm total heavy metals.

growing on the hills above the refinery contained 41–160 ppm lead in the dry weight of the leaves, depending on the distance from the refinery. Leafy vegetables contained 4.4–260 ppm lead in the dry weight, root vegetables < 0.02–63 ppm, and fruits of vegetables <0.4–11.0 ppm. A particular moss that covers the garden soils contained 370 ppm lead in the dry weight, 7,010 zinc, and 61 ppm cadmium. The lead uptake thus varies with species and plant part as well as distance. It was observed that the principal source of metals in the vegetation was by absorption through the roots from polluted soil rather than from direct deposition of metals from the air.

A comprehensive study by the U.S. Environmental Protection Agency was conducted in the Helena Valley area of Montana to determine the effects on vegetation of pollutants from the American Smelting and Refining Co. smelter (Hindawi and Neely, 1972). The lead content of vegetation was found to decrease with distance from the stack. Gordon (1972) reported samples from east Helena of plants and the soils in which they were grown to contain lead in the dry weight, in parts per million, as follows:

	Vegetation lead	*Soil lead*
Washed lettuce	<10– 26	49– 550
Unwashed lettuce	26–460	370–1,400
Conifer needles	40–125	370–1,100

Hindawi and Neely (1972) grew alfalfa, pinto beans, carrots, beets, petunias, and tobacco in greenhouses in vermiculite, exposing the growing plants to ambient air, and in garden soils outdoors, at the same distances from the stack, in order to test how much lead might be absorbed from the soil and how much from the air in the vicinity of a smelter. Their results, reported for unwashed produce, in parts per million, are as follows:

Distance from smelter (mi)	Distance from smelter (km)	Vermiculite (A)	Local garden soil (B)	Absorbed from soil (B-A)
0.4	0.6	7.4	48.3	[1]40.9
.8	1.3	3.0	5.4	2.0
2.5	4.0	1.5	3.0	1.5
4.5	7.2	.6	1.0	.4

[1] Believed to reflect contamination by duststorm that arose during sampling.

If one assumes that the plants grown in vermiculite in the greenhouse but receiving ambient air are receiving the same atmospheric lead insult as the outdoor plants, then by subtraction it would appear that about half of the lead measured in unwashed produce may be absorbed from the soil and half from the air.

During the 19th century, several parts of Wales were intensively mined for lead. Fields adjacent to and downstream from the mines became contaminated by airborne and waterborne heavy-metal compounds; these fields still contain high concentrations of these metals. Work by Alloway and Davies (1971) showed that herbage, consisting largely of the grasses *Festuca* and *Lolium,* and soils in this area have the following lead contents in parts per million dry weight:

	Range	Mean	Standard deviation
Herbage	30– 100	63.2	24.5
Soil (total)	90–2,976	1,652.0	878.3
Soil (available[1])	16–1,020	323.8	292.7

[1] Acetic acid extractable.

Radishes were then grown in 15 gardens of north Cardiganshire, some close to and some remote from mines. The radishes had lead contents ranging from 4.6 to 33.1 ppm dry weight, with a mean content of 13.1 ppm and standard deviation of 7.4.

Lagerwerff, Brower, and Biersdorf (1972) collected soil and grass samples along 4 transects extending 6,684 feet (2,400 m) from a smelter in Galena, Kan., near the Missouri border, after the smelter had discontinued operations involving lead production. In the direction of prevailing winds, lead content of the unwashed grass ranged from 98.4 ppm (dry weight) at 1,082 feet (330 m) from the smelter to 16.2 ppm at 6,684 feet (2,400 m). They also observed that the pastures near the smelter had been invaded by switchgrass (*Panicum virgatum*) and broomsedge (*Andropogon virginicus*), which are both tolerant of the combination of low pH and high heavy-metal concentration in the soil.

In 1968 the U.S. Geological Survey sampled birch and oak trees, their humus, and the alluvium in which they were growing, along a stream in a forested mining area near Joplin, Mo.; old mine diggings and pits were visible under the undergrowth. Although this locality had no air contamination from lead at the time of sampling, concentration of lead in the bark was comparable to that in the first-year twigs. The lead content was higher in the birch, which is an accumulator, than in the oak. Results of the study are as follows (number of samples collected are given in parentheses):

	Lead (ppm)	
	In ash	*In dry weight*
Betula lutea (birch) (2):		
Leaves	345	25.0
Twigs (1st-year)	4,600	175.0
Wood	900	14.0
Bark	2,900	73.0
Roots	1.600	50.0
Quercus muhlenbergia (oak) (2):		
Leaves	140	6.4
Twigs (1st-year)	1,200	48.0
Wood	375	9.4
Bark	1,500	178.0
Humus		1,700.0
Alluvium		2,000.0

Smelters and refineries, commonly located in well-populated areas, may contribute considerable amounts of lead to the atmosphere; this airborne lead, in turn, contaminates the soil and vegetation. Warren, Delavault, and Cross (1966) found as much as 1,600 ppm lead in the ash of birch leaves growing 3 miles (5 km) from the Trail smelter in British Columbia.

Studies have been made by the U.S. Geological Survey near several zinc-lead smelters. Analyses of plants and soils collected near the Bartlesville, Okla., and Leadville, Colo., smelters are given in table 32. The tree sampled at Leadville was the nearest pine to the smelter able to grow in the contaminated soil and was considerably dwarfed. The smelter had not been operative for 15 years at the time of sampling.

TABLE 32.—*Lead contents of plants and soils as related to smelter contamination in Colorado and Oklahoma*

[Leaders (...) indicate no data. From Cannon and Anderson (1971); analysts, T. F. Harms and C. S. E. Papp]

Sample No. D413-	Material analyzed	Lead (ppm)	
		In ash	Converted to dry wt
	Bartlesville, Okla. 1,500 ft (460 m) from smelter		
387	*Populus deltoides* (cottonwood), leaves	120	11.2
410	*Populus deltoides* (cottonwood), wood	190	2.5
411	*Populus deltoides* (cottonwood), bark	500	34
406	Top 0.5 in. (1.25 cm) soil	2,500	......
407	1–5 in. (2.5–12.7 cm) soil	2,500	......
	7,000 ft (2,100 m) from smelter		
390	*Ulmus americana* (elm), leaves	120	7.2
388	*Asparagus officinalis* (asparagus), tops	40	2.4
389	*Allium porrum* (onion), bulb	200	11
408	Humus	1,000	......
409	Soil	125	......
	Leadville, Colo.[1] 1,000 ft (300 m) from smelter		
452	*Carix* sp. (sedge), tops	500	49
	3,200 ft (975 m) from smelter		
453	*Pinus edulis* (pine), needles	2,500	40
454	*Pinus edulis* (pine), branch wood (including bark)	18,000	342

[1] Smelter inoperative since 1956.

LEAD ACCUMULATION RELATED TO AGRICULTURAL ACTIVITIES

Contamination of the soil due to agricultural activities stems generally from efforts to reclaim or increase the fertility of the land, or from sprays used on crops to combat insect or fungal infestation. Tailings from lead-zinc mines are occasionally used for fertilizer, but a study by Hawkes and Lakin (1949) in east Tennessee where such practice is common showed that the amounts added were small and did not affect the level of lead in the soil. Residual lead can be detected in soils that have been sprayed in the past and this lead may be translocated to the edible parts of produce. Warren (1961) compared trees in orchards in Okanogan County, Wash., that had been sprayed 10 years earlier with trees that had never been sprayed. The unsprayed trees contained less than 1 ppm lead whereas sprayed trees contained 40, 50, and 100 ppm. A garden in Canadaigua, N.Y., which had been sprayed repeatedly, but which was well protected from street contamination, was sampled by the author and found to contain 300 ppm lead in the soil, 700 ppm in the ash (44 ppm in dry weight) of raspberry canes, and 300 ppm lead in the ash (12 ppm in dry weight) of the berries.

LEAD ACCUMULATION RELATED TO URBAN AIR POLLUTION

The effects of lead in the atmosphere on the lead content of vegetation were pointed out by Warren and Delavault (1960), who found higher values in Canadian plants collected near roadsides than in those remote from roads. Warren and Delavault (1962) further investigated this anomaly by sampling similar vegetation in two localities in England—in an area of Sussex remote from a road and in London. Their results for twigs of the previous year's growth showed these lead contents, in parts per million:

Species	Sussex locality		London locality	
	Dry weight	*Ash*	*Dry weight*	*Ash*
Lime	0.4	8	5	50
Yeco (needles)	.4	7	6	100
Willow	1.0	35	2	30
Birch	1.0	36	8	160
Oak	.8	30	20	280
Ash	2.0	30	14	160
Hazel	2.0	50	52	680

In Maryland the lead content of the ash of vegetables collected near roads was also shown to be higher than that of vegetables farther from roads (Cannon and Bowles, 1962), as shown in the following table (analyst, E. F. Cooley):

Distance from road		Number of samples analyzed	*Lead content (ppm)*	
(ft)	(m)		Mean	Range
1- 25	4-8	29	80	10-500
25- 50	8-16	29	66	10-700
50-500	16-160	45	45	<10-150
>500	>160	28	20	<10-200

To test the significance of these findings, Cannon and Bowles (1962) sampled grass in four directions for 1,000 feet (304 m) from major highways in the Denver area in early June of 1961. The samples were washed in tapwater and analyzed using an emission spectrograph. The lead contents along all four traverses decreased logarithmically with distance from the highway, from 30 ppm to a background of 2 ppm at 900 feet (274 m). In 1969, the samples were re-collected in early June along the only traverse remaining in pasture. The lead content had risen about 1,000 percent and had spread considerably farther from the highway. The highest lead content, 222 ppm dry weight, was found at a distance of 5 feet (1.5 m) from the highway, and grass at 1,000 feet (304 m) contained 28 ppm (fig. 11) (Cannon and Anderson, 1971). Washed grass contained less than unwashed, although the samples were collected during a period of heavy rains.

