Source of lead in humans from Broken Hill mining community

by

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Editorial Board

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Abstract

This paper documents the first precise lead isotope measurements for men, women and children from the same family in an attempt to determine the source of lead in their blood. The subjects reside in one of the world's largest lead mining cities, Broken Hill, NSW, Australia. Biological and environmental samples have been compared using isotopic compositions and lead contents. Adult males have isotopic profiles (or compositions) which appear to be related to their occupations. Adult females have low blood leads (<10 $\mu g\ dL^{-1}$) and their main source of lead is not from the mine dumps around which the city is built but probably from a mixture of petrol, food and perhaps water.The blood lead contents in children from 1 to 14 years old vary and are partly dependent on age. There is a moderate correlation of blood lead and isotopic compositions (r = 0.73) indicating that a significant component of blood lead derives from the mine dumps in children with elevated blood leads. Some children with blood leads <20 $\mu g\ dL^{-1}$, however, also have a dominant component of mine lead in their blood

Keywords: Blood lead level, isotope measurement, lead mining community.

Introduction

Most investigations of the correlations between blood lead (PbB) and environmental lead have focussed on urban environments and point sources such as lead smelters (see references in, for example, the ATSDR report to Congress, 1988). Few studies have addressed the problem around lead mining centres (*e.g.,* Barltrop *et al.,* 1974, 1975; Barltrop and Strehlow, 1988; Heyworth *et al.,* 1981; Gallacher *et al.,* 1984; Bornschein *et al.,* 1988; Moffat, 1989; Cotter-Howells and Thornton, 1991).

This research addresses the problems of the source of lead, especially in mothers and their children, from one of the largest lead-zinc-silver mines in the world, Broken Hill. Broken Hill is a city of about 25,000 people located about 930 km west of Sydney. It is an isolated desert area subject to intense dust storms. It has operated for over 100 years, initially as shallow mining and smelting and later in an underground mode. During the past 20 years the tailings dumps and oxidised surface ore have been reprocessed resulting in an increased volume of fine-grained lead-rich dust (containing up to 3% Pb) available for wind- dispersion. Broken Hill is an ideal site for investigation because of its isolation and the probable major source of lead pollution is easily identified as the city surrounds the mine dumps.

Our interest in Broken Hill arose from media publicity of the results of a PhD student at the University of Adelaide. In this study, Van Alphen showed that the ceiling dusts in a number of houses from Broken Hill were up to 100 mm thick and contained up to 3.6% Pb, along with elevated levels of other metals such as zinc and cadmium (personal communication, 1991). He attributed the source to the mine dumps. At about the same time, Donald Howarth and a colleague identified three cases of the extremely rare condition, delayed visual maturation of the optic nerve. These subjects resided in houses undergoing renovation during their mothers' pregnancy and it was suggested that exposure to elevated sources of lead may have been one of the factors contributing to the condition. Because of the probable single point source of lead and its well-documented isotopic composition, Broken Hill was considered to be a potential site for inclusion in an ongoing project "Biokinetics of Lead in Human Pregnancy".

The publicity, combined with reports of the high incidence of dogs dying from lead poisoning, led to a blood lead survey of children aged from 1 to 4 years by the NSW Department of Health. Of 600 children tested so far, over 25% have PbB >25 $\mu g\ dL^{-1}$ (S. Corbett, personal communication, 1991).

To evaluate the source of lead we have used the lead isotope fingerprinting method. Lead has four isotopes, 208, 207, 206 and 204, which vary in abundance depending on their geological and/or industrial source. The abundances ("fingerprint", signatures, isotopic composition or profiles) are generally expressed in terms of ratios such as

Figure 1 *Blood lead vs isotopic value ($^{206}Pb/^{204}Pb$) showing .possible mixing relationships between the mine Pb and other sources of lead. On such a diagram, mixing between two end-members is a hyperbola.*

$^{206}Pb/^{204}Pb$; a $^{206}Pb/^{204}Pb$ value of 16.0 found, for example, in the Broken Hill mines, means that the abundance of ^{206}Pb is 16 times that of ^{204}Pb.

The lead isotope fingerprinting method makes use of the fact that the abundance of the isotopes of Pb from one geological source can be quite different to the abundance of the isotopes from another geological source. For example, the Pb from the Broken Hill zinc-lead-silver ores has a totally different profile (a $^{206}Pb/^{204}Pb$ of 16.0) to that of Pb,

from say, the Rosebery ores on the west coast of Tasmania ($^{206}Pb/^{204}Pb$ of 18.3). The profiles or abundances of the Pb ores are also usually quite different from those of Pb in the common rocks which surround the mineral deposits.

In using the fingerprinting method for determining the source of Pb in, for example, people, the Pb isotope profiles in blood and/or urine are compared with those found in the potential environmental sources such as air, food, water and dust. In simple terms, the closer the similarity in isotope profiles between that in blood and an environmental source or sources indicates that the environmental source may be a significant contributor to the Pb in blood. In practice, the isotope profiles are mixtures of lead from a number of sources. Simple mixing relationships are shown in Figure 1 where one major potential source is the mine lead and 100% of this end member will lie on or close to the value of the ore (16.00 ± 0.02) and may be close to a PbB of 25 μg dL⁻¹. The 0% end member for the mine lead is assumed to approximate the female with the lowest PbB of 2.8 μg dL⁻¹. Because of the potential number of 'other sources', the relationships are more diffuse. However, for simplicity, if a 0% end member for other sources is assumed to intersect the 0 - 16.0 point and the 100% end member is placed at 25-17.0 point then combining the mine lead and 'other sources' on the graph in Figure 1 gives the mixing

Figure 2 *Sketch of Broken Hill city showing locations of houses/subjects sampled with respect to the mining activities in the centre of the city.*

relationships between the two main source groups. A simple two- component mixing on the diagram is a well-defined hyperbola, or on a $^{206}Pb/^{204}Pb$ vs $1/PbB$ is a straight line (Faure, 1986).

The aims of this research are:

(1) To compare the lead isotopic profiles and lead contents in blood and urine from women and children, especially of the same family, as a guide to current and perhaps past exposure.

(2) To compare the lead isotopic profiles and lead contents in the subjects with environmental samples, to assess the sources of lead in the biological samples.

(3) To assess the reliability of urine compared with blood as an indicator of current and past exposure of lead for potential serial testing of infants. Ongoing investigations involve lead isotopic measurements of deciduous teeth profiles to determine past exposure in early childhood and speciation of the lead in dusts using SEM, XRD and 0.12M HCl leaching methods. These preliminary results were presented at a symposium on "Lead in Adults" held at Research Triangle Park, North Carolina, in December 1991

Methodology

Sample collection

Early subjects were recruited on a voluntary basis when attending Donald Howarth's surgery. The intention was to obtain an estimate of the isotopic profiles for 10 women of child-bearing age in Broken Hill as a possible prelude for recruitment into the project on "Biokinetics of Lead in Human Pregnancy". Following the media publicity, later volunteers were mainly families that expressed concern for their children and/or fitted the criterion that they had been renovating their houses when the children were young, or the children had demonstrated excessive hand-to-mouth activity. Presently 14 families consisting mainly of mother and child(ren) are enrolled. The other subjects are four fathers from the same families and 10 female adults. The families are of varying socio-economic status and are located randomly throughout the city (Figure 2).

