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# Use of Lead Isotopes in Soils To Identify the Source of Lead Contamination Near Adelaide, South Australia

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■ Soil profiles from an urban–rural transect near Adelaide, South Australia, have been analyzed by using lead isotopes as a discriminant for the source of soil lead. Analyses of the top 10 cm of soil profiles taken from sites up to 50 km from Adelaide show that this surface horizon mainly contains Precambrian lead, such as that found in the Broken Hill or Mount Isa deposits. There is also a small amount of younger lead present, similar to that derived from Missouri and young Canadian deposits. Both types of lead are used in the manufacture of tetraethyllead for Adelaide gasoline. Natural soil lead, derived from parent rock, occurs throughout the profiles; however, it is only a relatively minor component in the surface horizons but is the major component at depths greater than 30–40 cm. Assessment of the data suggests that orchard sprays, power stations, and smelters are not the main source of lead in the surface horizons—rather, contamination derived from tetraethyllead from gasoline is indicated.

An ongoing study by the CSIRO Division of Soils of metal cycling in an urban–rural transect east of Adelaide, South Australia, is resulting in the collection of information on soils, plants, stream waters, and atmospheric accession. This transect includes a variety of soils and rocks and is ca. 100 × 30 km. It comprises urban, intensive agricultural, and extensive dryland agricultural environments, as well as an important water catchment.

A survey of surface soils in the transect suggests that, with increasing distance from Adelaide, the concentrations of lead and zinc decrease in the surface horizons, whereas the distributions of copper and cadmium show no such relationship to distance from the city (1). Furthermore, the decrease in concentration of lead with depth in the profiles is more pronounced closer to Adelaide, in the western part of the transect. The higher lead levels in the surface soils nearer to the city were initially considered to be related to the parent rocks and to enhanced biological activity due to higher rainfall. However, more recent investigations suggest that atmospheric fallout may have contributed significantly to the lead present in these surface soils.

Apart from some soils obviously affected by agricultural sprays or mineralization, the range of lead concentrations found in most of the surface soils taken from the transect was not significantly greater than normal.

The aim of the lead-isotope investigation was to determine the sources of the lead found throughout the soil profiles of the transect and, if possible, to evaluate the regional extent of urban pollution.

Four lead isotopes, three of which are the stable end product of the radioactive decay of a parent element, are measured. The radiogenic isotopes are $^{208}Pb$ (from $^{232}Th$), $^{207}Pb$ (from $^{235}U$), and $^{206}Pb$ (from $^{238}U$). The fourth isotope, $^{204}Pb$, has no known radioactive parent.

Since the formation of the earth, the three radiogenic lead isotopes have exhibited a smooth increase in abundance with time compared to the nonradiogenic isotope $^{204}Pb$. The relative increase for each radiogenic isotope is in accord with the rate of radioactive decay of its parent. The various ratios of the isotopes to each other are conventionally plotted in diagrams such as those of Figures 2 and 3. By plotting the ratios of the relatively abundant radiogenic isotopes, for instance, in a diagram of $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$, one can minimize errors that may arise during mass-spectrometry measurements of the less abundant $^{204}Pb$.

The growth curves are also plotted on the diagrams and represent the changing ratios of the isotopes with time in a closed system. In theory this variation in relative abundance is dependent not only on time but also on the Th/Pb and U/Pb ratios of the parent material. However, in practice there are complications, such as the mixing of lead from different sources. On the ratio plots, this is shown by the straight mixing lines.

Each lead–zinc ore body has its own specific set of isotope ratios (i.e., its "isotopic fingerprint"). For example, large "massive sulfide"-type ore bodies—such as those at Mount Isa and Broken Hill in Australia and at Sullivan in Canada—contain lead that has uniform isotope ratios. The isotopic data plot on or near to the growth curves. However, the "Mississippi Valley"-type ore bodies—such as those in Missouri in the United States—are very different and contain lead that has diverse isotope ratios. The isotopic data are of a more radiogenic nature (i.e., $^{206}Pb$, $^{207}Pb$, and $^{208}Pb$ are relatively abundant) and do not plot on the growth curves.

In soils, the lead isotopic data can show even more variable and more radiogenic isotopic patterns than "Mississippi Valley"-type ore bodies.

## Study Area

The study area is shown in Figure 1. It extends from the Adelaide urban area (Adelaide Plains) in the west to the Murray River (Murray Plains) in the east. These regions are predominantly underlain by Quaternary sediments, whereas the central Mount Lofty Ranges, in the center of the area, are underlain by mainly Upper Proterozoic, Cambrian and Ordovician rocks, although a small area is underlain by lower Proterozoic rocks (e.g., at site 694).