Salmi (1969) reported a decrease in lead content of *Sphagnum tuscum* (moss) on the surface of a bog at distances of 0–984 feet (0–300 m) from a road in Finland. At about 33 feet (10 m) on one traverse, 27 ppm lead was measured, in contrast to a norm of 2 ppm. Purves and Mackenzie (1969, 1970) reported on significant differences in lead content of herbage in parklands of Scotland. The mean for rural herbage was 30.3±2.3 ppm and that for urban (Edinburgh) herbage was 44.6±4.2 ppm in dry weight. On the other hand, the inner leaves of cabbage collected from rural and urban areas showed significant

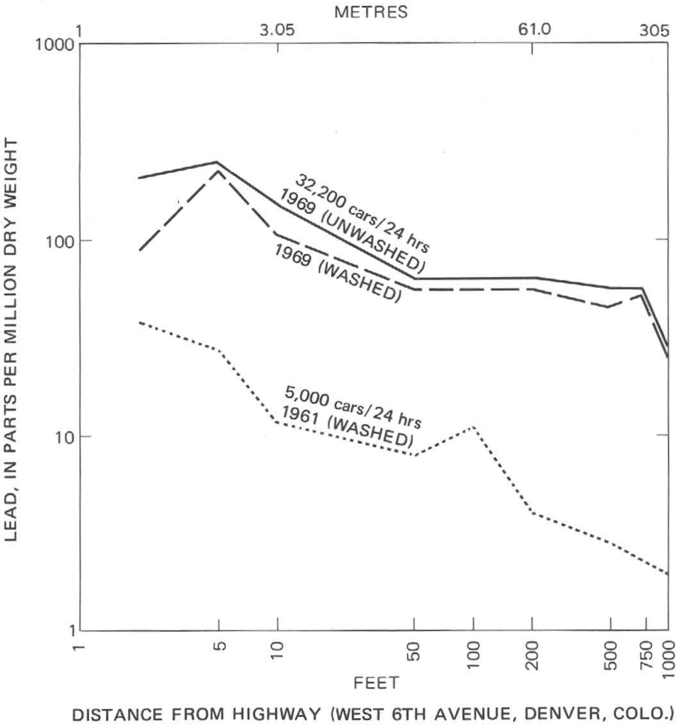

FIGURE 11.—Lead in grass collected for 1,000 feet (304 m) from highway in 1961 and 1969.

differences in boron, molybdenum, and zinc, but none in lead. Unwashed privet leaves were collected by Everett, Day, and Reynolds (1967) in areas close to and remote from highways in England. Leaves near highways had an average of 86 ppm dry weight, and leaves remote from highways had an average of 45 ppm dry weight.

A U.S. Geological Survey study in Missouri (Connor, Erdman, and others, 1971) found that roadside contamination has a much greater effect on the lead content of vegetation than it does on soils or rock outcrops. Thirty-two samples of cedar and 60 samples of grass were collected from locations both on (< 50 ft (15 m) away) and off (> 500 ft (152 m) away) secondary roads. The collections from these locations consisted of the terminal branches of cedar (*Juniperus virginiana*) and above-ground portions of grasses at a specified stage of development. The mixed grasses were mostly *Triodia flavens, Festuca elatior,* and *Setaria viridis.* The samples, which were not washed, were analyzed by emission spectrography. The results are shown in table 33. The differences in both cedar and grass are significant at the 0.05-ppm probability level; those in subsoils and rocks are not. These data show that lead reported in roadside soils is confined to surface soils, and that soils at a depth of several inches are unaffected. Cedar, which is an evergreen and thus exposed to contamiination throughout the year, contained no more lead than did the grass. That cedar is an accumulator of lead was shown by one sample collected near Centerville, which contained 1,200 ppm lead dry weight (Connor, Shacklette, and Erdman, 1971). Further investigation has shown a geometric mean of 348 ppm dry weight in 15 cedar samples from the area. It is believed that the soil here has been contaminated by ore dust from trucks transporting ores from mine to smelter. These data can be compared with those of Lagerwerff and Specht (1970), who sampled grass at 8, 16, and 32 feet (about 2, 4, and 9 m) from major freeways near Washington, D. C., and soil at these sites at depths of 0–5, 5–10, and 10–15 cm. Lead contents in grass and soil decreased with distance; the levels of lead in grass ranged from a maximum of 68.2 ppm dry weight at 8 feet (2 m) to a minimum of 7.5 ppm at 32 feet (9 m) and in surface soil ranged from 540 ppm to 55 ppm. The data also show a reduction in lead content with depth. Dedolph, Ter Haar, Holtzman, and Lucas (1970) were able to correlate the amounts of lead in grass with concentrations in air. At 40 feet (12 m) from the road, the air contained 2.3 $\mu g/m^3$ and the grass averaged 15 ppm dry weight, and at 120 feet (36 m), the air contained 1.7 $\mu g/m^3$ and the grass 8.4 ppm lead.

TABLE 33.—*Comparison of lead content between on-road and off-road samples of some soils and plants in Missouri*

[Data from Connor, Erdman, and others, 1971; analyst, Harriet Nieman]

Locality	Sample type	Number of samples	Lead content (ppm)[1]	
			On-road[2]	Off-road[3]
Various	Cedar branch tips	32	16	7
Do	Soil	32	17	14
Kansas City, Mo	Grass	30	29.0	9.7
Do	Soil	30	10	14
Pacific, Mo	Grass	30	17.0	4.5
Do	Soil	30	10.0	3.5

[1] Dry weight, geometric mean.

[2] Samples taken < 50 ft (15 m) from road.

[3] Samples taken > 500 ft (152 m) from road.

An increase in the lead content of plant foliage in the winter months has been reported by several workers and generally attributed to increased exposure time to air-pollution lead. Mitchell and Reith (1966) found an increase in pasture herbage from 1 ppm lead (dry weight) in early autumn to 30–40 ppm in the winter. However, they attributed the increase to either a translocation of lead from roots to tops during the winter months or a loss of organic matter through respiration rather than to surface contamination from the air.

The effects of washing on the lead values varies with season and rainfall conditions. In the study reported by Cannon and Anderson (1971), on grass collected in the spring shortly after a heavy rain, no great difference in lead content between washed and unwashed samples was noted. Ganje and Page (1972) compared the lead content of washed with unwashed samples of lima-bean leaves and pods, corn leaves, sugar-beet leaves, and tomato fruits collected in California near the Santa Ana and Riverside Freeways; they found a 30–70 percent decrease, depending on such factors as the extent of plant surface exposed, roughness of surface, and duration of exposure. Motto, Daines, Chilko, and Motto (1970) also found a ±40 percent decrease in washed grass collected within 225 feet (68 m) of highways. Rains (1971), on the other hand, could not wash lead from *Avena fatua* (wild oats) that had grown in a lead-fallout region, nor could he extract it with water. He was, however, able to extract 50 percent with 0.01 *M* HCl and 95 percent with 0.01 *M* NH_4 EDTA.

Whether the lead that cannot be washed from roadside plants is absorbed directly from the air through the leaves or is taken up from the contaminated soil has been debated. Certainly there can be no doubt concerning absorption from the air in regard to *Tillandsia usneoides* (Spanish moss), which has no root system and obtains all essential elements from the atmosphere. Analyses of 123 samples of Spanish moss collected by H. T. Shacklette (written commun., 1971) from the Atlantic and Gulf Coastal Plain areas ranged from 3.2 to 230 ppm lead in dry weight and had a geometric mean of 192 ppm; the contrast between samples from urban industrial areas and rural areas indicated the influence of atmospheric pollution in raising lead levels. Wherry and Buchanan (1926), who analyzed Spanish moss for some of the essential plant nutrients, found no difference between washed and unwashed samples. Martinez, Nathany, and Dharmarajan

(1971) in most instances found no significant difference between unwashed samples of Spanish moss and those washed with ammonium acetate, but were able to extract more than one-third of the lead from a sample collected near a four-lane highway. These plants, however, have a highly developed system for extracting nutrients from the air and cannot be considered as representative of the entire plant kingdom.

Rühling and Tyler (1968) grew plants from roadside seed in contaminated soils obtained near highways. The plants contained only 5–10 ppm lead in the dry weight of the plant, whereas the same species of weeds that grew in the same soils along the roadside contained 68–950 ppm lead in the dry weight of washed samples. These data indicate absorption of lead from the atmosphere. Crops were grown by Ter Haar (1970) both in greenhouses supplied with filtered and ambient air and in plots planted in rows perpendicular to a busy highway. Of the 10 crop plants studied, only leaf lettuce, bean leaves, and the husk of sweet corn showed significant increases in lead content in unfiltered air compared to filtered air. In crops grown 30–520 feet (9–158 m) from a highway, soybeans and snap beans also showed higher lead contents nearer the highway. He concluded from these studies that natural lead in the soil is the main source of lead in edible crops and that airborne lead contributes only 0.5 to 1.5 percent of the lead content of the U.S. diet. More sophisticated experiments (Dedolph and others, 1970) at the Argonne Laboratory consisted of growing six harvests of ryegrass and three harvests of radishes in chambers ventilated with filtered and unfiltered air and in a field adjoining a highway traversed by about 29,000 vehicles per day. The data obtained from analyses of coded samples were subjected to statistical evaluation. Clearly defined differences in plant-lead content attributable to differences in the lead concentration of the atmospheric environment could be discerned in leaves of both species. Lead-enriched water applied to the plants had no effect on their lead content. Atmospheric lead had no effect on the lead content of the root or edible portion of the radish. They concluded that the radish and rye leaves contain on the order of 2.5 ppm lead dry weight, which is soil derived. Lead concentrations above this base level (maximum 15 ppm) reflect the average lead concentration in the atmosphere in which the plants were grown.

Schuck and Locke (1970) investigated crops routinely grown in fields near highways in the vicinity of Riverside, Calif., and concluded that lead particulate particles are not absorbed but exist as a topical dust coating, of which at least 50 percent can be removed by washing. In a cauliflower head, interior florets contained less lead than did the outer florets; maximum amounts were contained in the outer leaves of cabbage heads growing 25 feet (7 m) from the highway. No evidence of absorption through the roots from water or from the high-lead soils that had been treated in the past with lead arsenate was observed.

Zimdahl and Arvik (1972) believed that the leaf cuticle is a primary barrier to entrance of atmospheric lead into the leaf and plays a more important role than stomatal penetration. Experiments with penetration of lead through cuticle membrane from leaves and fruits showed that less than 1 percent of the lead is able to penetrate the cuticular barrier. Whether atmospheric lead can be absorbed through the stomata of the leaf and translocated to other parts of the plant has not been determined, although lead isotopic studies should be able to resolve this question. Chow (1970) has shown that the isotopic composition characteristic of gasoline lead is of greater abundance in grass near highways and in surface soils than in soils at depth. Ault, Senechal, and Erleback (1970) studied tree rings and found no significant difference in isotopic ratio (Pb^{206}/Pb^{204}) with age. The ratios in all rings of wood were lower than that of roadside grass or of gasoline lead. The lead abundance in the outermost tree rings (0.34 ppm) was twice that of the 15- and 30-year-old rings (0.15 ppm). Either the uptake of lead was less in the past or lead is removed from the xylem layers after formation—perhaps along the radial ray cells of the woody part of the tree.