.(a) *Blood*: Venous blood samples were collected in Donald Howarth's surgery following a rigorous protocol which involved washing the arm with soap and water, swabbing with alcohol, rinsing with MilliQ water, and drying with a Kleenex tissue; disposable gloves were worn during the operation. Needles and syringes of the same brand that had been tested earlier for Pb contents were used for venipuncture. One to 5 ml of blood was placed into a cleaned Savillex Teflon vial without Heparin or EDTA and immediately frozen.

(b) *Urine*: Spot urine samples were collected by the subjects in their homes into cleaned 125 mL polyethylene containers and also frozen. Prior to lead isotope analysis, a sub-sample was taken for creatinine determination.

(c) *Water*: Cold water from the kitchen faucet was collected in cleaned 125 ml polyethylene bottles after a 30 second flush. Early samples were not acidified with 1% nitric acid. Acidification of these samples after >6 months showed them to have the same lead isotopic compositions but the lead content doubled; at the low levels measured in the waters, these changes do not affect the conclusions.

(d) *Ceiling dust*: Was scraped into plastic bags. Sub-sampling of the upper and lower parts of the dust accumulations to evaluate any historical changes showed there to be no isotopic variation with time.

(e) *Vacuum cleaner dust*: This dust was an integration of that removed from the floor over periods from days to weeks. Part of the contents was shaken into plastic bags. No attempt was made to size or pulverise the sample.

(f) *Kitchen wipes*: This dust was collected onto a ~75x75 mm acid-washed polyethylene sheet from bench tops, window ledges, refrigerator tops or anywhere dust fall-out had taken place in the kitchen.

Sample preparation

All operations were carried out in a "clean" laboratory in Class 100 laminar flow work bench stations. Biological samples (blood, urine, food) were digested in double quartz-distilled nitric acid in a microwave oven. After digestion, the lead was separated in a 0.5 cm^3 bed volume of AG1-X4 anion exchange resin in 1M HBr medium. Further purification was achieved using the same acid in a 0.1 cm^3 bed volume of AG1-X8 anion exchange resin. Approximately 50 mL water was evaporated to dryness under a clean nitrogen flow and then treated in the same manner as for the biological samples. Vacuum cleaner and ceiling dust were leached with clean 7M HNO$_3$/7M HCL for ~1 hour; the kitchen wipes and air filters were leached with the same acid in an ultrasonic bath for ~15 minutes. Lead was separated using a 0.5 cm^3 resin bed as for the biological samples. Further purification of the lead was achieved using anodic electrodeposition.

Lead content

Was measured by isotope dilution mass spectrometry for all samples except the ceiling dusts and kitchen wipes. A 46% pure ^{202}Pb solution, whose isotopic composition and concentration were accurately known, was added to the samples prior to digestion.

Isotope ratios

Were measured on a solid source thermal ionisation mass spectrometer (Isomass 54E) in fully automatic mode. The precision of the measurements is discussed in the following section on Quality Control. To allow interlaboratory comparisons, the data have been normalised to National Bureau of Standards SRM 981 Common Lead Standard and SRM 982 Equal Atom Standard by applying a

correction of + 0.08% per mass unit.

Quality control

Because of the absence of international biological standards for lead isotopic compositions, quality control is maintained through a number of approaches

.*(a) Replicate analyses*: An estimate of the precision of the lead isotopic ratios (and lead contents) in blood and urine is obtained from duplicate analyses of blood and urine samples from different subjects.

(b) Blood/urine pairs: Additional quality control can be gauged from the isotopic analyses of blood/urine pairs from the same subjects. Such analyses incorporate not only the laboratory errors but also a component of contamination arising from sample collection, a potential problem especially for urine. Good agreement for blood/urine pairs has been obtained for > 30 females and children from Broken Hill.

(c) Serial testing of blood/urine: Probably the best estimate of the precision of the isotopic analyses can be obtained from weekly urine and monthly blood samples of a 49 year-old male subject. These data include sampling and laboratory errors, the latter encompassing measurements by 2 analysts and probably reflect the optimum estimate of analytical precision currently in the CSIRO laboratories. From 21 separate urine measurements, the mean and standard deviation of the $^{206}Pb/^{204}Pb$ ratio is 16.745 ± 0.022 (1 σ).

(d) NBS SRM 981: To minimize interlaboratory bias, an aliquot of the NBS Common Lead Standard SRM 981 is analysed with each batch of samples, *i.e.* almost on a daily basis. Over 1,600 measurements of SRM 981 have been accomplished over an 11 year period with up to nine different operators. The analysis of this standard allows comparisons to be made between different laboratories around the world.

(e) CH-6 Quality Assurance Program: CSIRO participates in the Standards of Australia CH-6 Pb and Cd in blood program each month, in which porcine blood is "doped" with varying amounts of Pb and Cd. Unfortunately, the amounts of Pb are >10 $\mu g \, dL^{-1}$.

(f) Duplicate sampling and analysis for lead content: Some children (n=6) were re-sampled and lead contents measured according to the protocol outlined above, the day after having a sample taken by the NSW Health Commission and whose lead content was measured by graphite furnace AAS in the Adelaide Childrens Hospital. Excellent agreement was obtained for these trials.

Results and Discussion

Lead sources

The major point source of lead in Broken Hill is attributed to the mining operations, especially the mine dumps. The lead isotopic compositions of the Broken Hill mines and mineral occurrences in the surrounding areas are well-documented (*e.g.* Reynolds, 1971; Gulson, 1984). Analyses of sulfide minerals (n=33) from different parts ('lodes') of the Broken Hill deposit show it to have a uniform isotopic composition with the $^{206}Pb/^{204}Pb$ values of 16.00 ± 0.02 and that the oxidised surface material has the same isotopic compositions as the primary sulfide ore (Gulson and Mizon, 1979). Although lead- rich ore of a different geological origin and isotopic compositions ('Thackaringa' ore) from outside of Broken Hill was processed in the early history of the city, its contribution to the lead budget is insignificant (*e.g.* estimated 100's of thousands of tonnes of Thackaringa ore was processed compared with > 120 M tonnes of the main Broken Hill lodes). The limited contribution of the Thackaringa ore to the lead budget is confirmed from the analyses of ceiling dusts which, in many cases, provide a historical record of lead production in the city; the lead isotopic compositions of the dusts shows them to be overwhelmingly from the main Broken Hill lodes, as discussed in the following section.

House dust

Encompasses windblown dust in the ceilings, vacuum cleaner dust, and surface dust especially from the kitchen.

