Reports

Lead Aerosols in the Atmosphere: Increasing Concentrations

Abstract. *The concentrations of atmospheric lead around San Diego, California, have been determined and their geographic and seasonal variations are explained. The lead aerosol concentration at San Diego is increasing at a rate of 5 percent per year. The isotopic composition of lead aerosols is similar to that of the lead additives isolated from gasoline, which are the largest contributors to atmospheric lead pollution.*

The distribution of industrial lead as a toxic pollutant in the environment has been the subject of concern since the advent of antiknock lead additives in gasoline (*1*). The U.S. Department of Health, Education, and Welfare, in conjunction with the manufacturers of the lead alkyl additives, has conducted a joint survey known as the Tri-City Project on the lead concentrations in the ambient atmospheres of Los Angeles, Philadelphia, and Cincinnati (*2*). The literature dealing with lead concentrations in the atmosphere is reviewed every 2 years by Altshuller (*3*). We here report the concentration of lead aerosols around San Diego, California.

Samples consist of filters through which air is drawn by vacuum pumps (Gelman Little Giant). Cellulose ester membranes (MF-Millipore, type HAWP) with a 0.45-μm mean pore size and a retention efficiency of greater than 95 percent for 0.05-μm particles are used. The filter holder is made of anodized aluminum with a gold-plated screen and a clamp ring to support the filter. The filter holder is housed in an inverted polyethylene cup for protection from rain, dust, and sea-salt spray and is suspended from a wooden pole extending from the building roof. Air flow is monitored with a Sprague gas meter placed between the pump and the filter holder. Flow rates average 1 m^3/hour. We determined the lead concentrations in the samples by the stable isotope dilution method, using an enriched Pb^{206} tracer obtained from the Oak Ridge National Laboratory. The lead blank for fixed aliquots of chemical reagents averages 0.03 μg per run. The mass spectrometric method has been described by Chow (*4*). Lead aerosols are isotopically determined as common lead with a ratio of Pb^{206} to Pb^{208} of 0.481.

The histogram (Fig. 1) shows the weekly average lead concentrations in the atmosphere of various environments around San Diego during the years 1968 and 1969. The abscissa is the frequency of occurrence of lead concentrations for air samples measured weekly, and the ordinate is the atmospheric lead concentration plotted on a logarithmic scale. The air at Mount Laguna [6100-foot (1850-m) elevation] contains several hundredths of a microgram of lead per cubic meter; the air at the La Jolla seashore (Scripps Institution) contains several tenths of a microgram of lead per cubic meter; and the air in downtown San Diego contains several micrograms of lead per cubic meter. If the previously reported lead concentrations in mid-Pacific Ocean air of several thousandths of a microgram per cubic meter (*5*) are included, the frequency of the atmospheric lead distribution shows a trend that increases logarithmically from the mid-ocean to remote high mountains to seashore to suburban and urban environments.

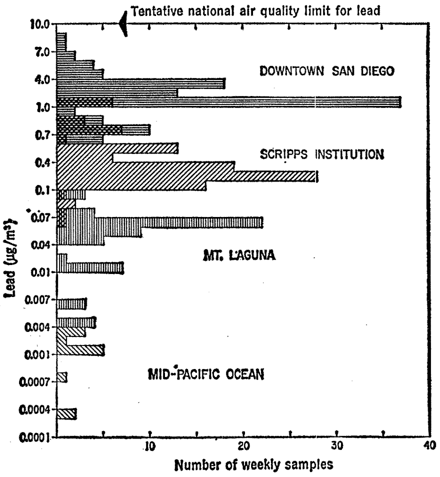

Fig. 1. Trend of atmospheric lead concentrations in various environments.

The Mount Laguna station, located at the San Diego State College Astronomical Observatory on the crest of the Peninsula Range, is remote from any industrial sources of pollution. The San Diego metropolitan area is approximately 45 miles (72 km) west of this site. Automotive traffic is probably less than a dozen cars per week within ½ mile of this location. A mountain road over which approximately 200 to 300 cars travel per day is about 1 mile west of the site. The lead aerosol concentration at this site is uniformly low throughout the year, with an average of 0.05 μg/m^3 (values range from 0.01 to 0.07 μg/m^3). In the winter months when strong radiation inversions cause the atmospheric lead contents in the foothill and coastal regions to be high, remarkably low lead concentrations which are almost as low as those found over the mid-Pacific are encountered here. This is attributable to the fact that the site is well above the inversion base at these times. The Scripps Institution sampling site is located at the end of the observation pier, which extends 1000 feet into the Pacific Ocean. The surrounding area is mostly residential. As might be expected, this site shows relatively low lead concentrations, with a yearly average of 0.4 μg/m^3, especially during the summer months when the prevailing sea breezes are from the west and northwest so that fresh marine air is brought in. The Mission Valley station is located at the California Highway Patrol Office about 10 miles inland from the ocean and is in a broad, flat-floored valley transecting the heavily populated San Diego Mesa. The valley floor is being increasingly developed with major shopping centers, hotels, and sports facilities. Traffic flow in the vicinity of the sampling site is about 175,000 cars per day. Within the last 3 years, the concentration of atmospheric lead in Mission Valley has increased about 15 percent per year. A comparison of the concentration of atmospheric lead during the winter months of 1967 with that during the winter months of 1969 reveals a drastic increase of 50 percent. The downtown San Diego station is located at the Central Public Library in a commercial district. Following the trends prevalent in most center city areas, the traffic flow in the downtown region has remained rather constant during the past decade.