Algae, mosses, lichens, and others of the lower plant groups, because of their slow growth and unusually high concentrations of metals, have been proposed by several scientists as indicators of lead contamination. Ruhling and Tyler (1968) suggested that mosses growing on trees in urban areas be used as an index for surveying deposition of airborne heavy metals. They found that the contents of lead in mosses in southern Sweden had risen from about 25 to 100 ppm from 1860 to 1968. Martinez, Nathany, and Dharmarajan (1971) suggested that Spanish moss, which is not a true moss but a highly specialized epiphytic angiosperm, be used as a sensor for lead in the Gulf States; they were able through this medium to establish gradients from line-and-point sources to pollutants. Rains (1971) found a particular species of *Avena fatua* (wild oats) to be highly tolerant of lead and suggested its use as an indicator.

Two sources of pollution-caused lead in the atmosphere that have not been mentioned in previous sections have been reported in British Columbia and England. Warren, Delavault, Fletcher, and Wilks (1971) described an episode in Richland, B.C., in 1970, when dust falling in a particular area of the town was found to contain 4.2 percent lead, soil within a radius of a few hundred feet contained as much as 4,000 ppm lead, and forage grown in this locality contained from 1.5 to 8.5 percent lead in the ash. Lead in unwashed vegetables contained as much as 6.5 ppm in wet weight but a maximum of 0.6 ppm after washing. Although, for the most part, the lead is not absorbed into the plant tissue, the lead on the plants was being consumed by cattle. The industrial plant credited with being the source of the lead pollution has been closed voluntarily until control devices can be installed. Dunn and Bloxam (1932) reported on livestock deaths in England, which, although widely separated, were all on pastures near coke ovens. Soil downwind from the ovens contained as much as 7 ppm lead and grass contained as much as 46 ppm in the dry weight. Soils and grass upwind from the ovens had considerably lower lead contents. Further analysis showed the chimney soot to contain 342 ppm lead and the flue soot, 68 ppm.

SUMMARY

Plants absorb available lead from soils. Natural lead in plants growing in uncontaminated and unmineralized areas averages 2 ppm in the dry weight. As much as 350 ppm lead has been measured in the dry weight of vegetation rooted in soils developed from rocks containing lead ores; concentrations of as much as 664 ppm have been reported in vegetation subjected to the industrial and agricultural activities of man. A large percentage of lead in soil is not available to plants, and only in mining areas where high lead levels in soils occur is the growth of plants seriously affected. Of greater environmental significance is atmospheric lead from lead smelters, other types of industrial plants, and automobile emissions. Concentrations of lead in or on plants exposed to contaminated air decrease logarithmically with distance from the source. There is no clear evidence that lead from the atmosphere enters into the plant, except in the case of Spanish moss, which is highly specialized for absorbing atmospheric elements into the plant tissue. Washing and preparation of vegetables reduces the lead content to levels acceptable for human consumption, with the possible exception of lettuce and other leafy vegetables that are consumed raw; however, atmospheric lead in or on forages remains a hazard to livestock. Lead levels are increasing markedly and should be monitored on a continuous basis in urban and industrial areas.

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LEAD IN THE ATMOSPHERE, NATURAL AND ARTIFICIALLY OCCURRING LEAD, AND THE EFFECTS OF LEAD ON HEALTH

By H. L. CANNON

The amount of lead introduced into the environment from natural sources appears to be small compared to that made available in one way or another by man. This lead, in turn, is being absorbed by man at rates estimated by Patterson (1965) to be 30 times higher than inferred natural rates. Any discussion of lead in the environment must consider, therefore, the sources and effects of contamination lead in the world today. We are all exposed to lead in the air we breathe and in the food and water we ingest; furthermore, workers in particular industries and residents of particular areas are also exposed to occupational and industrial lead.

NATURAL ATMOSPHERIC LEAD

The amount of lead from natural sources that is released into the atmosphere is small, as shown by the following estimates by Patterson (1965):

Source	Lead ($\mu g/m^3$)
Silicate dust from soils	0.0005
Volcanic halogen aerosols	.00003
Volcanic silicate smoke	.000006
Forest fire smoke	.000006
Aerosolic sea salts	.000001
Meteorites and meteoritic smoke	.000000002

The calculation of these values involved many assumptions, and the total of about 0.0005+ $\mu g/m^3$ in the atmospheric reservoir is probably low. One source of lead in the atmosphere that may be important in mineralized areas is the exudate from vegetation. Curtin, King, and Mosier (1974) showed that heavy metals, including lead, are given off in vapor by vegetation; lead in condensed tree exudate measured from 1 to 12 ppb. Although the exudate in nonmineralized areas has a much lower lead content, the overall contribution is considerable. A small amount of lead is also released from the decay of radioisotopes. Inasmuch as emanations from the volcano, Mauna Loa, Hawaii, affect the general circulation of the trade winds, Kruger (1969) measured Pb^{210} levels as a means of studying atmosphere chemistry and transport processes. The comparatively large values of Pb^{210} in Hawaii indicate that little is removed from the atmosphere during the trade wind transport over the open ocean. The release of Pb^{210} from radon decay has been estimated at $2,260 \times 10^{-12}$ curies per m^2 per year for annual rainfall in Great Britain, with a mean air residency time of about 4 weeks (Hill, 1960). Because of man's widespread contamination of the air with lead throughout the world, data on natural levels of lead in the atmosphere are difficult to obtain. Certainly, in noncontaminated areas of the world, lead in the atmosphere averages less than 0.01 $\mu g/m^3$ and perhaps less than 0.001 $\mu g/m^3$. A median lead value of 0.019 μg-m^3 was reported by the U.S. National Air Pollution Control Administration (1968) from 29 nonurban collections made in 1965; likewise, no significant lead (< 0.001 $\mu g/m^3$) was detected in the fourth quarter of that year at six stations in remote areas of the country, using especially sensitive methods of analysis.

LEAD CONTAMINATION OF THE AIR

Although the quantity of lead ingested from food and water is much higher than that taken in from urban air, inhaled lead is much more readily absorbed; probably some 20–40 percent of lead absorbed is derived from the air (Carroll, 1970). In general, the higher the atmospheric level the higher the blood level of lead and, presumably, the total body burden. The differences in the concentrations of lead in surface air collected by the Atomic Energy Commission along their 80th Meridian network in 1967 are shown in table 34 (Harley, 1970).

In data compiled by McCaldin (1966), mean atmospheric lead concentrations for particular sets of samples ranged from 0.3 ng/m^3 of lead in 149 samples from suburban stations of the National Air Sampling Network to 44.5 ng/m^3 in 7 samples collected from Boston's Sumner Tunnel. Lazrus, Lorange, and Lodge (1970) reported on atmospheric precipitation samples collected from a nationwide network of 32 stations in the United States. The lead values averaged for each station ranged from 0 to 138 g of lead deposited on 1 hectare by 1 cm of precipitation.

An increase with time in lead in the atmosphere has been shown by Murozami, Chow, and Patterson (1969) who studied the annual ice layers in dated sections in northern Greenland. The lead content of the ice was less than 0.0005 $\mu g/kg$ in 800 B.C.; 0.01 $\mu g/kg$ in 1750, at the beginning of the Industrial Revolution; 0.07 $\mu g/kg$ in

TABLE 34.—*Lead concentrations in surface air in 1967 from selected sites along the 80th Meridian*

[Data from U.S. Atomic Energy Commission (cited in Harley, 1970)]

Site sampled	Latitude	Lead (ng/m^3)
Thule, Greenland	70° N.	<0.01
Moonsonee, Canada	56° N.	0.06
New York, N.Y	41° N.	2.5
Sterling, Va	39° N.	.74
Miami, Fla	26° N.	1.7
Bimini, Bahama Islands	26° N.	0.10
San Juan, P.R	18° N.	0.80
Balboa, Panama	9° N.	0.23
Guayaquil, Ecuador	2° S.	0.35
Lima, Peru	12° S.	0.50
Chacahaya, Peru	16° S.	0.09
Antofagasta, Chile	24° S.	0.06
Santiago, Chile	33° S.	0.87
Punta Arenas, Chile	53° S.	0.06

1940; and 2.5 μg/kg in 1965. Lead contents of Antarctic ice are much lower, probably because much less lead is introduced by man into the air of the southern hemisphere than into that of the northern hemisphere.

Estimates of the residence time of lead in air range from 1 to 4 weeks depending on the size of the particulate matter with which the lead is associated (Lagerwerff, 1972). Measurements of aerial concentrations of Pb^{210} show an upward transport of the finer particulates into the troposphere and beyond. The aerosols then travel toward the poles, where they become concentrated and sink again into the atmosphere. The cycle is closed by surface air currents which move toward the equator.

The most significant contribution of lead to the atmosphere is from the combustion of leaded gasoline, as table 35 shows. According to TerHaar and Bayard (1971) the lead originates in the antiknock fluid, which contains $PbBr_2$, PbBrCl, Pb(OH)Br, $(PbO)_2PbBr_2$, and $(PbO)_2PbBrCl$. After burning, the compounds recombine, so that after 18 hours 75 percent of the bromides and 30–40 percent of the chlorides disappear, and the proportion of lead carbonates and lead oxides are increased. A study of the aerosols in Fairbanks, Alaska, by Winchester, Zoller, Duce, and Benson (1967) showed that although the weight ratio Cl:Pb averages close to that of ethyl fluid (0.34) the Br:Pb ratio is 4 times less than that of ethyl fluid (0.39). This information supports the theory that lead halide particles, formed initially by combustion of ethyl fluid, lose bromine by oxidation and volatilization. The extent of the lead contribution to the atmosphere from ethyl gasoline was proved by Chow and Johnstone (1965), who determined that the isotopic composition of the lead from ethyl gasoline and of aerosols from the Los Angeles basin were the same. The lead from car exhaust was identified also in mountain snows and in the surface waters of the ocean. This identification followed a joint study by the U.S. Public Health Service and the petroleum industry of the lead in the atmosphere of three cities—Cincinnati, Philadelphia, and Los Angeles—which was conducted from June 1961 to May 1962 (Ludwig and others, 1965), during which time 3,400 samples were collected from 20 stations. They found an average concentration of 1.4 ng-m^3 in Cincinnati, 1.6 ng/m^3 in Philadelphia, and 2.5 ng-m^3 in Los Angeles. Concentrations as high as 44 ng/m^3 were measured in a vehicular tunnel. The highest concentrations were found during the autumn and winter months and in the early morning hours. Other studies in the United States and elsewhere have substantiated these findings. Temperature inversion phenomena in San Diego, which prevent the vertical movement of air above the base of the inversion layer, were studied by Chow and Earl (1970). Although pollution in San Diego is relatively low compared to that of other cities, average weekly lead concentrations of as much as 8 ng/m^3 were measured.