Soils are mainly loam, sandy loam, or loamy sand surface soils overlying yellow or red clay B horizons, which vary considerably in depth to weathered rock. Average annual rainfall is largely topographically controlled and varies in amount from ca. 900 to 300 mm. The higher average rainfalls occur on the western side of the Mount Lofty Ranges, declining both to the east and to the west. Frontal rains approach from the west, the prevailing wind direction, and provide the major part of the annual rainfall, ~70–80% of which falls between April and October (2).

Although other winds do occur, the predominant winds in Adelaide during the wet months of the year are from the northwest to southwest direction, both close to the ground and at ~1000 m (Bureau of Meteorology, Adelaide, personal communication). Southwesterly sea breezes predominate during the daytime in the summer months.

## Site Selection

The 12 soil sample sites used in this study are representative of others along the transect and are shown in Figure 1. They were chosen mainly on the basis of surface-soil lead concen-
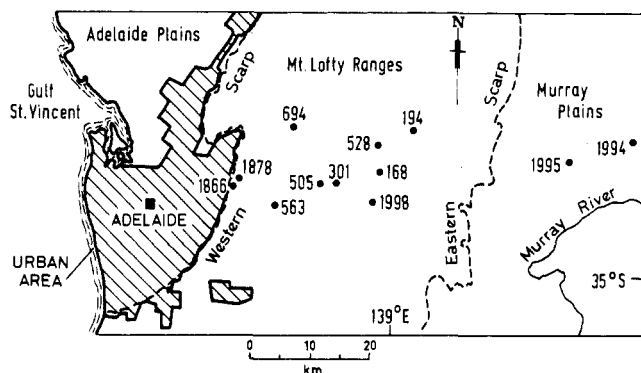
**Figure 1.** Locality map for soil samples from the study area.

tration and for remoteness from busy roads, although the two sites nearest to the Adelaide urban area (1878 and 1866) are closer to roads carrying high traffic volumes. The sites have a westerly aspect (i.e., toward Adelaide) or are unobstructed for a considerable distance in that direction. All sites are in open grassland or pasture (except 694, which is in dry sclerophyll woodland).

The distance of each site to the nearest main road (for which the traffic volume in a westerly direction had been measured in 1974) is shown in Table I. Samples were normally collected at least 50 m from local roads and tracks, which have much lower traffic volumes (less than ~20 vehicles/day) than the nearest main road.

### Soil Sampling

Soil cores were obtained by driving a steel tube (5-cm diameter) to a depth of 1 m, or less if the soil was shallow. The cores either were cut into 10-cm sections immediately on extrusion from the tube and stored in plastic bags or were extruded directly into a plastic sheath for later subsectioning in the laboratory. The individual samples were then dried at 35 °C, ground to pass a 2-mm sieve, and stored in plastic containers before analysis. The sections of the profile selected for isotope analysis were the 10-cm surface, the deepest subsample, and an intermediate subsample, which was taken either from the B horizon, where clearly defined midway down the profile, or from the 30–40-cm section if there was no clearly definable pedological change. Organic matter (such as roots and seeds) present in the surface soil was not separated.

### Techniques

Contaminant lead present in surface soil is more easily removed than the lead in the lower horizons, which is an inherent part of the soil and is tightly bound in minerals such as feldspars. Consequently, for most of our analyses, only dilute HCl was used to extract the lead. To investigate the inherent lead in the whole soil, the sample was attacked with $HF–HNO_3$.

For the acid leaches, ~0.5–1 g of soil was weighed into a 10-mL PTFE beaker. Ca. 3 mL of 1.2 N HCl was added and the mixture stirred overnight (for ~16 h). The material was then transferred in 1.2 N HBr to a 10-mL polypropylene centrifuge tube and centrifuged. In most samples, the supernatant liquid was split: one aliquot was retained for isotope ratios and the other mixed with a $^{207}Pb/^{204}Pb$ spike for concentration measurements and to correct for mass fractionation during mass-spectrometric analysis. The spiked aliquot was evaporated to dryness and taken into solution with ~2–3 mL of 1.2 N HBr and 1 mL of 1.2 N HCl. The solutions were transferred to a 2-mL anion-exchange column (AG 1-X8, 200–400 mesh) previously conditioned with 1.2 N HBr. Washings (10 mL of 1.2 N HBr, 10 mL of 1.2 N HCl) were

discarded, and the lead was eluted with 6 N HCl. A second-stage purification was achieved by anodic electrodeposition.