Table 1. Percentage of lead in suspended particulate matter at San Diego during 1969.

Station	Lead (% by weight)			
	January–March Average (range)	April–June Average (range)	July–September Average (range)	October–December Average (range)
Scripps Pier	0.48 (0.34–0.64)	0.37 (0.24–0.60)	0.42 (0.17–0.59)	0.68 (0.29–1.19)
Mission Valley	3.23 (2.37–4.79)	2.26 (1.50–4.15)	2.16 (1.85–2.49)	4.61 (2.85–6.92)
Downtown	3.51 (2.13–4.98)	1.97 (1.11–4.41)	1.71 (1.19–2.47)	4.62 (1.95–7.22)
Mount Laguna		0.40 (0.32–0.47)	0.33 (0.23–0.42)	0.32 (0.30–0.34)

This site is only 1 mile from the Pacific Ocean and San Diego Bay, which are located to the west and south, so that when the winds are from those directions, as during the summer months or a winter storm, relatively low lead concentrations are observed. On the basis of 3 years of sampling in the downtown area and some earlier analyses by the California Bureau of Air Sanitation and the National Air Sampling Network for this site, for which an annual average lead concentration of 1.12 and 1.84 μg/m³ for 1957 and 1966, respectively, were reported, the lead concentration appears to be increasing at a rate of about 5 percent per year.

Figure 2 shows the seasonal trend of weekly lead concentrations at downtown San Diego, Mission Valley, and Scripps Institution stations for the years from 1967 through 1969. The atmospheric lead concentrations show an annual cycle with a winter high and a summer low. The amplitude of the lead contents of the downtown air from winter to summer is about 3 and that of the Mission Valley and Scripps Institution is about 2. This pattern of seasonal variation is attributed to local meteorological conditions. Summer months in southern California are usually cloudy, with overcast mornings along the coast. Although the coastal sky is covered by a thick cloud cover during the night and early morning hours, the temperatures increase inland where skies are clear, thus creating a thermal low-pressure region in the interior and setting in motion the summer sea-breeze circulation. Therefore, the lead concentration in the inland atmosphere is reduced by this dilution with clean marine air. During the winter months there is little difference between land and sea temperatures and so the sea breezes are usually diminished; the reduced wind velocity cannot effectively dissipate the pollutants, and, as a result, the lead aerosols accumulate in the inland air.

Air temperature normally decreases with increasing altitude. Occasionally, however, a layer of warmer air overlies cooler air and creates the phenomenon known as a temperature inversion. There are two major types of temperature inversions: radiation and subsidence. The subsidence inversion, which occurs generally during the summer months, has its origin in the subsiding air of the high-pressure belt encircling the earth in the vicinity of northern latitudes 30° to 35°. As the subsiding air is heated by compression, it produces a warm dry layer aloft that is markedly different in temperature from the layer of air near the surface. The boundary between the cold and warm air masses, that is, the inversion base, varies from time to time, but it is usually several thousand feet above sea level.

The other type of inversion, the radiation inversion, is common in southern California during the early mornings of the winter months. Inversions develop when the wind is light and air layers above the ground are dry, a situation contributing to rapid heat loss from the ground into the overlying air. Under these conditions the lowest temperature is found near the ground, and the base of the inversion is generally within several hundred feet of the surface. Thus the air chamber is much smaller during a radiation inversion. When the inversion phenomenon occurs, the upward diffusion is inhibited. This gives little opportunity for vertical movement above the level established at the base of temperature inversion. As a result, the pollutants are trapped in this limited air space.