TABLE 35.—*Lead emissions in the United States, 1968*

[Data from U.S. Environmental Protection Agency (cited in National Research Council, 1972)]

Emission source	Lead emitted	
	(tonnes/yr)	(tons/yr)
Gasoline combustion	181,000	199,000
Coal combustion	920	1,000
Fuel oil combustion	24	26.5
Lead alkyl manufacturing	810	890
Primary lead smelting	174	192
Secondary lead smelting	811	892
Brass manufacturing	521	573
Lead oxide manufacturing	20	22
Gasoline transfer	36	39.5
Total	184,316	202,635

A study by Daines, Motto, and Chilko (1970) has shown that a relationship exists between the amount of lead in the air and traffic volume, proximity to the highway, engine acceleration, and wind direction. They also found that traffic markedly affected lead content of air only in a relatively narrow zone along the highway, with the lead content decreasing more than 50 percent in the interval from 10 to 150 feet (3 to 46 m). Ault, Senechal, and Erlebach (1970) demonstrated that there are significant differences in lead isotopic ratios found in rock, soils, grasses, tree leaves, normal air particulate, and those found in coal, fly ash, gasoline, and fuel oil. The Pb^{206}/Pb^{204} ratio of 18.2 in air within 500 feet (152 m) of a turnpike approached that of gasoline (18.3), whereas at greater distances the ratio averaged 18.7.

A less serious source of atmospheric lead is in fly ash which originates mainly from the burning of coal by power plants, steel mills, cement plants, and other industries. In a recent U.S. Geological Survey study of the coal and fly ash produced by power plants in the Southwest Energy Program, it was found that coal being produced for 10 power plants had a median content of 50 ppm lead in ash (73 samples), with a range of 30–200 ppm. Bottom ash had a median content of 30 ppm, with a range of 20–30 ppm; fly ash had a median content of 50 ppm lead with a range of 20–70 ppm. At the Four Corners plant, in San Juan County, N. Mex., fly ash collected in the stack was compared with the effluent falling on vegetation and soil of the surrounding area. The fly ash in the stack averaged 70 ppm lead and the effluent only 20 ppm. Analyses of the top one-half inch of soil along two 6.5-mile (10.4-km) traverses from the power plant indicated, for 1.5 miles (2.4 km), a lead content above the 20 ppm reported by Shacklette, Hamilton, Boerngen, and Bowles (1971) as average for U.S. soils, but the lead value at no point was greater than 30 ppm (Cannon and Anderson, 1972).

A major but relatively local source of atmospheric lead is the effluent from mining and smelting operations. Djurić, Kerin, Graovac-Leposavic, Novak, and Kop (1971) reported on a detailed study of lead levels in air, water, plants, and urine in the environs of a lead smelter in Yugoslavia. The smelter lies in a basin, has been operative since 1746, and currently produces 22,000 tons (19,800 t) of lead annually. The stack had no filtering devices until 1969. Samples of air collected in 1967 from three villages in the valley had a lead content ranging from 1.3 to 84.0 ng/m^3, with considerable variation on different sampling dates. Lead contents in soils ranged from 91 to 24,880 mg/kg, compared with 0.8–37.4 mg/kg in uncontaminated soil. The river that received effluent from the smelter ranged in lead content from 685.12 mg/l at the smelter to 2.89 mg/l 22 km below the smelter. Above the smelter the river contained only 0.001–0.02 mg/l. Analyses of food and forage show relatively low lead levels in peeled produce but high levels of lead in lettuce and hay; the lead levels in hay are toxic to cattle if the hay is used exclusively and continuously as forage. Milk, meat, and honey were also contaminated, the lead content in milk being 40 times the national average in the United States. Lead in the environment is being absorbed by the inhabitants at levels sufficient to induce a physiologic response.

A study has been made of the distribution of lead around two smelters in Toronto, Canada, and of blood lead levels in the local families. The lead fallout was shown to originate from episodic large-particulate emissions from near-ground sources rather than from stack fumes. Between 13 and 30 percent of the children living in the contaminated areas had absorbed excessive amounts of lead, but probably the lead was ingested from contaminated dusts rather than from drinking water, home-grown vegetables, air, or paint pica. Of the children who had absorbed excessive lead, most of those selected for special study showed metabolic changes; 10–15 percent of this selected group showed subtle neurological dysfunctions and minor psychomotor abnormalities (Roberts and others, 1974).

Cases of lead poisoning have been reported among workers and residents near a lead smelter in India where the daily flue emissions contained almost 2,000 lb (900 kg) of lead; in Colombia, families living in lead foundries exhibit chronic symptoms, and many children die from lead poisoning (Haley, 1969).

Lead poisoning in 75 children in Smeltertown, an area of 120 families near El Paso, Tex., where lead has been smelted since 1887 (Wall Street Journal, 1972a, b), has recently shown the urgency of the problem in this country. An intensive monitoring program has been initiated to study the effects on the environment of the so-called New Lead Belt (Wixson and others, 1972) in Missouri, which accounted for more than 80 percent of the total United States lead production in 1973. Lead levels in soils, air, plants, and water are being carefully checked and the effects of lead pollution on grazing animals are being studied. Long-term studies should contribute much to our knowledge of the long-range effects of low-level lead contamination on the health of animals, including man.

Cigarettes represent a minor but common source of lead. Although most of the lead remains in the ash, an intake of 20 ng per pack from the smoke has been estimated by Horton (1966). Studies by the Air Pollution Control Administration have demonstrated that in urban areas smokers have 1.24 times more blood lead than nonsmokers and in rural areas, 1.42 times more blood lead (Hofreuter, 1960).

LEAD CONTAMINATION OF WATER AND FOOD

Pollution lead may be ingested from several sources. A main source of lead poisoning in underprivileged children is pica, or an abnormal craving to ingest odd things including fragments of lead-based paint from cribs and walls (Haley, 1969). A decrease in plumbism from this source can be expected as current laws ordering the substitution of titanium-based paints on nursery furniture become effective. Cooking in earthenware pottery with a lead glaze or the use of such pottery as containers for acid foods can be a cause of lead poisoning (Klein and others, 1970). Vegetables and fruits are easily contaminated by lead-arsenate sprays and, although less lead arsenate is used than formerly, a buildup of the metals occurs in the soils of old orchards where a reservoir of lead is available to crops long after the use of lead arsenate has ceased. Experimental work by Jones and Hatch (1945) showed that crops grown in soil taken from an orchard with a spray record of 22 years assimilated from 1 to 3 times more lead in the above-ground portions and 2 to 8 times in the below-ground portions than the same crops grown in unsprayed soil; a maximum lead value of 35 ppm in dry weight of peeled eggplant was recorded.

Lead may also be introduced into cultivated land through the use of tailings from lead-zinc mines or of high-lead limestones for fertilizer. Warren, Delavault, and Cross (1966) have reported on the use of a limestone containing 45 ppm lead for fertilizer on land which then produced oats containing 3–4 ppm lead in the dry weight.

The soil and vegetation in the vicinity of mining operations (even though long defunct) may be contaminated by waste and spoil piles. The lower part of the Tamar Valley district of west Devon and Cornwall in Great Britain is a richly mineralized area which was mined for base metals in the 19th century. Soils from pastures and gardens contain unusually high contents of lead; garden soils had a maximum of 522 ppm total lead and 36 ppm available lead (extractable with acetic acid) (Davies, 1971). Radishes were used as a convenient test crop to measure actual uptake. They contained as much as 74 ppm lead in the ash. Davies (1972) concluded that the inhabitants of this valley are exposed to a greater lead insult than similar populations elsewhere in Great Britain.

Drinking water standards have been set by the U.S. Public Health Service at 0.5 mg/l maximum for lead. Although ground-water lead levels have remained relatively unaffected, man has increased lead in surface waters through agricultural practices, fallout of lead alkyl aerosols, contact with scrap and waste heaps, and mining activities. However, according to Patterson (1965), in rural areas the atmospheric washout of lead alkyl products should immediately be fixed in the clay fractions of the soil and thus make little contribution to the surface waters except through storm sewers. Sewer treatment plants contribute lead to surface waters, although about 65 percent of the lead in drinking water is removed in treatment processes, according to Horton (1966). He stated that lead is frequently present in unfiltered surface waters at levels well above the maximum permissible concentration but is generally much lower in filtered water. Analyses of 42 sewage sludges from rural and industrial towns in England and Wales show very large concentrations of certain trace elements. The sludges contained from 120 to 3,000 ppm lead and had a median content of 700 ppm in dry weight (Berrow and Webber, 1972).

Contributions of lead to ground and surface waters from rainfall can range as high as 0.49 mg/l in areas of industrial contamination or high traffic volume. However, Lazrus, Lorange, and Lodge (1970) have shown that there is, on the average, twice as much lead in atmospheric precipitation as in municipal water supplies, suggesting that the lead precipitates or is adsorbed on suspended matter and is thus filtered out in processing. Ettinger (1966) showed maximum lead in surface water to be associated with metal-working and chemical industries, but concluded that only a fraction of the lead in surface water remains dissolved.

Lead piping and lead solder used with copper tubing may also be a significant source of lead in water distribution systems. According to Patterson (1965) many of our largest cities use lead pipe exclusively for water service connections. She has estimated a per capita contribution of 5 μg/l of lead from lead used in water distribution systems.

EFFECTS OF INGESTED LEAD ON LIVESTOCK

In animals, the toxic effects of lead ingested in contaminated vegetation have often been noted. Horses, especially young ones, are particularly susceptible to lead poisoning. Chronic lead poisoning in six foals on three different properties within 5 miles (8 km) of the Trail smelter in British Columbia and subsequent poisoning of introduced horses has been described by Schmitt and others (1971). The symptoms were loss of weight, muscular weakness, stiffness of joints, and harsh, dry coats. A thorough investigation showed that young horses were more susceptible than old horses, and that lead rather than zinc, arsenic, or cadmium was the cause of the illness. Soil, forage, and blood levels of the horses on the three properties were as follows:

Property	Distance from smelter (miles)	Lead in top 1 inch soil (ppm)	Lead in forage (ppm dry weight)	Mean lead in blood (μg/100 g)
A	2.0	750	38	22.6
B	1.5	620	90	31.6
C	.5	2,900	264	37.6

In all but a few fruits and vegetables grown within 5 miles (8 km) of the smelter, lead concentrations were considered to be acceptable for human consumption, and human-urine lead levels were not elevated.