Ceiling dust is a potential major source of contamination because of the old nature of the houses and the dust is easily disturbed during renovations. The lead isotopic compositions of the dust were measured for 10 randomly located houses, only one of which coincides with the biological samples, because the dust measurements were made prior to the major study. The lead isotopic compositions of eight of the 10 dusts lie within the range measured for the mine lead, *i.e.* the $^{206}Pb/^{204}Pb$ ranges from 16.00 to 16.02, and could be attributed solely to a source from the mine. The other two houses are located within 2 km of the mine dumps and although their $^{206}Pb/^{204}Pb$ values are slightly higher at 16.08 and 16.16, the dominant proportion (>80%) of lead is attributed to mine dust. Preliminary lead speciation using SEM, XRD and HCl methods indicate that much of the lead in the ceiling dusts is a complex Pb Fe Ca P Al Si "mineral" with rare galena. The complex material is a weathering product of the primary ore. XRD analyses indicate that >90% of the dusts consist of minerals common to the surrounding country rocks (*e.g.* quartz, feldspar, sillimanite, Fe and Mn oxides). For two samples containing 1% and 0.6% Pb respectively, about 30% of the lead was extracted with 0.12 M HCl, indicating a very high degree of bioavailability, which would be of major concern if children were to ingest such dust.

Vacuum cleaner dust has variable amounts of lead partly dependent on the distance from the dumps and partly because the samples were not sized or crushed to a fine homogeneous powder prior to analysis. For houses within about 1 km from the dumps, the vacuum cleaner dust contains up to

Figure 3 *Blood lead* vs *isotopic values compared with the range in isotopic values measured in a quarterly market basket survey of food from Adelaide, from whence most of the Broken Hill food is derived. Circles; adult females: squares; fathers: triangles; children.*

~3,000 ppm Pb and the $^{206}Pb/^{204}Pb$ ratios range from 16.0 to 16.13, consistent with their main source of lead deriving from mine dust. At distances greater than 1 km, the lead contents are less than 1000 and usually less than 500 ppm with $^{206}Pb/^{204}Pb$ values from 16.2 to 16.6. There are, however, exceptions such as a house located within a few hundred metres of mining operations and whose vacuum cleaner dust has $^{206}Pb/^{204}Pb$ values of 16.98 and 16.38 on two separate occasions. The isotopic variability in the floor dust, a sample integrated over days to weeks, is probably mirroring the same sources as observed in the air filter sampling, discussed later.

The dust wipes, usually obtained from the kitchen, exhibit less variation in isotopic profile with $^{206}Pb/^{204}Pb$ ratios from 16.02 to 16.16. One house has a value of 16.44, consistent with the vacuum cleaner dust but in some of the other houses, there is no agreement between vacuum cleaner dust and that from the wipes. Notwithstanding these differences, the lead in kitchen dust from the majority of houses is attributed to a mine source.

Blood samples
Blood levels of 25 adult females are low (none >10 $\mu g\ dL^{-1}$) and are similar to levels found in 25 women from each of Adelaide and Hobart and most from Port Pirie. The lead isotope profiles in the women are quite different from those in the house dust. No systematic relationship exists between PbB and isotopic profiles and geographical distance from the dumps although the subjects with the lowest PbB and highest $^{206}Pb/^{204}Pb$ (most different from the mine lead) live furthest from the dumps. The isotope profiles in the women indicate that although a small amount of lead in their blood could come from the mine, other more dominant sources have to be considered, the most likely being uncontaminated food, water and air.

Levels of lead and isotopic compositions for three adult males appear partly related to occupation or activities. For example, one subject, with the highest PbB of any adult, has worked all his life in a service station. His isotopic composition is the same as that for gasoline distributed at the time of biological and air sampling. Likewise, another subject, also has a high PbB for an adult (16.4 $\mu g\ dL^{-1}$) and a $^{206}Pb/^{204}Pb$ of 16.36 at the lower end of the range for 'average' adults; he has worked for >19 years as an underground miner. Yet another subject suffered lead poisoning symptoms (nausea, vomiting, headaches) after considerable exposure to lead-rich ceiling dust during renovations.

At the time of the conference, none of the children aged between 1 and 14 years had a PbB of >25 $\mu g\ dL^{-1}$. The lead isotope profiles in the children are generally different from those of their mothers and most are quite different from the mine lead profile. Recent analyses of two children identified by the NSW Department of Health survey as having PbB >25 $\mu g\ dL^{-1}$ have $^{206}Pb/^{204}Pb$ values which lie within the range for those of the mine and most house dust (16.0 - 16.2). One of these children has a PbB of 40.4 $\mu g\ dL^{-1}$ and a $^{206}Pb/^{204}Pb$ of 16.17. These results would be interpreted to mean that the dominant source of lead is from the mine dust. Unfortunately, there are a number of other children whose PbB is <20 $\mu g\ dL^{-1}$ with similar low isotope ratios of ~16.2; the dominant source of lead in their blood is also interpreted to come from mine lead. With the levels of concern in 1991 of 25 $\mu g\ dL^{-1}$ recommended by the Australian National Health and Medical Research Council, intervention or follow-up for these children would not be forthcoming even though the lead isotope measurements indicate a significant exposure to mine lead.

Source of lead
The variability in lead isotope profile and the difference between young children and adult females indicates that there are other sources of lead in their blood besides that derived from the mine. The scatter in the data also indicates that there are more than two sources of lead; a simple two-component mixing on the diagram of $^{206}Pb/^{204}Pb$ vs PbB is a well-defined hyperbola, or on a $^{206}Pb/^{204}Pb$ vs 1/PbB is a straight line (Faure, 1986).

Accepting that mine dust is one end-member (the low $^{206}Pb/^{204}Pb$ end) of a mixing relationship, the other higher $^{206}Pb/^{204}Pb$ end is attributed to at least three possible sources: food, water and air.
(a) Food as a possible lead source: The majority of packaged food available in Broken Hill comes from Adelaide, some 600 km to the south. As part of the project 'Biokinetics of Lead in Human Pregnancy', quarterly market basket surveys were conducted in Adelaide, Port Pirie and Hobart in Tasmania. Except for one seasonal aberration in Port Pirie, the lead content of the 12 month market basket survey was <10 ppb. The very low lead contents of the food indicate that it is only a minor contributor to PbB in the cities examined. For example, it only

Figure 4 *Blood lead vs isotopic values compared with the range in isotopic values measured for cold water from houses in Broken Hill. Symbols as for Figure 3.*

Figure 5 *Blood lead vs isotopic values compared with the range in isotopic values in air dust from 24-hour high volume filters located in three sites shown in Figure 2. Symbols as for Figure 3.*

contributes an estimated 3.5 µg to the daily uptake of lead from the gastrointestinal tract.

It should be noted that the measured lead contents do not include a 'preparation' component, a contribution of variable significance in an environment such as Broken Hill. If, however, mine lead from 'fall- out' during food preparation was a major contaminant, it would be reflected in the blood isotopic compositions.

The range of isotopic compositions of the Adelaide food overlaps that of the blood for the female adults (Figure 3) and thus food could be a contributor to their overall lead budget. To better define the real contribution of lead from food to PbB, it is intended to carry out Duplicate Diet surveys in a small number of homes.