During such a temperature inversion phenomenon, high concentrations of atmospheric lead are encountered as evidenced by the "spiked-peak" lead concentrations superimposed on the general seasonal trend at all urban stations (Fig. 2). This effect is most pronounced at the downtown station. Average weekly lead concentrations of as much as 8 μg/m³ have been observed. The tentative national air quality limit for lead proposed by the American Industrial Hygiene Association is 10 μg/m³ (*6*). Even though the ambient atmosphere of San Diego is less polluted than that of other major metropolitan areas, its average annual lead concentration has already exceeded the World Health Organization air quality guides for the level I criterion of 2 μg/m³ (*7*).

"Deep valleys" on the general seasonal trend were observed during the rainy periods or periods of persistent westerly winds. Rain washes out the lead aerosols from the atmosphere but the lead aerosol concentration builds up quickly after the storm front passes. During the first quarter of 1969, the San Diego area had an unusually heavy rainfall of 10 inches (25.4 cm), an amount which equals the entire normal yearly precipitation. Thus, the atmospheric lead content for this quarter showed a much lower value than that of the preceding year, and this is also reflected in the annual average for 1969. This explanation is supported by

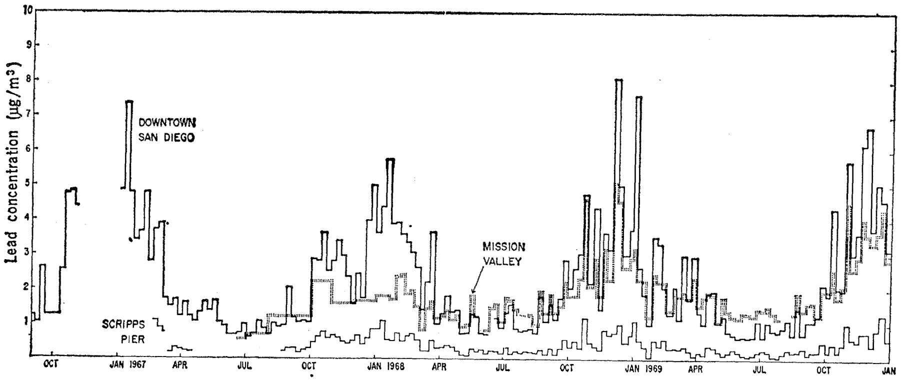

Fig. 2. Atmospheric lead concentrations around San Diego, California, September 1966 to December 1969.

the fact that the lead concentrations during the first quarter of 1970 show a continually increasing trend.

Concentrations of suspended particulate matter present in the atmosphere at various San Diego stations are given in Table 1. Lead aerosols constitute about 3 to 4 percent of the total suspended particulate matter in downtown San Diego and Mission Valley, with a range from 1.2 to 7.2 percent. Lead concentrations at Scripps Institution and Mount Laguna average about 0.49 and 0.35 percent, respectively. The Scripps samples contain relatively high concentrations of sea-salt constituents and thus have a low lead content.

Each lead ore deposit has its characteristic isotopic composition which is fixed during mineral genesis, and this unique chemical property can be used in the identification of the source of the industrial lead pollutants. Various brands of gasoline samples were purchased from San Diego service stations, and simultaneously aerosol samples were gathered. Gasoline and aerosol samples from other cities were also obtained. Leads in gasolines and in the aerosols were chemically extracted and their isotopic compositions were determined. The results are plotted in Fig. 3.

The average isotopic composition of marine sediments represents a lead from the Quaternary Period which was deposited onto the ocean floor millennia ago and typifies the results of natural weathering (*8*), whereas the lead in coastal surface seawater, which isotopically has a model age of Tertiary time, is no longer the sole product of natural weathering. The isotopic composition of lead in gasoline additives and in the aerosols represents a mined ore lead of typical Tertiary or older age, which is less radiogenic than that of the Quaternary lead. This means that the lead aerosols could not be derived from the surface soils of natural weathering. Comparison of the isotopic composition of lead in the southern California aerosols with that of the average of local gasoline leads shows that these two kinds of lead are identical within experimental error. Isotopic compositions of lead aerosols in Denver, Boston, Bern, and other cities are also identical with those of the respective gasoline leads of those cities. This indicates that the excess lead in the aerosols can only be attributed to automotive exhausts.

The two major lead-producing mine districts in the United States are located at southeast Missouri (St. Joseph) and Coeur d'Alene, Idaho (Bunker Hill). The isotopic composition of these two ore leads (Fig. 3) are on the extreme ends of the isotopic scale for lead ores. So far no gasoline lead additive with these specific compositions has been encountered. The isotopic compositions of gasoline leads approximate those of lead deposits in Mexico and Canada (*9*).