The death of four horses that had been corralled on the tailings pond of an old gold mine near Evergreen, Colo., was investigated by D. M. Sheridan and H. L. Cannon of the U.S. Geological Survey (unpub. data, 1970). The drinking water for the horses contained high concentrations of fluorine but the autopsy report showed lead poisoning. A noxious weed, *Grindelia squarrosa,* evident in the hay fed to the horses, which had been cut at a city country club, was subsequently found to contain 1,540 ppm lead in the dry weight. Inasmuch as the grass in the hay contained only 5.2 ppm, *Grindelia* appears to be an accumulator of toxic levels of lead.

Horses subsequently died in a pasture near Centerville, Mo., where 15 samples of cedar were reported by Connor, Shacklette, and Erdman (1971) to contain as much as 1,200 ppm lead in the dry weight, with a geometric mean of 348 ppm dry weight. The area was believed to have been contaminated by lead from ore trucks.

An outbreak of acute lead poisoning among cattle pastured near a lead smelter was studied by veterinarians from the University of Minnesota (Hammond and Aronson, 1964). The forage contained 148–285 ppm lead in the dry weight. Acute bovine lead poisoning resulted from long-term continuous intake of contaminated forage, whereas horses in the same environment responded by long-delayed onset of the classical syndrome of chronic equine plumbism. These and other case histories suggest that airborne lead absorbed by and adhering to plants may be more hazardous to grazing animals than to man.

OCCUPATIONAL LEAD

Plumbism from occupational lead used in automobile body manufacture and repair, foundries, electrotype printing, storage battery manufacture, secondary smelters, and munition plants was a hazard in this country before 1945. Improved occupational practices since that time and the introduction in 1945 of safe working standards for lead levels in air and urine have been responsible for decreasing exposure to airborne lead in dust and fumes by several orders of magnitude (Stokinger, 1966). In a study of workers who are regularly exposed to gasoline additives, it was found that garage mechanics show elevated lead levels in urine, but the levels are below the present acceptable limits. Although inhalation intoxication and skin absorption have caused problems in other countries (Haley, 1969), controls instituted in the United States have resulted in safe handling of lead alkyls, tetraethyl lead, and tetramethyl lead during manufacture. Nevertheless, after the manufactured products leave the plant, they may still pose a hazard through careless handling by the consumer; for instance, acute plumbism among children has been caused by burning old battery cases for fuel in fireplaces and cookstoves (National Research Council, 1972).

The contributions of lead to the environment that result from man's activity are much greater, therefore, than the lead that is available in the environment from natural sources. Considerably improved controls and monitoring programs are indicated.

ABSORPTION AND EFFECTS OF LEAD ON HEALTH

The human body tends to discriminate against the heavier metals in favor of the lighter, using the lighter in metabolic processes and being poisoned by the heavier (Patterson, 1965). The chemistry of lead is similar to that of barium in its behavior in the body, particularly in regard to deposition in and mobilization from the skeleton.

Lead in animals (including man) is concentrated largely in bone, although small amounts of lead occur in other types of tissue. Amounts that have been reported are as follows (Haley, 1969):

Tissue	*Lead (μg/100 g)*
Long bone	670–3,590
Flat bone	210–1,110
Liver	40– 280
Kidney	15– 160
Muscle	10– 170
Brain	10– 90

Bone represents the greatest storage site of lead, which is bound to bone by absorption or exchange at the surfaces of bone salt crystals, or is combined with the sulfate in the organic matrix. However, according to work by Kehoe (1961), the average individual appears to be in lead balance; the body burden of lead is established early in life and does not change appreciably throughout the life span. Haley (1969) reported lead concentrations in blood from 10 to 26 μg/ml; however, the lead levels of blood can be raised experimentally to as much as 450 μg/100 g by heavy dosages in food and air, with accompanying increases in urinary and fecal lead (Kehoe, 1964). Lead interferes with normal maturation of erythroid elements in the bone marrow and inhibits hemoglobin synthesis in precursor cells (Kench and others, 1952). Lead also affects prophyrin metabolism and interferes with the activity of several enzymes.

Although less than 10 percent of lead ingested by man is absorbed, 20–25 percent of respiratory intake may be retained and absorbed. Epidemiologic studies of blood lead levels show a logarithmic regression on estimated atmospheric exposure, according to Goldsmith and Hexter (1967), who postulated that further increases in atmospheric lead will result in predictable, progressively higher lead levels in the population. In a group of workers who were exposed to industrial lead and who had blood lead levels of 0.045–0.14 mg/100 g, the serum transaminase activity was increased, suggesting that subclinical liver impairment may occur at levels below the "safe" level of 0.07 mg/100 g (Hofreuter, 1960). Experiments by Schroeder, Vinton, and Balassa (1963) with lead-fed rats showed increased mortality rates in both sexes and renal and hepatic accumulations of lead similar to those in adult humans. However, there is evidence that the average intake of lead from food has not changed from its level during the three-decade period prior to 1965, because the increase in environmental lead in food has been balanced by the decrease in use of lead in agricultural chemicals and in food processing and packaging (Lewis, 1965).

In children, overt manifestations of acute lead poisoning, plumbism, differ from those of adults, and the mortality rate is relatively high. Symptoms may include anemia, gastrointestinal distress, and encephalopathy. The last may result in early death, permanent symptoms of brain damage, or complete recovery (Haley, 1969). Adult or chronic lead poisoning requires years to develop to the critical level, which is recognizable by symptoms such as headache, muscle pains, constipation, abdominal tenderness, colic, weight loss, and fatigue (Johnstone, 1964). Kidney damage from lead has not been identified in the United States although it is commonly reported in European countries; this difference may be due to poorer industrial hygiene in European countries. Renal lesions, which may be caused by lead ingestion, have been shown to lead to hypertension and may also predispose to gout as a result of defective urate secretion (Emmerson, 1965). An important symptom of chronic plumbism is the neuromuscular involvement, usually of the extensor muscles, as in wrist drop. Chronic exposures to lead in the water supply have been shown to result in increased miscarriages and stillbirths; the pregnant woman and her fetus are highly susceptible to lead poisoning (Wilson, 1966).

The poisoning of industrial workers with organic lead alkyls—tetraethyl or tetramethyl lead—causes a different set of symptoms called the acute brain syndrome. These symptoms include irritability, insomnia, emotional instability, tendon reflexes, and tremor. Delusions and hallucinations may occur (Sanders, 1965). However, lead alkyls decompose rapidly and are largely handled physiologically as inorganic water-soluble lead (Tepper, 1966). Although, according to Haley, there are no documented cases of lead poisoning in children or adults attributable to airborne lead from the combustion of leaded gasoline, continuous monitoring has been advised and realistic lead tolerance levels advocated after further study.

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ANALYTICAL METHODS FOR THE DETERMINATION OF LEAD

By F. N. Ward and M. J. Fishman

DETERMINATION OF LEAD IN SOILS AND ROCKS

Methods of chemical analysis with enough sensitivity to measure the low concentrations of lead in soil an rock samples are numerous. Such methods are based on familiar operations of optical emission spectrography, X-ray spectrography, molecular absorption (colorimetry), and atomic absorption. In a review of available methods, a certain amount of judgment has to be exercised in choosing those to be discussed; accordingly, the following discussion will be devoted to the methods most commonly used by the U.S. Geological Survey.

OPTICAL EMISSION SPECTROGRAPHY

Optical emission spectrographic methods are used to determine the lead content of soils, rocks, and minerals at the 5- to 10-ppm level, with a relative standard deviation of 10–20 percent. Such precision is attained with a semiquantitative procedure variously designated as the three-step or six-step semiquantitative spectrographic method. Better precision is attained with strictly quantitative procedures, but the semiquantitative methods are so widely used in the Geological Survey that some discussion of them is in order.

Quantitative data are achieved by comparing the spectra from unknown soil and rock samples with spectra of standard mixtures obtained under identical conditions of instrumental parameters, sample handling, and so on. The standard spectra are produced from mixtures of different amounts of pure compounds incorporated in matrices whose chemical compositions are similar to those of the host materials of the unknowns. The mixtures of pure compound plus matrix material are accordingly referred to as standard mixtures or simply as standards.

Within an order of magnitude, the concentration of lead in standards differs by a common factor, the cube root of 10 (Myers and others, 1961; Barnett, 1961). An explanation of the theoretical basis of this common factor is beyond the scope of this paper. It suffices to say that within an order of magnitude a series of lead standards would contain the following amounts of lead: the first standard, 1 percent; the second standard, 0.464 percent; the third, 0.215 percent, and so on.

Ward and others (1963) stated that these values could be rounded off respectively to 1, 0.5, 0.2, and 0.1 percent. Within an order of magnitude change in lead concentration, three standards were used and the method was called a three-step semiquantitative spectrographic method. The differences between the standards were called concentration ranges, and these ranges were rather broad. Many spectrographers felt that by inserting additional standards at the logarithmic midpoints of these ranges they could achieve better precision and accuracy. The method henceforth became known as a six-step semiquantitative spectrographic method.

After using both three-step and six-step procedures for a few years many Survey spectrographers concluded that the value of the additional midpoint standards for obtaining more accurate results was debatable and that the time required to prepare the midpoint standards as well as the extra space required on the photographic plate might offset any advantage.

Currently both methods are used in the Geological Survey, although most appraisal studies and exploration programs need only the three-step, or three-standards, procedure.

In applying the method, the spectrographer prepares a standards plate having spectral lines produced by lead concentrations of 1.0, 0.5, 0.2, and 0.1 ppm, and he designates the midpoints of the ranges delineated by these standards as 0.7 0.3, and 0.15 ppm, respectively. He compares the spectral line of lead from an unknown with the line produced by one of these standards or, if the unknown lies at a midpoint between two standards, with the range delineated by two standards lines. This range is often called a bracket and the midpoint further specified as the geometric midpoint.

Shacklette and others (1971, p. 225) described this method for reporting semiquantitative results as follows.

> The values obtained by spectrography were reported in geometric brackets having boundaries 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12 and so forth, percent; the brackets are identified by their respective geometric midpoints, 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, and so forth. Thus, a reported value of 0.3 percent for example, identifies the bracket from 0.26 to 0.38 percent as the analyst's best estimate of the concentration present. The precision of a reported value is approximately plus or minus one bracket at the 68-

percent level of confidence, and plus or minus two brackets at the 95-percent level.

The lead content of the unknown is thus reported with one of the following numbers: 1.0, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, and the reported value for lead will always be one of these numbers expressed as a power of 10 that depends on the relative concentration.

Ideally, the composition of the matrix or material to which pure lead compounds are added to form this series of standards should approximate the composition of the samples as closely as possible, especially with regard to major components. These major components cause changes in the sample excitation, which, along with the spectral lines and physical nature of the samples, affect spectral lines and intensities of the lead analyte. These effects are magnified because of the predominance of the matrix in the standard mixture. For highest accuracy, therefore, standards would have to be incorporated in several different kinds of matrices—for instance, gossan, silicate, or carbonate—and ultimately the number of standards would become unwieldy.