(b) Water as a possible lead source: Drinking water is another possible source of lead in blood. Cold waters from 19 of 20 houses have lead contents <0.5 ppb; one house had a lead level of 3 ppb when first sampled but this was collected whilst house renovations were in progress. Repeat collection 5 months later gave a level of 0.4 ppb.

These lead contents are low and are consistent with low values found in 25 houses from each of Adelaide, Port Pirie and Hobart during the Biokinetics project. They are consistently lower than the current Maximum Contaminant Level of the U.S. EPA of 50 ppb.

The lead isotopic compositions of the waters exhibit considerable variation between houses (Figure 4) as we have found in the other three cities mentioned above.

The isotopic variations possibly arise from differences in the plumbing systems for the individual houses although in the samples with <0.1 ppb, may partly arise from a small amount of laboratory contamination. As a further control of the individual variability, point source collections are to be made.

The low lead contents in the water contribute an insignificant amount to lead body burden although the isotopic compositions would permit it a minor role. Furthermore, in almost every

household tested, cooking is mainly with microwave ovens.

(c) Air as possible lead source: Dust collected on the high volume air filters, the locations of which are shown in Figure 2, could derive from a number of possible sources such as the mine dumps, the surrounding country side (with other small mine dumps and the rocks which host the mineral deposits) and from leaded gasoline.

Lead from the surrounding country side is considered to contribute insignificantly to the lead budget because the dust in the house ceilings is predominantly from the main Broken Hill lodes and the lead associated with the host rocks is in tightly bound silicate minerals such as potassium feldpsar which would not be bioavailable.

Results for the dust from high volume filters appear to be dependent on the prevailing wind directions. Where the prevailing wind is blowing over the mine dumps, the isotopic compositions reflects a significant mine contribution. In contrast, if the prevailing direction is over the city, the $^{206}Pb/^{204}Pb$ values are >16.4. One possible source for this lead is from gasoline and measurements of two gasoline samples bracketing the air sampling period have the same isotopic compositions and could constitute one of the main end members of the mixing relationships shown in Figure 1. The isotopic variations noted in the air dust could also account for some of the variability found in vacuum cleaner dust, mentioned earlier.

(d) Paint as a possible lead source: In view of the antiquity of many houses in Broken Hill, paint is a possible source of lead in children, especially through pica. Paint flakes will be analysed in the future but paint is not considered as critical as dust at this stage because a number of children with PbB ~20 µg dL^{-1} and low $^{206}Pb/^{204}Pb$ values live in relatively new, lead-free painted houses.

Blood and urine correlations

Because of the potential difficulty in obtaining venous samples from newborn infants and trauma

often induced from serial sampling of children, we have been evaluating the potential of urine to complement or replace blood as an indicator of body burden.

The high correlations of isotopic compositions in blood and urines are extremely encouraging especially given the relatively unconstrained urine sampling. In the reverse mode, the high correlation of blood and urine isotopic compositions is a good monitor of quality of blood analyses.

At this stage, the usefulness of a spot PbU is uncertain even when normalized to creatinine; once again, contamination arising during sampling is a major concern.

Conclusions

Preliminary results from adults and children at Broken Hill have shown that the adult females have generally low PbB and variable isotopic compositions. Their current blood lead is attributed to a mixture of sources and could include mine dust, gasoline, food and water. The lead in adult males appears to be related to their occupation and activities. The blood lead of children is highly variable and partly related to age, with older children (up to 14 years) having lead similar to that in adult females. Younger children (< 6 years) also have variable PbB and isotope profiles although there is a moderate correlation (r = 0.73) between PbB and isotopic compositions, indicating that the higher PbB reflects a larger component of mine lead. A number of children with PbB >15<20 µg dL^{-1} have isotopic compositions which indicate a significant exposure to mine lead and yet would not be considered at risk based solely on PbB levels. Detailed evaluation of deciduous teeth are currently underway, especially from children whose houses were being renovated during pregnancy and/or early childhood.

Acknowledgements

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Lead Bioavailability in the Environment of Children: Blood Lead Levels in Children Can Be Elevated in a Mining Community

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ABSTRACT. Lower blood lead averages in mining communities, compared with other child exposure settings, e.g., innercity areas of the United States and smelter communities, have been attributed to lower bioavailability of lead to children in the mining areas. Direct supporting evidence of the lower bioavailability has, however, generally been lacking. Elevated blood lead levels for approximately 85% of children with > 10 µg/dl have been reported from the Broken Hill mining community in Australia. Lead isotope, optical, and scanning electron microscope analyses on the lead species from soils and dusts show them to be derived mainly from weathered ore body material. Solubility tests using 0.1M HCl on the $-53+38$ µm fraction of soil and dust show the lead species to have a high degree of bioavailability. Ingestion of soil and dust, either directly or via mouthing activity, is the main source and pathway for elevated blood lead in children from this community.

LEAD as an environmental toxin continues to garner considerable media and scientific attention, especially its potential negative effects on children. The generally accepted indicator of lead exposure is blood lead (PbB), and most investigations of the correlations between PbB and environmental lead have focused on urban environments and point sources such as lead smelters (see references in, for example, ATSDR[1]). There are, however, considerably more mining sites throughout the world with their associated waste rock dumps, tailings ponds, contaminated soils, etc., that pose potential environmental hazards. Until Superfund legislation was introduced in the United States, investigations of the relationship between PbB and environmental lead were minimal. Furthermore, many of the more recent investiga-

tions[2,3] and evaluations[4,5] of the relationships of PbB and soil/dust lead in mining communities have found lower PbBs (generally < 10 µg/dl) than the averages in urban and smelter communities, and this has been attributed to the low "bioavailability" of the lead species. ("Bioavailability" is the proportion of lead considered to be extracted in the gastrointestinal tract, compared with the total available lead.) The low PbB found in these communities led Steele et al.[4] and Woodward-Clyde[5] to state that lead in soils (or dusts) from mine wastes has a low impact on PbB.

A critical review, however, by Mushak[6] (and personal communication, 1993) showed that some reports and investigations of PbB levels in children from mining communities provided an uncritical or narrowly focused

look at these sites, that a portion of the historical data-base from mining areas is of questionable quality by current epidemiologic and biostatistical criteria, and that a more analytical assessment of a number of these studies indicates that bioavailability is not low with reference to new childhood lead exposure and toxicity guidelines.

A number of these same reviews and investigations have also assumed, absent clear evidence, that any differences in PbB between mining and other lead exposure settings arose from differences in bioavailability, rather than differences in other critical parameters of childhood lead exposure that also determine daily lead absorption—particularly the amount of ingested lead-contaminated dusts and soils.