The lead pollutants originate overwhelmingly from the burning of lead alkyl additives in automotive fuels. In the United States in 1968 alone, more than 5×10^8 pounds (2.3×10^8 kg) of lead were combusted as antiknock additives. About 10 percent of this amount, that is, 5×10^7 pounds of lead, were emitted into the ambient atmosphere within the State of California; most of these lead pollutants were discharged in the densely populated San Francisco Bay area and southern California (*10*). About 75 percent of the lead burned in gasoline is introduced into the atmosphere as finely divided aerosols. Since the advent of leaded gasoline, a cumulative amount of more than 12×10^9 pounds of lead have been marketed and consumed as antiknock additives in the United States.

By comparison with the burning of gasoline, the burning of coal has never been a significant contributor of lead aerosols in the atmosphere. In recent years, about 5×10^8 tons (4.5×10^{11} kg) of coal were burned annually in the United States. The average lead content of the coal is about 10 parts per million (ppm) (*11*). The atmospheric lead contributed by the burning coal would amount to only about 3 percent of that contributed by gasoline lead if both were introduced into the atmosphere with equal efficiency. In modern furnaces that burn pulverized coal, more than 95 percent of the fly ash is removed by electrostatic precipitators so that only a small fraction of the lead in coal ash is emitted as lead aerosols. At present, the atmospheric lead contribution from coal smoke is therefore insignificant.

Lead is a naturally occurring, widely dispersed element. The lead content of the earth's crust is between 10 and 15 ppm (*8*). As we have shown above, the lead aerosols constitute, on the average, about 3 percent of the total suspended particulate matter in the San Diego and other metropolitan air (*2*). Any airborne virgin soil particles could not possibly account for this high concentration of lead. Therefore, soil lead is not the source of the lead pollution. On the contrary, the earth's soils are being contaminated by the gasoline leads.

Lead aerosols are eventually removed from the atmosphere by precipitation either in rainfall or as dust. Most rain in southern California occurs in connection with large, general storms that originate in higher latitudes and move southward into the region during the winter season if the storms are not blocked by high-pressure cells in the

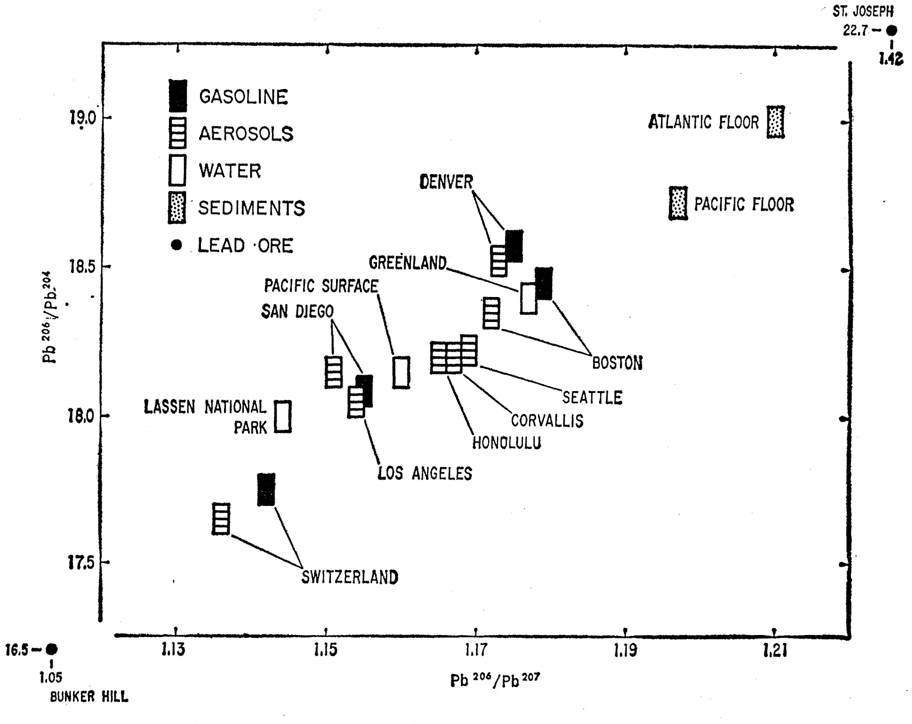

Fig. 3. Isotopic correlation of lead in various specimens.

Pacific. Few storms have the intensity to penetrate as far as San Diego; thus the annual rainfall averages only 10 inches per year. We have collected rainfall at the La Jolla station and analyzed it for lead during the past 3 years. Lead concentrations range from 3 to over 300 μg per liter of rainwater, and there is an inverse relationship between the amounts of rainfall and the lead concentration. The average lead contents in La Jolla rainwater is about 40 μg/liter. Lazrus *et al.* (*12*) reported an average of 36 μg of lead per liter for a U.S. nationwide sampling network. They concluded that the lead content in rainwater at various cities is correlated with the gasoline consumption there. According to the U.S. Public Health Service drinking water standard, the "grounds for rejection" limit for drinking water is 50 μg of lead per liter (*13*).