For some samples, the whole soil or the centrifuged residue from the acid leach was dissolved in $HF–HNO_3$, and the lead leached out with 1.2 N HBr–1.2 N HCl. The lead separation method was the same as that used for the supernatant from the acid leaches.

The lead was analyzed by using the silica gel–phosphoric acid method on an AVCO 35-cm radius 90°-sector mass spectrometer. Data for the preliminary study (which was carried out 18 months prior to the present results) were usually taken with the largest peak $^{208}Pb$ at ca. $1 \times 10^{-11}$–$3 \times 10^{-11}$ A, by using a peak switching unit arranged in the order 206–207–zero–208–zero–204–206. The data from a DANA digital voltmeter were recorded with a Hewlett-Packard printer taking five 20-ms readings per peak. This prototype system was less sophisticated and gave less satisfactory data than the present arrangement, which is under computer control. Also, on occasion, it was difficult to obtain a clean sample for the mass-spectrometric analysis, even with electrodeposition. For a set of 10 ratios, the internal standard deviations were as follows: $^{208}Pb/^{206}Pb$, 0.02–0.2%; $^{207}Pb/^{206}Pb$, 0.03–0.1%; and $^{206}Pb/^{204}Pb$, 0.10–0.3%. Some runs (as indicated in Table II) had a standard deviation of 0.3–0.5% for the $^{206}Pb/^{204}Pb$.

The most recent data were acquired under computer control and with small changes in the chemical separation method. Two to four blocks of 16 ratios, measured in the sequence 206–204–206–207–206–208–206, typically gave the following standard errors of the mean: $^{208}Pb/^{206}Pb \leqslant 0.01\%$; $^{207}Pb/^{206}Pb \leqslant 0.02\%$; and $^{206}Pb/^{204}Pb \leqslant 0.1\%$. Eight analyses of the National Bureau of Standards SRM 981 over a 2-week period gave the following results, expressed as standard error of the mean: $^{208}Pb/^{206}Pb = 0.005\%$; $^{207}Pb/^{206}Pb = 0.02\%$; $^{206}Pb/^{204}Pb = 0.035\%$. The results in Table II were normalized to SRM 981 and Broken Hill lead. Processing blanks ranged from 8 to 12 ng of lead.

### Results

In view of the number of data in Table II, and to avoid confusion, we have plotted only representative sites and usually the highest-precision data in Figures 2 and 3. Mixing lines are drawn in these figures to join isotopic values of Broken Hill–Mount Isa and Missouri ("Mississippi Valley")