Blood lead levels in children from the Broken Hill mining community in Australia are not low. A 1991/1992 survey by the NSW Health Department showed that of 899 children aged 1–4 y, approximately 20% had PbB > 25 μg/dl and approximately 85% > 10μg/dl.[7] Data for an additional 48 children were consistent with these results.[8]

Broken Hill is a city populated by approximately 25 000 people located about 930 km due west of Sydney. Broken Hill is an isolated desert area that was previously subject to intense dust storms. It has operated for more than 100 y, initially as shallow mining and associated smelting and later deep underground mining. During the past 20 y, the tailings dumps and oxidized surface ore have been reprocessed resulting in an increased volume of fine-grained lead-rich dust (containing up to 3% Pb) available for wind dispersion. This recent activity is, however, possibly overshadowed by ancient weathering processes in which the primary sulfide ore body was oxidized approximately 30 million y ago. It has been estimated by geologists familiar with the Broken Hill ore body that possibly 40 million tons of ore have been removed by natural processes (G. McIlveen, personal communication, 1993) and could have been dispersed into the countryside. Nevertheless, Broken Hill is an ideal site for investigation because of its isolation and the mining activities are the most easily identifiable major source of lead pollution, hereafter referred to as ore body lead.

In an effort to better understand sources and pathways of lead in children at Broken Hill, our investigation, using the lead isotope fingerprinting method of biological and environmental samples—complemented with optical and scanning electron microscopic methods, x-ray diffraction analyses, and solubility tests of environmental samples containing the lead species—has shown that the lead species are highly bioavailable.

Materials and methods

Soil and dust samples were dried and sieved, and the −53 +38 μm fraction was subjected to gravity separation using methylene iodide (density 3.2). The −53+38 μm fraction was chosen because it has been shown that the −100 μm fraction of soils and dusts adheres strongly to the hand,[9] and recent bioavailability experiments in the United States have been performed on material with a mean size of about 50 μm.[10] The bulk and −53/+38 μm fractions were subjected to leaching with 0.1M HCl for 2 h at 37 °C to obtain an estimate of the bioavailability of the lead species. It should be noted that the 0.1M HCl leaches, although simulating stomach conditions, are only an approximation and give indications of the gross relative solubility of the lead-bearing phases. This is illustrated by the often widely differing percentages of 0.1M HCl/total extractable lead (derived from the HNO_3/HCl leaches) measured by two different analysts on different sample aliquots and by different measuring techniques. For ease of analyses, and quantity of material available for analysis, we have used a ratio of approximately 70–100/l of liquid/sample, which is far in excess of the 14/1 ratio used in the bioavailability studies with New Zealand white rabbits.[11] Repeat extractions on two samples using a 14/1 ratio did not alter the conclusions significantly (Table 1). Lead isotopic compositions were measured by high-precision thermal ionization mass spectrometry on blood, urine, and teeth and compared with data for water and house dust from all dwellings, and selected paint, street dust, external air, internal house air, and gasoline samples. Lead contents were measured either by isotope dilution mass spectrometry or by ICP-AES.

Results

The major point source of lead in Broken Hill is the mining operations, especially the mine ("skimp") dumps. The lead isotopic compositions of the Broken Hill mines and mineral occurrences in the surrounding areas are well-documented.[8] Analyses of sulfide minerals from different parts ("lodes") of the Broken Hill deposit show it to have a uniform isotopic composition with $^{206}Pb/^{204}Pb$ values of 16.00 ± 0.02 (1 σ) and that the oxidized surface material has the same isotopic compositions as the primary sulfide ore.[8] Thus, material that may have been subjected to weathering for more than 30 million y has the same isotopic composition as the primary sulfide ore.

Other major sources of lead could be from gasoline and paint. Gasoline in Broken Hill contains about 0.85 g/l and has $^{206}Pb/^{204}Pb$ values of 16.56 ± 0.07 (1 σ). Paint has been largely ignored as a potential contributor to PbB in children in Broken Hill, but there are many old houses, some of which have lead paint. In the earliest days, lead in paint came from Europe and its $^{206}Pb/^{204}Pb$ ratios would have been approximately 18 or greater. Later, the lead in paint could have come from the Broken Hill ore body, and it appears that the earliest residents mixed lead from the mine workings with the red dust and solvents to form a paint mix. Certainly, some of the paint we have analyzed has the isotopic ratios of ore body lead.

The lead content of the finer fractions (−53+38 μm fraction) of soils and house dust can be > 0.3% and occasionally up to 1% Pb, with isotopic compositions consistent with derivation of the lead from an ore body source (Table 1). Lead isotopic measurements on 60 children demonstrate that, for some children with elevated PbB (> 15 μg/dl), > 80% of the lead comes from an ore body source via ingestion of soil/dust (Fig. 1) if the

Table 1.—Comparison of Solubility for Bulk and Fine Fractions of Different Environmental Samples from Broken Hill

	Total leachable*		0.1M HCl Pb			Bulk	
	Pb (ppm)	^{206}Pb/^{204}Pb	Pb	^{206}Pb/^{204}Pb	%0.1M HCl/total	Pb (ppm)	^{206}Pb/^{204}Pb
Vacuum dust −53 + 38μm							
541	3 750	16.20	1 660	16.24	41	615	16.25
(−125 μm	2 320	16.24)					
541†	—	—	760	16.32	13		
526	8 300	16.00	2 580	16.02	26		
557	2 600	16.03	1 550	16.04	121	590	16.04
556	1.21%	16.06	3 390	16.07	30	4 490	16.09
(−125 μm	7 400	16.05)					
536	4 300	16.05	2 390	16.09	55	1 290	16.06
536†	—	—	1 220	16.12	46		
553	3 010	16.13	1 810	16.18	51	—	—
Soils −53 + 38μm							
541 −1	2 415	16.11	1 470	16.13	64	665	16.12
−1†	—	—	930	16.15	37	—	—
−2	3 225	16.10	1 820	16.13	59	2 080	16.13
526 −1	3 815	16.01	2 630	16.00	57	2 370	16.02
−1†	—	—	2 480	16.02	76		
−2	3 165	16.03	2 610	16.01	84	1 990	16.02
557 −1	4 475	16.02	2 010	16.03	63	2 060	16.06
−2	4 735	16.00	2 930	16.01	54	570	16.03
556 −1	4 540	16.02	2 510	16.00	60	500	16.04
−2	8 500	16.01	3 070	16.01	41	2 000	16.03
553 −1	2 910	16.26	1 870	16.34	61	1 430	16.32
−2	3 150	16.13	1 680	16.16	58	780	16.17
Footpath and gutter sweepings −53 + 38μm							
Gutter	2 010	16.07	1 540	16.09	79	620	16.13
Gutter	1 620	16.09	610	16.09	44	420	16.15
Gutter	2.05%	16.02	6 600	16.02	37	5 400	16.05
Soil/gravel	1.00%	16.01	6 400	16.01	61	5 300	16.02
Soil/gravel	9 700	16.02	5 500	16.00	52	9 300	16.01
Gravel	1 015	16.11	520	16.09	57	280	16.27
Gutter	4 080	16.07	1 410	16.09	33	880	16.14

Percentage of 0.1 M HCl/Total leachable Pb is calculated from the amount of Pb extracted per unit weight in μg, compared with the total amount extracted in μg.
*1/~14—sample /0.1 MHCl; −1, −2—separate soil samples.

main end-members are ore body (16.00) and gasoline (16.56). It is clear from Figure 1, however, that there are other sources of lead in the children's blood and that almost one-third of the 60 children studied have more than 50% of their lead derived from gasoline or paint or both.