In the San Diego region the amount of dust falling was 72 and 113 mg/m^2 per day for the fourth quarter of 1969 for our La Jolla and downtown San Diego stations, respectively. About two-thirds of the La Jolla dust consists of water-soluble matter primarily composed of sea salts. The gross lead content of the La Jolla dust is 0.09 percent, which corresponds to a lead precipitate of 65 μg/m^2 per day. San Diego dust, about one-third of which consists of soluble matter, contained 0.84 percent lead, equivalent to 950 μg/m^2 per day. On the basis of a comparison of the lead contents in the La Jolla and downtown San Diego dust (0.09 and 0.84 percent, respectively) with those of the lead aerosols in the suspended matter (0.68 and 4.62 percent, as given in Table 1), it is clear that only a fraction of the lead aerosols precipitate out near the source of emissions. The remainder of the lead aerosols are carried in the air currents and spread around the globe (*14*).

A portion of these lead pollutants have undoubtedly been incorporated into plants and animals (*15*). Long-term increases in atmospheric lead concentration will result in predictably higher concentrations of lead in the blood of the exposed populations (*16*). Because of the well-known toxicity of lead, the health hazard of increasing lead pollutants in the environment cannot be ignored.

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17. We thank C. Snyder for technical assistance. Supported by the PHS grant No. 5-R01-AP-00875 and the Office of Naval Research contract No. Nonr 2216(23). This paper was presented at the Symposium on Geochemical Atmospheric Constituents of the American Chemical Society National Meeting in Houston, 25 February 1970.

6 April 1970; revised 25 May 1970

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Gadolinium: Distribution between Aqueous and Silicate Phases

Abstract. *Studies of the partition of trivalent gadolinium between aqueous and silicate phases have been made at temperatures from 800° to 900°C and at pressures from 500 to 1000 bars. Constant values for the distribution coefficients for forsterite, enstatite, and diopside were obtained over a concentration range from 0.6 part per billion to 4 parts per thousand in the solid phases. Ratios of silicate crystal–aqueous phase distribution coefficients to silicate melt–aqueous phase distribution cofficients are close to the values for silicate crystal–silicate melt distribution coefficients estimated from natural systems. The free ion activity of trivalent gadolinium in the silicate melts appears to be less than one-hundredth of its value for aqueous phases of the same concentration.*

The number of thermodynamic parameters that would have to be evaluated in order to predict the behavior of a trace element during solidification of a natural silicate liquid is prohibitive. A promising approach is to measure distribution coefficients for trace elements in the hope that they will be constant over a useful variety of silicate compositions. Such seems to be the case for the rare earth elements since estimates of their distribution coefficients lie within a narrow range. These estimates are derived from studies of several natural systems which include phenocrysts and host matrices treated as equilibrium solid-liquid pairs (*1*), ultramafic rocks and basalts treated as partial melt–residue pairs (*2*), and minerals and estimated residual liquids from the Skaergaard intrusion (*3*). We have obtained laboratory values for distribution coefficients of Gd that are similar to those found for natural systems. Our measurements also show a strong affinity of silicate liquids for that element.

Most of the cations that are essential components of common silicate minerals are mono- or divalent. Entry of Gd^{3+} into one of the silicate structural sites, therefore, requires charge compensation. In natural silicate melts the concentrations of both major cations and possible compensating anions presumably exceed that of Gd by several orders of magnitude. If so, no conceivable distribution of the Gd between the solid phase and its parent liquid will significantly affect the activities of those ions in either phase. The equilibrium distribution of Gd will then be given by the ratio of the activities of that element for the two phases according to Eq. 1

$$K = \frac{A(\mathrm{Gd}^{3+},\ \text{solid solution})}{A(\mathrm{Gd}^{3+},\ \text{liquid})} \qquad (1)$$

where K is a constant.

In this paper we define a distribution coefficient D as the ratio at equilibrium of the bulk concentration of the trace element in the solid to its bulk concentration in the liquid. This distribution coefficient is related to the constant K as follows, where γ represents the activity coefficient of Gd^{3+}

$$K = \frac{\gamma(\mathrm{Gd}^{3+},\ \text{solid solution})}{\gamma(\mathrm{Gd}^{3+},\ \text{liquid})} D \qquad (2)$$