# Table II. Lead Isotopic and Concentration Measurements for Soils from Urban–Rural Transect [f]

| sample no. [a] | depth, cm | treatment | Pb [b] µg/g | $^{208}Pb/^{206}Pb$ | $^{207}Pb/^{206}Pb$ | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ |
|---|---|---|---|---|---|---|---|---|
| | | | | Mt Lofty Ranges Profiles | | | | |
| 694/1 [c] | 0–10 | AL | 47 (53) | 2.1026 | 0.8414 | 18.87 | 15.87 | 39.67 |
| /4 [c] | 30–40 | AL | 25.6 (25) | 2.0600 | 0.8042 | 19.84 | 15.96 | 40.87 |
| /7 [c] | 60–73 | AL | 28.9 (24) | 2.0475 | 0.7980 | 20.06 | 16.01 | 41.07 |
| /7 [c] | 60–73 | WS | 14 | 1.9937 | 0.7782 | 20.94 | 16.30 | 41.75 |
| 1878/1 | 0–10 | AL | 25 (30) | 2.1793 | 0.9140 | 16.964 | 15.505 | 36.970 |
| /4 | 30–40 | AL | 10 (10) | 2.1159 | 0.8510 | 18.395 | 15.654 | 38.922 |
| /9 | 80–93 | AL | 16 (12) | 2.0755 | 0.8051 | 19.717 | 15.874 | 40.923 |
| 1866/1 | 0–10 | AL | 23 (15) | 2.1925 | 0.9322 | 16.469 | 15.352 | 36.108 |
| /4 | 30–40 | AL | 3.1 (—) | 2.1611 | 0.9074 | 17.041 | 15.463 | 36.827 |
| /6 | 50–57 | AL | 2.2 (1.6) | 2.1221 | 0.8751 | 17.732 | 15.517 | 37.629 |
| 563/1 [cde] | 0–10 | AL | (21) | 2.183 | 0.915 | 16.98 | 15.54 | 37.06 |
| /1-1 [cd] | 0–10 | AL | (21) | 2.172 | 0.910 | 17.08 | 15.55 | 37.09 |
| /1-2 [c] | 0–10 | AL | (21) | 2.1769 | 0.9112 | 17.02 | 15.51 | 37.05 |
| /1-2 [cd] | 0–10 | res | 10 | 2.124 | 0.848 | 18.57 | 15.75 | 39.44 |
| /1-3 | 0–10 | AL | 23 | 2.1760 | 0.9097 | 17.061 | 15.520 | 37.125 |
| /1 [c] | 0–10 | WS | | 2.1538 | 0.8847 | 17.65 | 15.62 | 38.02 |
| /4 [c] | 30–40 | AL | (3.6) | 2.1344 | 0.8349 | 18.75 | 15.65 | 40.01 |
| /6 [cd] | 50–60 | AL | (2.3) | 2.140 | 0.854 | 18.52 | 15.82 | 39.63 |
| /6 [cd] | 50–60 | WS | | 2.119 | 0.820 | 19.34 | 15.86 | 40.98 |
| 168/1 | 0–10 | AL | 13 (12.5) | 2.1901 | 0.9272 | 16.686 | 15.471 | 36.544 |
| /3 | 20–30 | AL | 10 (11.0) | 2.1532 | 0.8977 | 17.230 | 15.467 | 37.100 |
| /9 | 80–90 | AL | 6.4 (3.7) | 2.1062 | 0.8516 | 18.025 | 15.350 | 37.964 |
| 301/1 [c] | 0–10 | AL | (12.7) | 2.1785 | 0.9260 | 16.75 | 15.51 | 36.49 |
| /4 [c] | 30–40 | AL | (3.8) | 2.0963 | 0.8422 | 18.95 | 15.96 | 39.72 |
| /10 [c] | 90–100 | AL | (3.9) | 2.0867 | 0.8283 | 19.06 | 15.79 | 39.77 |
| /10 [c] | 90–100 | WS | 13.8 | 2.0833 | 0.8253 | 19.68 | 16.24 | 41.00 |
| 528/1 | 0–10 | AL | 4.2 (3.9) | 2.1871 | 0.9254 | 16.684 | 15.439 | 36.490 |
| /5 | 40–50 | AL | 2.3 (2.1) | 2.0976 | 0.8531 | 18.287 | 15.601 | 38.359 |
| /9 | 80–90 | AL | 1.9 (0.8) | 2.0868 | 0.8469 | 18.376 | 15.563 | 38.347 |
| 194/1-1 [c] | 0–10 | AL | 3.0 (3.1) | 2.1608 | 0.8896 | 17.23 | 15.33 | 37.23 |
| /1-2 [c] | 0–10 | AL | (3.1) | 2.1590 | 0.8875 | 17.55 | 15.58 | 37.90 |
| /3 [c] | 20–30 | AL | 1.9 (1.1) | 2.0690 | 0.7712 | 20.48 | 15.80 | 42.38 |
| /10 [cd] | 90–100 | AL | 1.3 (0.73) | 2.057 | 0.758 | 21.18 | 16.06 | 43.58 |
| /10 [c] | 90–100 | WS | | 2.0659 | 0.7686 | 20.49 | 15.75 | 42.33 |
| | | | | Background Profiles | | | | |
| 1994/1 | 0–10 | AL | 2.4 (2.5) | 2.0869 | 0.8424 | 18.504 | 15.588 | 38.616 |
| /4 | 30–40 | AL | 1.2 (—) | 2.0542 | 0.8193 | 19.006 | 15.572 | 39.042 |
| 10 | 90–100 | AL | 2.1 (2.4) | 2.0647 | 0.8243 | 18.955 | 15.625 | 39.136 |
| 1995/1 [d] | 0–10 | AL | 3.6 (3.5) | 2.0924 | 0.8486 | 18.34 | 15.56 | 38.36 |
| /4 [d] | 30–40 | AL | 2.9 (—) | 2.0523 | 0.8129 | 19.21 | 15.62 | 39.43 |
| /10 [d] | 90–100 | AL | 1.5 (2.4) | 2.0682 | 0.8319 | 17.55 | 14.60 | 36.30 |
| | | | | Orchard soil | | | | |
| 505 | 0–10 | AL | 240 (265) | 2.2174 | 0.9524 | 16.171 | 15.401 | 35.858 |
| | | | | Mineralized Profile | | | | |
| 1998/1 | 0–10 | AL | 130 (120) | 2.1385 | 0.8780 | 17.716 | 15.554 | 37.886 |
| /5 | 40–50 | AL | 220 (190) | 2.1412 | 0.8765 | 17.813 | 15.613 | 38.141 |
| 10 | 90–100 | AL | 300 (340) | 2.1428 | 0.8774 | 17.791 | 15.610 | 38.123 |