In practice, a compromise is made, and most lead determinations are made on the basis of standards prepared in one or two matrices modified to approximate the vast number of geologic materials analyzed. Further modifications—such as the addition of graphite to the unknown sample in a 2:1 ratio—are made to promote uniform excitation and inhibit the effect of major components in the matrix.

In these semiquantitative methods, spectra of unknowns are compared visually with spectra of standards, and occasionally faulty comparisons along with possible computational errors give rise to shocking results which usually prove embarrassing. Aware of these possibilities, spectrographers of the U.S. Geological Survey worked for several years to develop systems in which human participation was minimized and as many operations as possible were performed instrumentally. The problem was twofold. First, they had to make an instrument to read the line intensities recorded on the plates; however, each plate is unique and has to contain built-in flagging so that the instrument will measure the intensity of the most appropriate line or lines of the elements of interest including lead. Second, the Survey spectrographers had to devise computer programs to perform as many computations as possible, including corrections for matrix and background; and present the final readout in a format useful to geologists. The computer program was devised first and is described by Helz, Walthall, and Berman (1969); the instrument development came later and is given by Helz (1973). Subsequent applications and improvements are described by Dorrzapf (1973).

X-RAY SPECTROGRAPHY

In the U.S. Geological Survey, lead determinations are made routinely by X-ray spectrographic methods. These methods are not generally considered as trace methods, but after chemical pretreatment sensitivities as low as 50 ppm with a relative standard deviation of about 20 percent are achieved.

MOLECULAR ABSORPTION (COLORIMETRY)

For more than 25 years, trace amounts of lead in soils and rocks have been determined by molecular absorption methods. The common name for this process—colorimetry—is descriptive, but the process is one of absorption. Under specific conditions lead reacts with certain organic reagents—for instance, dithizone—to form colored species which can be extracted into immiscible solvents such as carbon tetrachloride or xylene.

The absorption of the colored species by these solvents occurs maximally at discrete frequencies, and the amount of absorption can be related to the concentration of lead in the soil or rock sample.

Molecular absorption methods of lead analysis are so numerous that a thorough review is beyond the scope of this paper, but procedures included by Sandell (1959) illustrate some of the available methods. For real samples of igneous rocks the sensitivity of the method is as low as 1 ppm (Thompson and Nakagawa, 1960).

Rapid field methods based on the reaction of lead with dithizone have a sensitivity limit of 20 ppm, which is adequate for reconnaissance studies.

ATOMIC ABSORPTION SPECTROMETRY

Atomic absorption methods for lead in soils and rocks as used in our laboratory were described by Ward and others (1969). Sensitivities as low as 1 ppm are routinely achieved, and under special conditions, such as by using a Delves spoon, the sensitivity can be lowered by one or two orders of magnitude.

Some typical lead values determined routinely by an atomic absorption method are as follows: five repeat determinations on a sandstone yielded 12–16 μg/g lead, with a relative standard deviation of 12 percent; corresponding values on a granite were 22–24 μg/g, with a relative standard deviation of 5 percent.

ELECTRON PROBE

The electron probe is useful for determining lead concentrations greater than about 0.1 percent. In ordinary soils and vegetation and in many rocks, the lead concentration is too low for measurement by the probe. In minerals, however, the local concentration of lead may easily exceed the threshold amount, and the probe is most useful for determining such enrichments.

DETERMINATION OF LEAD IN VEGETATION

One routine spectrographic method for determining lead in plant ash calls for mixing equal parts of ash with quartz to simulate the silicic matrix in which the standard powders are incorporated. The obvious advantage is that the same standard plates can be used on plant ash and silicic rock samples. The obvious disadvantage is that the sensitivity given above for lead in soils and rocks by optical emission spectrography is only 10–20 ppm. This sensitivity is adequate for many species of vegetation, but is inadequate for some specific applications.

Recently Mosier (1971, 1972) incorporated standard powders in a plant-ash base and, with a split-slit technique using a Hartmann diaphragm and a step filter assemblage, achieved a simultaneous recording of 35 elements including such volatile elements as silver, arsenic, bismuth, antimony, and others. Using this procedure Mosier determined amounts as small as 1 ppm lead in plant ash, with a relative standard deviation of 20 percent.

Trace amounts of lead in organic matter can also be measured by analytical methods based on molecular absorption (colorimetry) and atomic absorption. Methods based on X-ray spectrography may also be used after special sample treatment, but many different species contain less than threshold amounts and such X-ray methods are less useful than other procedures discussed here.

Molecular absorption methods for determining lead in vegetation are similar to those for soils and rocks except in sample size and treatment before analysis. Usually a 2-g sample of air-dried and ground vegetation is used; the minimum lead content that can be determined is near 0.25 ppm.

Atomic absorption methods for lead in vegetation are again similar to those for lead in soils and rocks, except in sample size and treatment. Ashing is necessary and can be accomplished either with oxidizing acids or by ignition in a muffle furnace at temperatures of 450°–500°C under controlled conditions to avoid losses.

Detection limits for lead of 0.02 μg/ml are quoted in the literature (Perkin-Elmer Corporation, 1971). Such limits are achieved with conventional atomic absorption techniques, but with a flameless procedure, Fernandez and Manning (1971) detected as little as 0.4 μg/l. Ward and others (1969) defined sensitivity in more practical terms, and, using a new procedure, they achieved a sensitivity of 1 μ g/g in plant ash. Five samples of fir ash contain 30–60 μ g/g lead. On the basis of 4 percent ash, these values are equivalent to 1.2–2.4 μg/g lead in air-dry sample.

DETERMINATION OF LEAD IN WATER

The literature on analytical methods for the determination of lead in water is voluminous. U.S. Geological Survey personnel have periodically reviewed the literature of analytical chemistry applied to water analysis; the last such review was published in 1973 (Fishman and Erdmann, 1973). These reviews are a good source of references to published descriptions of analytical procedures for lead, and we will not attempt to duplicate these references here. The principal methods used by the U.S. Geological Survey for determining lead in aqueous solutions are atomic absorption spectrophotometry and emission spectroscopy. For example, the analyses for this report, which were performed by U.S. Geological Survey personnel using these techniques, and which are described by M. J. Fishman (this volume), were determined on water samples filtered at the time of collection through 0.45-μ m-membrane filters and acidified with nitric acid to a pH less than 3.

Atomic absorption spectrophotometric methods are being used routinely for the direct determination of many trace elements; however, lead normally occurs in freshwater at concentrations less than can be directly detected by atomic absorption. Therefore, a preconcentration procedure is essential if lead is to be determined by atomic absorption. Brown, Skougstad, and Fishman (1970) described a rapid simple accurate and sensitive preconcentration procedure in which lead is chelated with ammonium pyrolidine dithiocarbamate (APDC) at a pH of 2.8, and the chelate is then extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of an atomic absorption spectrophotometer. Water containing from 1.0 to 20.0 μg/l lead may be analyzed by this procedure; higher concentrations must be reduced by dilution. None of the substances commonly occurring in natural water interferes with this method. Fishman and Midgett (1968) reported that results obtained by this procedure are in good agreement with those obtained spectrographically.

With the emission spectrograph, lead in water is determined simultaneously with many other minor elements. Three methods are described by Barnett and Mallory (1971). The first method consists of evaporating the water and analyzing the residue, and is used for the analysis of samples whose dissolved-solids concentrations do not exceed about 1,000 mg/l. This method is sensitive, precise, and reasonably accurate. The lower limits of detection vary with the quantity of dissolved solids; however, in order to achieve lower limits of detection for water samples containing more than 1,000 mg/l dissolved solids, it is necessary to separate lead and other minor elements from the major constituents prior to analysis. In the second method, lead and 20 other metallic elements are precipitated with thioacetamide, and the resultant sulfides are converted to oxides and analyzed. With the third procedure, 18 elements, including lead, are precipitated by complexing with tannic acid, thionalide, and 8-hydroxyquinoline. The precipitates are ashed and the resulting oxides analyzed.

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TABLES 36 & 37

TABLE 36.—*Normal lead content of some uncontaminated natural substances*

[Estimated from data given in this report]

Material	Median	Normal range
	ppm	
Crust of the earth	15	Unknown
Common rocks:		
Granite	18	10 - 100
Rhyolite	18	10 - 100
Gabbro	4	<1 - 25
Basalt	4	<1 - 25
Schist	15	<1 - 50
Gneiss	12	<1 - 40
Amphibolite	10	<1 - 25
Sandstone	15	10 30
Siltstone and shale	15	3 - 50
Carbonaceous shale	20	5 - 70
Limestone	5	3 - 15
Sediments:		
Terrestrial	15	5 - 40
Marine	60	30 - 150
Soil	15	5 - 50
Fossil fuels:		
Coal	10	3 - 30
Oil	.02	.005- 1
Common minerals:		
Potassium feldspar	50	10 - 150
Plagioclase feldspar	15	5 - 50
Muscovite mica	20	5 - 70
Biotite mica	30	5 - 100
Hornblende	10	3 - 30
Quartz	3	1 - 10
Calcite	3	1 - 15
	µg/l	
Water:		
Rivers	8	0.1 - 100
Lakes	2	.1 - 50
Hot springs	100	10 -1,000
Oceans	.2	.01 - 10
	µg/m³	
Air	0.02	< 0.001- 0.1
	ppm in ash	
Vegetation:		
Evergreen trees	30	10 - 100
Deciduous trees	25	10 - 50
Shrubs	25	<10 - 50
Grasses	20	10 - 100
Mosses	100	10 -1,000
Fruits and vegetables	<10	<10 - 30

TABLE 37.—*List of minerals and alloys in which lead (Pb) is a major constituent*

[Compiled by Michael Fleischer. This list includes minerals considered to be valid or doubtful species. Minerals containing two anions are listed under both, with the exception of compounds containing halides. For example, hidalgoite, $PbAl_3(SO_4)(AsO_4)(OH)_6$, is listed both under sulfates and under phosphates, arsenates, vanadates, and antimonites; however, mimetite, $Pb_5(AsO_4)_3Cl$, is listed under phosphates, arsenates, vanadates, and antimonites, but not under halides. References for unnamed minerals, given in parentheses, show volume and page number of American Mineralogist where the mineral is described]