Surface morphology of most lead-bearing grains indicate they have undergone multiple episodes of intensive wind transport. The lead compounds can vary in size from more than 10 μ down to 1–2 μ. The finer particles are commonly agglomerated onto non-lead–bearing host minerals, such as are found in the rocks in which the ore body is located (Fig. 2a). These agglomerates, with their fine grain size and relatively loose bonding to the host minerals, would facilitate easy removal by leaching solutions such as gastric juices. The remobilized and cemented aggregates and crystalline products derive from the weathering and oxidation of the original sulfide ore body, but these processes probably have

taken place over the past 30 million y; it is estimated that during this period, approximately 40 Mt (20%) of the original ore body has been weathered away.

Scanning electron microscopic analyses of a bulk (un-sized) and the −53+38 μm fractions from soil, gutter sweepings, ceiling dust, vacuum cleaner dust, and long-term house dust (three monthly collections) show that the majority of lead species are a complex Pb, Fe, Mn, Al, Si, O, +Ca, +P material (Fig. 2b). Rare occurrences of the primary sulfide, galena, are found in locations such as in a house within the boundaries of the mining activities or in gutter sweepings from thoroughfares along which processed ore is transported.

Notwithstanding the difficulties in correlating in vitro solubility of lead with uptake from the human gastrointestinal (GI) tract, it is likely that if a lead species is highly soluble in a simple in vitro simulation of the GI tract, then that species would be at least as soluble and probably more soluble in the human GI tract.[6] Solubility tests

Fig. 1. $^{206}Pb/^{204}Pb$ ratio versus PbB ($\mu g/dl$) in children, generally 1–4y old, whose PbB is > 15 $\mu g/dl$. Samples whose lead isotopic composition is dominantly ore body are shown by solid squares and those with dominantly gasoline/paint are indicated by open squares. The circles are vacuum dust(vc). The isotopic composition for paint can be either approximately 16.0 or > 17.0. Given that there is evidence for some children deriving most of their lead from one of the major sources, the data for the other children show that the lead in their blood comes from gasoline and or paint or both. The dashed line represents the mixing relation between the child with the highest proportionof ore body lead and the female adults with the lowest PbB (approximately 3 $\mu g/dl$) representing air, gasoline, food, and water lead. The numbers 7, 9, and 11 are ages of the older children.

In U.S. mining communities, low PbBs are attributed to encapsulation of the lead species in, for example, quartz or pyrite or insoluble sulfates. Mining communities in the United States have been mainly studied by Bornschein and associates at the University of Cincinnati Medical Center. Blood lead levels in children vary from 4.8 $\mu g/dl$ ($n = 316$) in Leadville, Colorado; 2.6 $\mu g/dl$ ($n = 28$) in Aspen, Colorado; 5.9 $\mu g/dl$ ($n = 105$) in Central City, Colorado; 6.2 $\mu g/dl$ ($n = 94$); and 3.5 $\mu g/dl$ ($n = 294$) in Butte, Montana.[5] In all cases, soil and house dust lead contents can range up to several thousand ppm.

However, independent reanalysis by the U.S. Environmental Protection Agency (EPA) of the Bornschein studies of the mining towns shows that the relationship between outside soil and interior dust is quite different from, and anomalous to, most other contaminated sites and it is this that reduces PbB and not bioavailability, per se (Mushak, written communication, 1993). Specifically, if one analyses the relationship of interior dust Pb in

on the bulk and $-53+38$ μm fractions show a very high degree of bioavailability of the lead species from Broken Hill (Table 1). The 0.1M HCl leach extracts 46–79% of the total leachable lead from gutter sweepings, 50-> 100% of the soils, and 9-> 100% of the vacuum cleaner dusts. The > 100% probably arises from sample heterogeneity, even though the sample is the $-53+38$ μm fraction. These results are similar to the approximately 65% available lead obtained for urban and house surface dusts.[12,13]

Discussion

The very fine grain size, chemical composition, and solubility in 0.1M HCl of the lead species may be some of the physicochemical characteristics of Broken Hill lead that distinguish it from those in other mining communities. Nevertheless, elevated PbBs in some children can be also attributed to lead in gasoline and paint, socioeconomic status, and other factors.

Solubility data are generally not available for the other mining communities, except in the case of Skagway, where the galena and sphalerite ore have been shown to have low solubility.[14] Unfortunately, the Skagway investigations used rats as the bioavailability test species. Weis and LaVelle,[15] in evaluating the issues surrounding metal bioavailability, especially lead bioavailability, concluded that any such metal bioavailability studies conducted on rodents or lagomorphs (e.g., rabbits) should be viewed with caution.

Fig. 2. (a) Back scattered electron image in soil from a backyard showing microcrystalline lead phase (white) in soil adhering to detrital sillimanite(A) and Fe-Mn oxides (B). (b) Back scattered electron image showing cemented aggregate of irregularity oriented clasts from long-term (3-mo collection in a hallway) airborne house dust. The crystalline nature of this material (consisting of Pb, Zn, Fe, Mn, Ca, Al, Si, O) suggests that it is of recent origin.

these communities to children's PbB, the regression co-efficient or "slope" (change in PbB per 1 000 ppm change in dust and soil) is similar to the average of such relationships, approximately 2, for many sites described by EPA.[26]

Other investigations purporting to show a lack of relationship between PbB and soil/dust lead include those of Barltrop et al.[16] and Cotter-Howells and Thornton[17] in the Derbyshire area of the United Kingdom. Only 13 children were measured in the Cotter-Howells and Thornton study, and the low PbB of 6.9 μg/dl was attributed to the dominant lead species manifested in pyromorphite, $Pb_5(PO_4)_3Cl$. Both the earlier studies of Barltrop et al.[16] and the study in the Northampton community in Western Australia[18] have been criticized by Mushak[6] and, in fact, Mushak noted that the Heyworth et al.[18] data support an impact of lead tailings on PbB.

In support of a relationship between PbB and soil/dust lead in mining communities, significantly higher concentrations of blood and environmental lead were found by Moffat[19] in two mining villages (Leadhills and Wanlockhead), compared with a non-mining village (Moniaive) in Scotland. The mean PbB in children was 17.6 in the mining villages, compared with 10.4 μg/dl in the control village, but the author concluded that there were no significant correlations between PbB in the children and any environmental factors. Unfortunately, no information appears available on the lead species, nor from most of the above studies.

Apart from some cases in Broken Hill where the dominant source of lead in children appears to be from gasoline or paint or both, coupled with varying amounts of ore body lead, the major source is from the ore body with its highly bioavailable lead species. The pathway for this to the child is via wind, soil or house dust or both, hands, and mouth (Fig. 3). Neither food, town water, nor air are significant contributors to blood lead.[20]

Even though there are widely varying percentages of bioavailable lead within the one sample, the amounts of lead that can be potentially absorbed under simulated stomach conditions are very high. The size fraction tested here was $-53+38$ μm, and there is possibly twice as much material comprising the -100 μm fraction, with possibly even higher total lead (see for example, house 556, -125 versus $-53+38$ gmm vacuum cleaner dust result, Table 1). Thus, there is a significant amount of soluble lead available (> 10 μg) if 100 mg/d is ingested by an infant.