[a] 1-1, 1-2, etc., replicate analyses. [b] Concentrations in parentheses are by 1 N HCl extraction, 16 h, 10 g of soil with 25 mL of HCl, analyzed by atomic absorption. [c] Data from preliminary study. [d] Analyses with standard deviation of 0.3–0.5% for $^{206}Pb/^{204}Pb$. [e] Stirred 5 h longer than 563/1-1 and 563/1-2. [f] AL = acid leach; WS = whole soil; res = residue.

lead (3). Part of the growth curve for "massive sulfide" deposits is also drawn (4).

**Profiles from Mount Lofty Ranges.** Profiles from eight sites in the Mount Lofty Ranges were chosen to evaluate the extent of possible urban pollution. These profiles (168, 194, 301, 528, 563, 694, 1866, and 1878) are located at varying distances from Adelaide and have differing lead concentrations. They conform to a fairly standard pattern: (1) The lead concentration is usually highest in the top 10 cm of soil and decreases by 3–4 times in the middle and lower parts of the soil profile. (2) The lead isotope ratios become more radiogenic with depth, approaching the ratio expected of the parent rocks (i.e., higher in $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios or, conversely, lower in $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$). (3) The samples from each profile give results that lie on well-defined arrays, the goodness-of-fit being better for the more recent, higher-quality data than for the preliminary data (Figures 2 and 3, Table II). (4) The arrays intersect the Broken Hill–Missouri mixing line and the growth curve over a restricted range of isotopic ratios. (5) The slopes of most of these arrays depart significantly from those for the Broken Hill–Missouri mixing line and the growth curve, which suggests that the lead in these samples is not a simple mixture of lead from different ore bodies, such as from Broken Hill and Missouri.
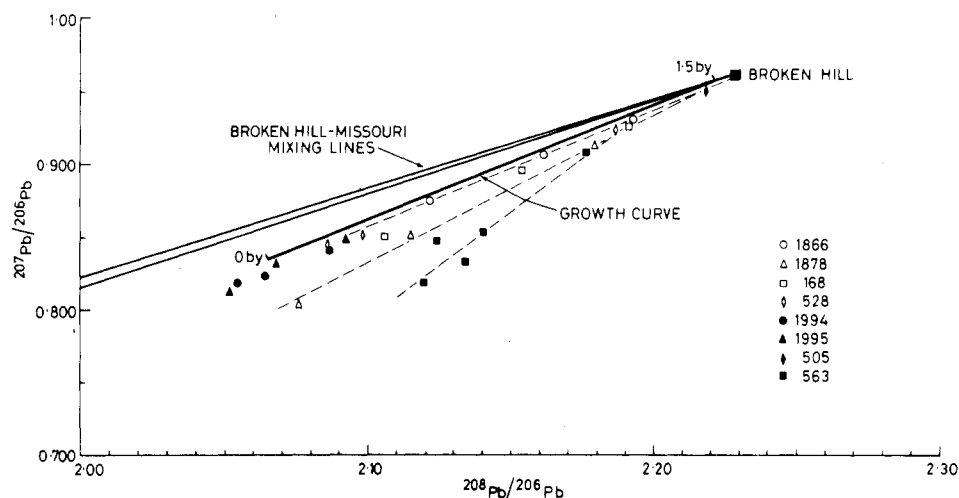
**Figure 2.** $^{208}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ diagram for representative soil profiles. The growth curve is taken from Cumming and Richards (4), and the Missouri data were taken from Sverjensky et al. (3). Dashed lines (eyeball fit) are the mixing lines between natural soil and contaminant leads.
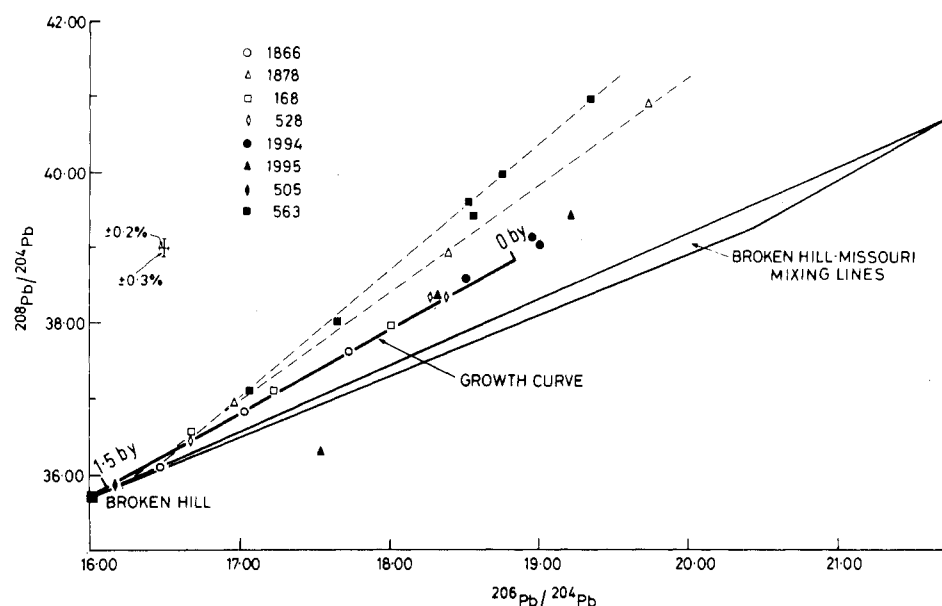