Name	Formula
Alloys	
Plumbopalladinite	Pd_3Pb_2
Polarite	$Pd(Pb,Bi)$
Unnamed (v. 46, p. 464)	Pd_4Pb
Unnamed (v. 53, p. 1063)	Pd_3Pb_3Bi
Minerals	
Arsenites:	
Finnemanite	$Pb_5(AsO_3)_3Cl$
Trigonite	$Pb_3MnH(AsO_3)_3$
Carbonates:	
Beyerite	$(Ca,Pb)Bi_2(CO_3)_2O_2$
Caledonite	$Pb_5Cu_2(SO_4)_3(CO_3)(OH)_6$
Cerussite	$PbCO_3$
Dundasite	$PbAl_2(CO_3)_2(OH)_4 \cdot 2H_2O$
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$

TABLE 37.—*List of minerals and alloys in which lead (Pb) is a major constituent*—Continued

Name	Formula
Minerals—Continued	
Carbonates—Continued	
Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$
Nasledovite	$PbMn_3Al(CO_3)_4(SO_4)O_5 \cdot 5H_2O$
Phosgenite	$Pb_2(CO_3)Cl_2$
Plumbonacrite	$Pb_{10}(CO_3)_6(OH)_6O(?)$
Schuilingite	$Pb_3Ca_6Cu_2(CO_3)_8(OH)_6 \cdot 6H_2O$
Susannite	$Pb_4(SO_4)(CO_3)_2(OH)_2$
Wherryite	$Pb_4Cu(CO_3)(SO_4)_2(Cl,OH)_2O$
Halides:	
Bideauxite	$Pb_2AgCl_3(F,OH)_2$
Blixite	$Pb_2Cl(O,OH)_2$
Boleite	$Pb_9Cu_8Ag_3Cl_{21}(OH)_{16} \cdot H_2O$
Chloroxiphite	$Pb_3CuCl_2(OH)_2O_2$
Cotunnite	$PbCl_2$
Cumengite	$Pb_4Cu_4Cl_8(OH)_8 \cdot H_2O$
Diaboleite	$Pb_2CuCl_2(OH)_4$
Fiedlerite	$Pb_3Cl_4(OH)_2$
Laurionite	$PbCl(OH)$
Lorettoite	$Pb_7O_6Cl_2(?)$
Matlockite	$PbFCl$
Mendipite	$Pb_3Cl_2O_2$
Naderite	$PbSbO_2Cl$
Paralaurionite	$PbCl(OH)$
Penfieldite	$Pb_2Cl_3(OH)$
Percylite	$PbCuCl_2(OH)_2$
Perite	$PbBiO_2Cl$
Phosgenite	$Pb_2(CO_3)Cl_2$
Pseudoboleite	$Pb_5Cu_4Cl_{10}(OH)_8 \cdot 2H_2O$
Pseudocotunnite	$K_2PbCl_4(?)$
Schwartzembergite	$Pb_6(IO_3)_2Cl_4O_2(OH)_2$
Unnamed (v. 55, p. 1814)	$Pb_6Cl_6(IO_3)_2O_2$
Iodates:	
Schwartzembergite	$Pb_6(IO_3)_2Cl_4O_2(OH)_2$
Unnamed (v. 55, p. 1814)	$Pb_8(IO_3)_2Cl_6O_2$
Molybdates, tungstates:	
Raspite	$PbWO_4$
Stolzite	$PbWO_4$
Wulfenite	$PbMoO_4$
Oxides:	
Bindheimite	$Pb_2Sb_2O_6(O,OH)$
Cesarolite	$H_2PbMn_3O_8$
Clarkeite	$(Na,Ca,Pb)_2U_2(O,OH)_7$
Coronadite	$Pb(Mn^{+2},Mn^{+4})_8O_{16}$
Curite	$Pb_2U_5O_{17} \cdot 4H_2O$
Fourmarierite	$PbU_4O_{13} \cdot 4H_2O$
Hematophanite	$Pb_4Fe_4O_9(OH,Cl)_2$
Litharge	PbO, tetragonal
Magnetoplumbite	$(Pb,Mn)_2Fe_6O_{11}$
Massicot	PbO, orthorhombic
Masuyite	Pb,U oxide(?)
Metavandendriesscheite	$PbU_7O_{22} \cdot nH_2O$, n less than 12
Minium	Pb_3O_4
Murdochite	$PbCu_6O_8$
Plattnerite	PbO_2
Plumboferrite	$PbFe_4O_7$
Plumbopyrochlore	$(Pb,Y,U,Ca)_{2-x}Nb_2O_6(OH)$
Quenselite	$PbMnO_2(OH)$
Rankamaite	$(Na,K,Pb,Li)_3(Ta,Nb,Al)_{11}(O,OH)_{30}$
Richetite	Pb,U oxide(?)
Senaite	$(Fe,Mn,Pb)TiO_3$
Uraninite	$(U,Th,Pb)O_2+X$
Vandendriesscheite	$PbU_7O_{22} \cdot 12H_2O$
Wölsendorfite	$(Pb,Ca)U_2O_7 \cdot 2H_2O$
Unnamed (v. 55, p. 1816)	Pb_8O_{16}
Phosphates, arsenates, vanadates, antimonites:	
Bayldonite	$PbCu_3(AsO_4)_2(OH)_2$
Beudantite	$PbFe_3(AsO_4)(SO_4)(OH)_6$
Brackebuschite	$Pb_4MnFe(VO_4)_4 \cdot 2H_2O$
Carminite	$PbFe_2(AsO_4)_2(OH)_2$
Caryinite	$(Ca,Na,Pb)_5(Mn,Mg)_4(AsO_4)_5$
Chervetite	$Pb_2V_2O_7$
Corkite	$PbFe_3(PO_4)(SO_4)(OH)_6$
Curienite	$Pb(UO_2)_2(VO_4)_2 \cdot 5H_2O$
Descloizite	$PbZn(VO_4)(OH)$
Dewindtite	$Pb(UO_2)_2(PO_4)_2 \cdot 3H_2O$
Duftite	$PbCu(AsO_4)(OH)$
Dumontite	$Pb(UO_2)_3(PO_4)_2(OH)_4 \cdot 3H_2O$
Ecdemite	$Pb_6As_2O_7Cl_4$
Ferrazite	$(Pb,Ba)_3(PO_4)_2 \cdot 8H_2O(?)$
Fornacite	$(Pb,Cu)_3[(Cr,As)O_4]_2(OH)$
Francevillite	$(Ba,Pb)(UO_2)_2(VO_4)_2 \cdot 5H_2O$
Gabrielsonite	$PbFe(AsO_4)(OH)$
Georgiadesite	$Pb_3(AsO_4)Cl_3$
Grayite	$(Th,Pb,Ca)PO_4 \cdot H_2O$
Hallimondite	$Pb_2(UO_2)(AsO_4)_2$

TABLE 37.—*List of minerals and alloys in which lead (Pb) is a major constituent*—Continued