Given such a potential hazard from soil/dust ingestion at Broken Hill, the amount of soil/dust ingested by children becomes important. Estimations of the amount of soil ingested vary widely from 4 to > 200 mg/d.[21,22] The U.S. Environmental Protection Agency IU/BK model to predict PbB has a default value of 100 mg/d of soil ingestion. Although very difficult to estimate at Broken Hill (or anywhere), the 100 mg may be a gross underestimate for some children at Broken Hill. For example, maternal anecdotes are that the child "eats handfuls of dirt" and this is supported by the abundant insoluble materials observed in feces. Furthermore, because of the climate, children in Broken Hill spend considerably more time outside than their counterparts in North America.

The relationship between PbB and soil lead levels in the Broken Hill children are similar to those found in smelter and urban communities (Fig. 4). The source of elevated lead in the urban communities is usually attributed to paint and past contamination of soils from gasoline, and in smelter towns, the point source is obvious. Pathways of soil, house dust, hands, and mouth in the urban and smelter environments are similar to Broken Hill.[2,23] Impacts of grain size and bioavailability of paint on PbB are poorly understood but the most severe cases of childhood lead poisoning over the past century in the United States were the result of paint ingestion.[24] The extremely fine grain size of smelter emissions would appear to be of greater significance than bioavailability of lead species; the latter are $PbSO_4$ and PbS (feedstock) with minor PbO.[25]

The problem of the sources and pathways of lead into humans and especially children in Broken Hill is quite different from several of the mining communities described in the literature and would appear to be mainly

Fig. 3. Provisional flow sheet for sources and pathways of Pb into children from Broken Hill.

Fig. 4. Comparison of PbB/soil dose response at mining, smelter, and urban sites in the United States, compared with Broken Hill (redrawn from Davis et al.[10]). Triangles denote children whose blood lead is attributed to paint or gasoline and solid circles whose lead is from an ore body source.

due to the bioavailability of the lead species. Statements that absorption factors of only 12% instead of 30% for PbB estimates using models should be applied to mining communities and that lead in soils or dusts from mine wastes has a low impact on PbB[4] should be treated with caution. In Broken Hill, both soil and house dust are derived from the same dominant source: ore body lead. House dust lead may be introduced by wind action, especially through open windows or spaces in roofs, or by human or animal transport. Thus, remedial actions in Broken Hill can be quite different from other mining communities and this reinforces the notion that each lead hazard to children needs individual consideration.

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Effect of plumbing systems on lead content of drinking water and contribution to lead body burden

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Abstract

Stable lead isotopes and lead contents in drinking water from a number of Australian cities have been measured to determine the contribution of drinking water to body burden. Lead contents are generally <2 $\mu g/l$ and thus contribute an insignificant amount to the lead budget in humans in Australia. First-flush and running water samples taken at intervals of up to 10 min show that equilibrium is reached within 1 min or ~ 10 l by volume. There is, however, large variability in both lead content and isotopic composition within the first minute which brings into question the reliability of the recommended sampling time of 30 s. Extremely large isotopic differences between individual dwellings within the one city and between dwellings and the storage tanks for the water supply are attributed to differences in lead residing in the plumbing within the dwellings, usually from lead solder in brass fittings. Isotopic analysis of solder and water from two dwellings confirm this relationship.

Key words: Lead; Water; First flush; Body burden

1. Introduction

With the introduction of regulations to minimize lead in gasoline and food in many countries since the early 1970s, drinking water may contribute increasingly to the body burden of lead. For example, Briskin and Marcus [1] suggest that, on average, drinking water constitutes 15–20% of total exposure to lead in the United States. WHO 1984 guidelines for lead in drinking water are 50 $\mu g/l$ and the USA EPA [2] has recently proposed

a non-enforceable goal for lead in drinking water at zero and the level for contamination of water supplied by the system to be lowered from 50 to 5 $\mu g/l$.

The pioneering investigations of Moore and his colleagues in Scotland established the relationship of plumbosolvency of water and blood lead levels (PbB), especially where the distribution systems consisted of lead. Furthermore, Moore [3] illustrated the potential health hazard of consuming first flush water with its generally higher lead content than running water. Later studies with copper plumbing systems have corroborated the earlier re-

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search [3,4]; relevant data sources and references are given in Levin et al. [5] and EPA [2]. Levin et al. [5] summarize the risk factors for elevated lead levels in drinking water as: (i) lead solubility of plumbing systems, (ii) age of plumbing systems, (iii) 'stagnation' time, (iv) temperature, (v) physical positioning of pipes and (vi) pattern of water consumption and volume of sample.

In our studies using stable lead isotopes for determining the source of lead in human blood, we have observed considerable isotopic variation in drinking water from different houses in the one community, even within a 200-m radius. To evaluate the cause of this variation and to repeat Moore's experiments on more modern houses and plumbing systems, we determined lead contents and isotopic ratio measurements on: (i) first flush and running water samples for up to 10 min from three houses of varying age, (ii) a repeat of (i) after 5 months, with water from the first flush and running water samples for up to 3 min, and (iii) water from houses in the one isolated mining community, and compared the results with water from distribution tanks.

2. Methods

2.1. Sampling

Plumbing for the three houses in Sydney used for the first flush testing was copper with lead-soldered brass joints. Cold water samples were taken from a kitchen tap (after standing overnight) into cleaned 125-ml polyethylene bottles at 1-min intervals, the flow rate being partly dependent on the age of the plumbing. From these results it was established that equilibrium (i.e. relatively uniform lead contents and isotopic compositions) was reached after about 3 min. One week later, samples were taken from two houses after 5 min of flushing. After an interval of 5 months, the first flush tests were repeated with samples being taken at intervals of up to 3 min. In one case, the flow rate was decreased to determine the effect of variation of flow rate on Pb content and isotopic composition. For routine sampling, water was taken after ~30 s flushing. In both Sydney and Broken Hill, samples were taken from draw-points off main storage tanks in the areas of interest. Except for early samples from Broken Hill, all samples

Fig. 1. Lead isotope ratios expressed as the $^{206}Pb/^{204}Pb$ value and lead contents in parts per million (or mg/l) as a function of volume of water for an inner Sydney residence (Burwood) with copper plumbing over 10 years old. No. 1 and No. 2 in this and Figs. 2 and 3 denote separate trials more than 5 months apart.

were acidified within days of collection to ~1% HNO_3 with twice sub-boiling distilled nitric acid.