**Figure 3.** $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram for representative soil profiles. The growth curve is taken from Cumming and Richards (4), and the Missouri data were taken from Sverjensky et al. (3).

The data clearly suggest that the surface soils in these profiles contain significant amounts of Precambrian lead from Broken Hill or Mount Isa, with a small amount of some younger lead, perhaps from Missouri or Canada. (No tetraethyllead is manufactured in Australia; both Missouri and Canadian lead—in addition to lead from Broken Hill and Mount Isa—are used to make tetraethyllead for the Australian market.) They also show that contamination of soil with this lead takes place up to at least 50 km east of the coastline at Adelaide. Calculations indicate that the Australian ore component of this contaminant lead is ~80–85% when based on Broken Hill lead ratios. The lead isotope ratios obtained from the soil profiles are essentially mixing lines of soil and contaminant Pb.

That the lead in the soils is a mixture of contaminant and soil lead is well illustrated by profile 563. The acid-leach data for the top 0–10 cm of 563/1 (the horizon with the highest· amount of extractable lead) lie close to the growth curve (Figures 2 and 3). Deeper in the soil profile, the lead concentration decreases to 3.6 and 2.3 $\mu g/g$, and the data become more radiogenic. This trend would be expected of the natural soil lead, which developed in a higher U/Pb and Th/Pb environment than ore lead.

The proposal that lead in surface soils has a component of

contaminant lead is further substantiated by whole-soil data and the residues from the acid leach. For 563/1, the data for acid leaching, whole soil, and residue lie approximately on a mixing line of contaminant and natural soil lead, with the residue, stripped of contaminant Pb, being more radiogenic than the acid leach or whole soil.

The whole-soil data for 694/7, 563/1, 563/6, and 301/10 (but not 194/10) are more radiogenic than their acid-leach counterparts, as expected for natural soil lead. In the case of the deepest samples, the whole-soil data (natural soil lead) define one end member of a mixing line, the other end member being the acid-leach values (contaminant lead) for the 0–10-cm samples.

The linearity of the lead-isotope data for the various profiles indicates that the soils throughout an individual profile had been weathered from source rocks of uniform isotopic composition. Local or regional transport of material of similar isotopic composition cannot be ruled out.

No relationship appears to exist between the lead isotope ratios and concentrations of lead in surface horizons or at lower depths. For example, in those soils nearest Adelaide, profile 1866 with the low lead values of 2–3 $\mu g/g$ (Table II) is less radiogenic and shows less dispersion (i.e., less variation of lead isotopes throughout the profile) than profile 1878,

which has 10–16 μg/g in the lower horizons. These differences are probably influenced by soil type. In profile 1866, a sandy, light-textured soil, leaching is possible to a greater depth than in profile 1878, which has a massive, heavy clay subsoil at 30 cm. In general, for a given input of contamination, the sandier soils (which tend to have both the lowest lead contents and the greatest potential for leaching) should exhibit the largest shifts toward the Broken Hill–Missouri mixing line or the growth curves.

A more general relationship describing the variation of radiogenic character of soil horizons cannot be established for the limited number of samples available, because of the extent of aerial contamination of lead, site-specific variations in original lead content of the soil, and soil properties affecting leaching. For example, profile 694 occurs in an area of high expected levels of contamination but also has high lead contents arising from the parent rocks. These lead concentrations are so high that contaminating lead does not markedly affect soil lead levels. Surface horizon isotopic data for profile 694 are thus closer to those of the lower horizons and do not exhibit the expected substantial shift toward the Broken Hill–Missouri mixing line. Despite the apparent anomalies, the majority of sites sampled in the Mount Lofty Ranges clearly indicate that there has been significant accession of aerosol lead.