Name	Formula
Minerals—Continued	
Phosphates, arsenates, vanadates, antimonites—Continued	
Hedyphane	$\mathrm{(Ca,Pb)_5(AsO_4)_3Cl}$
Hidalgoite	$\mathrm{PbAl_3(SO_4)(AsO_4)(OH)_6}$
Hinsdalite	$\mathrm{(PbSr)Al_3(PO_4)(SO_4)(OH)_6}$
Hügelite	$\mathrm{Pb_2(UO_2)_3(AsO_4)_2(OH)_4 \cdot 3H_2O}$
Lusungite	$\mathrm{(Sr,Pb)Fe_3(PO_4)_2(OH)_5 \cdot H_2O}$
Mimetite	$\mathrm{Pb_5(AsO_4)_3Cl}$
Monimolite	$\mathrm{(Pb,Ca)_3Sb_2O_8}$(?)
Mottramite	$\mathrm{Pb(Cu,Zn)(VO_4)(OH)}$
Mounanaite	$\mathrm{PbFe_2(VO_4)_2(OH)_2}$
Parsonsite	$\mathrm{Pb_2(UO_2)(PO_4)_2 \cdot 2H_2O}$
Plumbogummite	$\mathrm{PbAl_3(PO_4)_2(OH)_5 \cdot H_2O}$
Przhevalskite	$\mathrm{Pb(UO_2)_2(PO_4)_2 \cdot 4H_2O}$
Pyrobelonite	$\mathrm{PbMn(VO_4)(OH)}$
Pyromorphite	$\mathrm{Pb_5(PO_4)_3Cl}$
Renardite	$\mathrm{Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O}$
Sahlinite	$\mathrm{Pb_{14}(AsO_4)_2O_9Cl_4}$
Schultenite	$\mathrm{PbHAsO_4}$
Tsumebite	$\mathrm{Pb_2Cu(PO_4)(SO_4)(OH)}$
Vanadinite	$\mathrm{Pb_5(VO_4)_3Cl}$
Vauquelinite	$\mathrm{Pb_2Cu(CrO_4)(PO_4)(OH)}$
Unnamed (v. 51, p. 258)	$\mathrm{Pb_2Cu(AsO_4)(SO_4)(OH)}$
Unnamed (v. 52, p. 1585)	$\mathrm{PbFe_3(AsO_4)_2(OH)_5 \cdot H_2O}$(?)
Unnamed (v. 47, p. 418)	Pb,Fe arsenate
Unnamed (v. 47, p. 418)	Pb,Zn arsenate
Silicates:	
Alamosite	$\mathrm{PbSiO_3}$
Barysilite	$\mathrm{Pb_4MnSi_3O_{11}}$
Ekanite	$\mathrm{(Th,\ U)(Ca,Fe,Pb)_2Si_8O_{20}}$
Esperite	$\mathrm{(Ca,Pb)ZnSiO_4}$
Ganomalite	$\mathrm{Pb_3Ca_2Si_3O_{11}}$
Hancockite	$\mathrm{(Pb,Ca,Sr)_2(Al,Fe)_3(SiO_4)_3(OH)}$
Hemihedrite	$\mathrm{Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2}$
Hyalotekite	$\mathrm{(Pb,Ca,Ba)_4BSi_6O_{17}(OH,F)}$
Jagoite	$\mathrm{Pb_3FeSi_3O_{10}\ (OH,Cl)}$
Joesmithite	$\mathrm{(Pb,Ca,Mn)\ (Mg,Fe)_4Fe^{+3}Si_6O_{12}}$ $\mathrm{(OH)_4(O,OH)_8}$
Kasolite	$\mathrm{Pb(UO_2)SiO_4 \cdot H_2O}$
Kentrolite	$\mathrm{Pb_2Mn_2{}^{+3}Si_2O_9}$
Larsenite	$\mathrm{PbZnSiO_4}$
Margarosanite	$\mathrm{Pb(Ca,Mn)_2Si_3O_9}$
Melanotekite	$\mathrm{Pb_2Fe_2Si_2O_9}$
Molybdophyllite	$\mathrm{Pb_2Mg_2Si_2O_7(OH)_2}$
Nasonite	$\mathrm{Pb_6Ca_4Si_6O_{21}Cl_2}$
Plumalsite	$\mathrm{Pb_4Al_2(SiO_3)_7}$
Roeblingite	$\mathrm{Pb_2Ca_7Si_6O_{14}(OH)_{10}(SO_4)_2}$
Wickenburgite	$\mathrm{Pb_3CaAl_2Si_{10}O_{24}(OH)_6}$
Sulfates, chromates, selenates, selenites, tellurates:	
Anglesite	$\mathrm{PbSO_4}$
Beaverite	$\mathrm{Pb(Cu,Fe,Al)_3(SO_4)_2(OH)_6}$
Beudantite	$\mathrm{PbFe_3(AsO_4)(SO_4)(OH)_6}$
Caledonite	$\mathrm{Pb_5Cu_2(SO_4)_3(CO_3)(OH)_6}$
Corkite	$\mathrm{PbFe_3(PO_4)(SO_4)(OH)_6}$
Crocoite	$\mathrm{PbCrO_4}$
Demesmaekerite	$\mathrm{Pb_2Cu_5(UO_2)_2(SeO_3)_6(OH)_6 \cdot 2H_2O}$
Fleischerite	$\mathrm{Pb_3Ge(SO_4)_2(OH)_6 \cdot 3H_2O}$
Fornacite	$\mathrm{(Pb,Cu)_3[(Cr,As)O_4]_2(OH)}$
Hemihedrite	$\mathrm{Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2}$
Hidalgoite	$\mathrm{PbAl_3(SO_4)(AsO_4)(OH)_6}$
Hinsdalite	$\mathrm{(Pb,Sr)Al_3(PO_4)(SO_4)(OH)_6}$
Iranite	$\mathrm{PbCrO_4 \cdot H_2O}$
Itoite	$\mathrm{Pb_3Ge(SO_4)_2O_2(OH)_2}$
Lanarkite	$\mathrm{Pb_2SO_5}$
Leadhillite	$\mathrm{Pb_4(SO_4)(CO_3)_2(OH)_2}$
Linarite	$\mathrm{PbCu(SO_4)(OH)_2}$
Moctezumite	$\mathrm{Pb(UO_2)(TeO_3)_2}$
Molybdomenite	$\mathrm{PbSeO_3}$
Nasledovite	$\mathrm{PbMn_3Al_4(CO_3)_4(SO_4)O_5 \cdot 5H_2O}$
Olsacherite	$\mathrm{Pb_2(SeO_4)(SO_4)}$
Osarizawaite	$\mathrm{PbCuAl_2(SO_4)_2(OH)_6}$
Palmierite	$\mathrm{(K,Na)_2Pb(SO_4)_2}$
Phoenicochroite	$\mathrm{Pb_2Cr_2O_5}$
Plumbojarosite	$\mathrm{PbFe_6(SO_4)_4(OH)_6}$
Roeblingite	$\mathrm{Pb_2Ca_7Si_6O_{14}(OH)_{10}(SO_4)_2}$
Schmeiderite	$\mathrm{(Pb,Cu)_2SeO_4(OH)_2}$(?)
Susannite	$\mathrm{Pb_4(SO_4)(CO_3)_2(OH)_2}$
Tsumebite	$\mathrm{Pb_2Cu(PO_4)(SO_4)(OH)}$
Vauquelinite	$\mathrm{Pb_2Cu(CrO_4)(PO_4)(OH)}$
Wherryite	$\mathrm{Pb_4Cu(CO_3)(SO_4)_2(Cl,OH)_2O}$
Unnamed (v. 51, p. 258)	$\mathrm{Pb_2Cu(AsO_4)(SO_4)(OH)}$
Sulfides, selenides, tellurides:	
Altaite	PbTe
Betekhtinite	$\mathrm{Cu_{10}(Fe,Pb)S_6}$
Clausthalite	PbSe
Galena	PbS
Sulfides, selenides, tellurides—Continued	
Parkerite	$\mathrm{Ni_3(Bi,\ Pb)_2S_2}$
Shandite	$\mathrm{Ni_3Pb_2S_2}$
Unnamed (v. 53, p. 1421)	Pb-Bi-Te
Unnamed (v. 55, p. 1444)	$\mathrm{(Pb,Bi)_3Te_4}$
Unnamed (v. 55, p. 1067)	$\mathrm{(Pd,Pb)_3As}$
Sulfosalts:	
Aikinite	$\mathrm{PbCuBiS_3}$
Andorite	$\mathrm{PbAgSb_3S_6}$
Baumhauerite	$\mathrm{Pb_4As_6S_{13}}$
Benjaminite	$\mathrm{Pb_2(Cu,Ag)_2Bi_4S_9}$
Berryite	$\mathrm{Pb_2(Cu,Ag)_3Bi_5S_{11}}$
Bonchevite	$\mathrm{PbBi_4S_7}$(?)
Boulangerite	$\mathrm{Pb_5Sb_4S_{11}}$
Bournonite	$\mathrm{PbCuSbS_3}$
Bursaite	$\mathrm{Pb_5Bi_4S_{11}}$
Cannizzarite	Pb,Bi,S
Cosalite	$\mathrm{Pb_2Bi_2S_5}$
Cylindrite	$\mathrm{Pb_3Sn_4Sb_2S_{14}}$
Dadsonite	$\mathrm{Pb_{11}Sb_{12}S_{29}}$
Diaphorite	$\mathrm{Pb_2Ag_3Sb_3S_8}$
Dufrenoysite	$\mathrm{Pb_2As_2S_5}$
Fizelyite	$\mathrm{Pb_5Ag_2Sb_8S_{18}}$
Franckeite	$\mathrm{Pb_5Sn_3Sb_2S_{14}}$
Freieslebenite	$\mathrm{Pb_3Ag_5Sb_5S_{12}}$
Fülöppite	$\mathrm{Pb_3Sb_8S_{15}}$
Galenobismutite	$\mathrm{PbBi_2S_4}$
Geocronite	$\mathrm{Pb_5SbAsS_8}$
Giessenite	$\mathrm{Pb_9CuBi_6Sb_{1.5}S_{30}}$(?)
Gladite	$\mathrm{PbCuBi_5S_9}$
Gratonite	$\mathrm{Pb_9As_4S_{15}}$
Guettardite	$\mathrm{Pb_9(Sb,As)_{16}S_{33}}$
Gustavite	$\mathrm{Pb_5Ag_3Bi_{11}S_{24}}$
Hammarite	$\mathrm{Pb_2Cu_2Bi_4S_9}$
Hatchite	$\mathrm{(Pb,Tl)_2AgAs_2S_5}$
Heteromorphite	$\mathrm{Pb_7Sb_8S_{19}}$
Hutchinsonite	$\mathrm{(Pb,Tl)_2(Cu,Ag)As_5S_{10}}$
Jamesonite	$\mathrm{Pb_4FeSb_6S_{14}}$
Jordanite	$\mathrm{(Pb,Tl)_{13}As_7S_{23}}$
Kobellite	$\mathrm{Pb_2(Bi,Sb)_2S_5}$
Launayite	$\mathrm{Pb_{22}Sb_{26}S_{61}}$
Lengenbachite	$\mathrm{Pb_6(Ag,Cu)_2As_4S_{13}}$
Lillianite	$\mathrm{Pb_3Bi_2S_6}$
Lindströmite	$\mathrm{PbCuBi_3S_6}$(?)
Liveingite	$\mathrm{Pb_9As_{13}S_{28}}$
Madocite	$\mathrm{Pb(Sb,As)_{16}S_{25}}$
Marrite	$\mathrm{PbAgAsS_3}$
Meneghinite	$\mathrm{Pb_{13}CuSb_7S_{24}}$
Montesite	$\mathrm{PbSn_4S_5}$(?)
Nagyagite	$\mathrm{Pb_5Au(Te,Sb)_4S_{5-8}}$
Neyite	$\mathrm{Pb(Cu,Ag)_2Bi_6S_{11}}$
Nuffieldite	$\mathrm{Pb_{10}Cu_4Bi_{10}S_{27}}$
Owyheeite	$\mathrm{Ag_2Pb_5Sb_6S_{15}}$
Parajamesonite	$\mathrm{Pb_4FeSb_6S_{14}}$
Plagionite	$\mathrm{Pb_5Sb_8S_{17}}$
Platynite	$\mathrm{PbBi_2(Se,S)_3}$
Playfairite	$\mathrm{Pb_{16}Sb_{18}S_{43}}$
Ramdohrite	$\mathrm{Ag_2Pb_3Sb_6S_{13}}$
Rathite	$\mathrm{(Pb,Tl)_3As_5S_{10}}$
Rezbanyite	$\mathrm{Pb_3Cu_2Bi_{10}S_{19}}$
Robinsonite	$\mathrm{Pb_7Sb_{12}S_{25}}$
Sakharovaite	$\mathrm{(Pb,Fe)(Bi,Sb)_2S_4}$
Sartorite	$\mathrm{PbAs_2S_4}$
Schirmerite	$\mathrm{PbAg_4Bi_4S_9}$
Seligmannite	$\mathrm{PbCuAsS_3}$
Semseyite	$\mathrm{Pb_9Sb_8S_{21}}$
Sorbyite	$\mathrm{Pb_{17}(Sb,As)_{22}S_{50}}$
Sterryite	$\mathrm{Pb_{12}(Sb,As)_{10}S_{27}}$
Teallite	$\mathrm{PbSnS_2}$
Tintinaite	$\mathrm{Pb_5(Sb,Bi)_8S_{17}}$
Twinnite	$\mathrm{Pb(Sb,As)_2S_4}$
Ustarasite	$\mathrm{Pb(Bi,Sb)_6S_{10}}$
Veenite	$\mathrm{Pb_2(Sb,As)_2S_5}$
Wallisite	$\mathrm{PbTl(Cu,Ag)As_2S_5}$
Weibullite	$\mathrm{Pb_4Bi_6S_9Se_4}$
Wittite	$\mathrm{Pb_5Bi_6(S,Se)_{14}}$
Zinkenite	$\mathrm{Pb_6Sb_{14}S_{27}}$
Unnamed (v. 5, p. 136)	$\mathrm{Pb_3As_4S_9}$
Unnamed (v. 55, p. 1067)	Pb,Ag,Sb,S
Unnamed (v. 55, p. 1445)	Pb,Ag,Cu,Bi,S
Unnamed (v. 54, p. 990)	$\mathrm{(Pb,Ag,Bi)Cu_4Bi_5S_{11}}$
Unnamed (v. 38, p. 525)	Pb,Ag,Cu,Fe,Sb,S
Unnamed (v. 55, p. 533)	$\mathrm{Pb_8Bi_6S_{17}}$

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