**Background Profiles.** Site 1994 is an agricultural soil with calcareous subsoil on recent sediments and is farthest from Adelaide and remote from frequently used roads. The three samples from this profile contain 1–2 μg/g lead (Table II) and have radiogenic lead isotope ratios.

Site 1995 is also remote, but its soil has developed on metamorphosed granites. The data are similar to those for 1994, although more variable, perhaps reflecting a greater heterogeneity of lead in the source rocks or the contribution of other materials to the low lead levels present in the soil horizons. The surface soil could be expected to be similar to 1994, but at a depth of 90–100 cm it is quite different. In contrast to 1994, the acid-leachable lead concentrations of 1995 decrease down the profile from 3.6 to 1.5 μg/g.

The isotopic data for these two profiles suggest that they are uncontaminated, in that the analyses do not lie along mixing arrays but tend to form a cluster in the uncontaminated section of the soil mixing arrays (Figures 2 and 3). That is, their isotopic patterns are consistent with the deeper uncontaminated parts of the soil profiles from the Mount Lofty Ranges.

**Mineralized Profile.** Site 1998 is a lateritized soil (podzol) overlying the Nairne pyrite unit. Lead concentrations in the surface soil range from 130 to 300 μg/g. At the surface the mineral hinsdalite (Pb, Ba, Al phosphosulfate) is common, while at depth (up to 2 m) hinsdalite and lead sulfide occur (5). Lead isotopic ratios (Table II) are uniform, plot close to the growth curve, and are thus consistent with known "massive sulfide" deposits.

*Sources of Contamination*

The lead isotopic data from the soil profiles lie on mixing arrays whose end members are soil lead and contaminant lead. Intersection of the arrays on various isotopic plots allows the isotopic ratios of the contaminant lead to be obtained, so that its source can be determined.

The intersection of the arrays is close to Broken Hill–Mount Isa lead (Figures 2 and 3), but there is a small component of more radiogenic (probably younger) lead present. Calculations indicate that the Australian ore component of the contaminant lead is ~80–85% when based on Broken Hill isotope ratios. A number of possible sources could give contaminant lead with this isotopic signature: agricultural sprays, lead smelters, thermal power stations, and gasoline additives.

**Agricultural Sprays.** For many years, orchards in the study area have been sprayed with lead arsenate for control of various insect pests. It is conceivable that the contamination observed in some surface soils in the study area originates from this spray. The lead in the spray, manufactured in Australia, was undoubtedly from Broken Hill or Mount Isa.

The lead concentration for the orchard soil sample used in this study was 240 μg/g, but values of up to 600 μg/g have been measured (6). The lead isotope ratios for the orchard soil differed by less than 1% from Broken Hill lead (7) and less than 0.5% from Mount Isa lead (8). These small differences between the orchard soil ratios and those of Broken Hill and Mount Isa lead probably reflect a minor contribution from soil lead in the orchard soil (probably no more than 15–20 μg/g).

All of the arrays for contaminated samples intersect at, or very close to, the orchard-soil value. This may indicate that the samples are at least partly contaminated with lead arsenate spray, but there are several other factors to be considered:

(1) The main orchard area lies to the south and southeast of the study area, but the prevailing wind direction is from the northwest and southwest.

(2) Lead arsenate is no longer used as a commercial insecticide. Also, its total usage in the Mount Lofty Ranges is negligible in comparison to the amount of lead from automobile emissions in the Adelaide metropolitan area (in which there were 615 486 registered automobiles in 1975; data from the South Australian Department of Transport). In addition, lead accession to the area is a current phenomenon (1).

(3) Soil analyses from pastures adjoining the orchards suggest that lead from sprays does not drift more than ~30–50 m (1).

**Lead Smelters.** Lead smelters are another possible contaminating source. The feed stock for the Port Pirie smelter (which began in 1889 and is ~200 km NNW of Adelaide) is mainly Broken Hill ore. A detailed investigation by Cartwright et al. (9) showed that the greatest contamination from heavy metals is in the prevailing wind direction, and only background concentrations of lead can be measured beyond ~40 km from the smelter. The prevailing surface wind (at 2 m above ground level) direction in this area is from the south, with a component from the north (9). However, heavy-metal contamination is also significant in the hilly area to the east of the smelter, because of the prevailing high-level westerly winds (9).

**Thermal Power Stations.** Thermal power stations are another possible source of lead. However, in view of the young age of the coal used in power stations (compared with the Precambrian age of the major contaminant lead) and the expected radiogenic lead isotopes in coal (10), they are not considered a major source.

**Gasoline Additives.** On a worldwide basis, almost all of the isotopic data for gasoline additives (11) lie on the fan between the Broken Hill–Missouri mixing lines and the growth curve. Most of the tetraethyllead added to gasoline at the Port Stanvac (Adelaide) refinery is manufactured by a company that uses mainly Broken Hill and Mount Isa lead, with some Canadian lead. The isotopic ratios of this tetraethyllead are consistent with those estimated from the intersection of the arrays in Figures 2 and 3, but they are also consistent with the presence of up to 20% Missouri lead in the contaminant.

As it is impossible to obtain precise information on the isotopic composition of tetraethyllead used in Australia over a long time period, we can only conclude that, at the present stage of our investigation, gasoline additives appear to be the major source of contamination.

In fact, the absence of significant sources of contaminant lead other than automobile exhaust in the Adelaide metro-

politan area provides a unique opportunity to assess the spread of urban pollutants into adjoining areas. The long-range transport of the finest lead aerosols is exemplified by studies of accumulation of lead in the Greenland icecap (12) and by estimates of the long atmospheric residence times (7–30 days) of lead (13). The very short-range transport (less than 100 m) of coarser lead particles away from highways is also well documented. Intermediate-range transport of lead aerosols arising from automobiles is not as well understood, but Reiter et al. (14) concluded that nearly half of the lead emitted from automobiles was still airborne at the perimeter (>20 km) of their urban study area. Chow and Johnstone (15) showed that the high concentrations of lead in snow at the Lassen Volcanic National Park were derived from gasoline aerosols probably transported from San Francisco.

The spread of automobile lead aerosols with atmospheric residence times of some hours, and the precipitation of lead as dust or by rainfall, should indicate the potential for dispersal of many other urban pollutants which are emitted into the atmosphere. Because of the limited mobility of lead in soils, levels of contaminant lead in soils provide an approximation of the historic record of the extent of pollutant fallout. This approach was used by Cartwright et al. (9) in their assessment of accumulated fallout of heavy metals around a lead–zinc smelter in South Australia. The current isotopic study shows that surface soils are contaminated with lead at distances of ~50 km east of the city in the general direction of the prevailing winds. In other situations, this distance would be influenced by local topography and climate.

### Comparison with Other Isotope Studies of Soils

Ault et al. (16) analyzed surface samples across the New Jersey Turnpike, in a rural area approximately midway between New York City and Philadelphia. The isotope ratios of the topsoil close to the turnpike were less radiogenic (i.e., more similar to those measured for tetraethyllead) than samples more than 150 m from the turnpike. Soil samples from a depth of 12.5 cm had very similar isotope ratios to surface soils, implying further contamination at greater depths. The isotopic ratios of samples from a forested area in the Ringwood State Park, away from major roads, at depths of 0–2.5, ~19, and ~39 cm, showed trends similar to those observed in our samples. That is, isotope ratios of surface soils are more akin to those measured for lead in gasoline additives, but the ratios become progressively more radiogenic with depth and resemble those of the parent rock.

Rabinowitz and Wetherill (17) carried out a detailed study in southern Missouri and California, where they found that, although the lead concentrations from hot 6 N HCl acid leaches decreased 13 cm beneath the surface, the isotopic data showed no consistent trend. However, because some of the deeper soils were more radiogenic than the surface samples, they suggested that the surface soils were contaminated by automobile exhaust.

The data of Chow et al. (18) for Californian sediments show similar trends to our data. Their isotopic data for the top layers lie close to a "pollution line" plotted from isotopic data

for lead ores and gasoline additives (11). Also, Chow (19) had earlier sampled soils adjacent to major highways in the United States. He found that the 7 N HCl leaches of the 10–15-cm profile had a lower lead concentration and were more radiogenic than those of the 0–5-cm profile. Our data are consistent with this finding.

### Conclusions

A lead-isotope study of soil profiles on an urban–rural transect extending east from Adelaide, South Australia, suggests that, up to ~50 km from Adelaide in the prevailing westerly wind direction, the top 10-cm horizon at least is contaminated with lead from gasoline additives. The data indicate that appreciable lead contamination does not extend deeper than 30–40 cm. Using automobile lead as an indicator of urban pollution, this study indicates that pollutants have spread at least 50 km from their source.

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