2.2. Analysis and quality control

Approximately 25 g of sample was weighed into a cleaned Savillex Teflon beaker and a ^{202}Pb 'spike' solution added to enable the lead content and isotopic composition to be determined on the same sample. Thirty drops of concentrated clean nitric acid was added and the samples evaporated to dryness under a clean nitrogen flow in a 'clean' laboratory. Lead was separated on an anion exchange column in HBr medium. Isotope ratios and lead contents were measured on a thermal ionisation mass spectrometer (VG Isomass 54E) in fully automatic mode. Long-term precision for this instrument based on over 1500 measurements of the NBS SRM Common Lead Standard 981 for sample loads ranging from 10 to 300 ng is ±0.1% (2σ) on the ^{206}Pb/^{204}Pb, but is estimated to be about double this for low lead concentration waters, as shown from repeated measurements on the one sample of drinking water, used for quality control; i.e. 16.223 ± 0.025 (±0.30%, 2σ: $n = 11$). Repro-

ducibility of lead content in this water over an 18-month period was ±3% (3.1 ± 0.1 μg/l). Contamination levels for the analyses, estimated from processing without a water sample, range from ~70 to 130 pg Pb. No corrections have been made to the data for this blank.

3. Results

3.1. First flush and running water

Lead isotopic results (^{206}Pb/^{204}Pb value) are compared with total lead contents for the three Sydney dwellings in Figs. 1–3. The lead contents of the running water are low, usually <3 μg/l, and well within the current and proposed EPA limits of 5 μg/l. There are considerable variations in lead content from the first-flush water samples, which may partly reflect the different flow rates. The newest house (1 year old) had the highest lead content, of 64 μg/l for first flush, compared with running water of ~2, consistent with the conclusions of Sharrett et al. [6] that new housing under 5 years old, or residences in which recent plumbing renovation or repairs had been completed, has the

TURRAMURRA

Fig. 2. Lead isotope ratios expressed as the ^{206}Pb ^{204}Pb value and lead contents in parts per million (or mg/l) as a function of volume of water for a 1-year-old Sydney residence (Turramurra) with copper plumbing, but whose lead solder has a different geological source to that in Fig. 3.

EPPING

Fig. 3. Lead isotope ratios expressed as the $^{206}Pb/^{204}Pb$ value and lead contents in parts per million (or mg/l) as a function of volume of water for a Sydney residence (Epping) with copper plumbing more than 18 years old and whose lead solder is derived from the geologically ancient Broken Hill mines.

potential of producing higher lead exposure than older housing.

None of the results follow the pattern illustrated by Moore [3] in which he observed equilibrium being reached after 5 min (or 50 l). This difference probably arises from the lead versus copper or galvanized iron piping systems. In the Sydney houses, equilibrium was reached in approximately 1 min, or 10 l in terms of volume.

The isotopic patterns are also completely different for the three houses. The Turramurra and Burwood houses have similar patterns, allowing for the slower flow rate in the Burwood house, with a rapid decrease to the equilibrium value. In contrast, the $^{206}Pb/^{204}Pb$ value in the Epping house increases from 16.17 to 16.36, probably reflecting a difference in lead isotopes in the solder used for the brass joints; the solder in the Epping house has a $^{206}Pb/^{204}Pb$ of 16.00, demonstrating that the sole source of the lead was from the geologically ancient Broken Hill (Australia) mines. For the Turramurra house, the solder has a value of ~16.8, similar to the first-flush water.

Lead contents in the three samples from the Sydney water storage tanks in the vicinity of the Epping house are uniformly low: 0.36–0.64 μg/l. Two of the samples have similar isotopic values (16.97) but are quite different from the other sample (16.60).

3.2. Repeatability of the experiment

Re-sampling the water 1 week later in two houses after 5 min flushing showed them to have uniform lead contents and isotopic compositions (Figs. 1–3). However, a partial repetition of the first-flush experiment 5 months later gave entirely different results, especially in isotopic values. For example, in the Burwood house, the first-flush sample had a higher $^{206}Pb/^{204}Pb$ and then approached equilibrium in the same fashion, but the lead content showed a regular and rapid decrease to equilibrium with no 'spike' (Fig. 1). In the Turramurra house, the patterns were similar with an increase in lead content again obvious after 2–3 min (20–30 l) but little change in the isotopic ratios (Fig. 2). In contrast, with the change in flow

BROKEN HILL TAP WATERS

Fig. 4. Lead isotope ratios expressed as the $^{206}Pb/^{204}Pb$ value versus lead contents in parts per million (or mg/l) for waters from different residences in the Broken Hill mining community. The ellipse encompasses data from three storage distribution tanks in the city.

rate in the Epping house from 12 to 8 l/min, the approach to equilibrium was slower in lead content and a 'spike' in $^{206}Pb/^{204}Pb$, not observed with the faster flow rate, is present (Fig. 3). The irregularities in both lead content and isotopic composition within the first minute are cause for concern over the reliability of the recommended 30-s flush when sampling [2,5].

3.3. Variation within one community

The isotopic and total lead content variations have also been observed for 13 houses each from Port Pirie and Adelaide (South Australia) and Hobart (Tasmania) and the isolated lead mining community of Broken Hill. The results for 28 randomly distributed dwellings and three of the four storage tanks from Broken Hill are illustrated in Fig. 4. The lead contents are < 3 μg/l and most are below 1 μg/l. Six of the houses were re-sampled after periods ranging up to 7 months because of the initial concern over the variations within the city. Lead contents can vary by up to a factor of 2–6 in either direction and the isotopic composition by 0.2–4.4% in the $^{206}Pb/^{204}Pb$ value. In no case were the houses re-sampled at the same time of day (or night).

The samples from the three storage distribution tanks in Broken Hill have limited variations in both lead content (0.3–1.1 μg/l) and $^{206}Pb/^{204}Pb$ (16.41–16.52). The isotopic variations observed for individual houses, thus, can only be attributed to differences in the plumbing systems. There is no direct correlation of isotopic composition and lead content but this may be a reflection of different sampling time and residence times within the water pipes.

4. Discussion

The lead contents of drinking water from the five cities investigated so far are low by world standards. The majority of samples (51 of 57 houses)

have values <2 μg/l, well within the proposed USA EPA limits of 5 μg/l and WHO guidelines of 50 μg/l. Such low lead levels contribute insignificantly to PbB in the Australian population. For example, Briskin and Marcus [1] estimate that for drinking water levels of <50 μg/l, there is a contribution of 0.24–0.254 μg/dl PbB per μg/l lead in water. In Broken Hill, female adults have PbB ranging from 3 to 10 μg/l, and in young children PbB is above 10 pg/dl so that the contribution from drinking water is $<10\%$, even in female adults with the lowest PbB.

There is, however, the potential for significant contribution to blood lead if large amounts of the first flush water were consumed either after overnight standing or in the evening, if the residence is unoccupied throughout the day. Furthermore, the duration of the high lead 'spike' may vary widely depending on water usage and equilibrium may not be reached. Further testing of this aspect is currently in progress.

The variations in total lead content and isotopic composition within the one community have now been observed in five Australian cities. Similar variations with time in lead content were noted both within a water distribution system (Boston MA, Bennington VT, Seattle WA) and within a home (Chicago IL, Newport News VA, New Bedford MA) [2].

The uniformity in isotopic composition and lead content for water from the storage tanks and yet large variation in the 28 dwellings at Broken Hill demonstrates that the lead characteristics of drinking water are dominated by the individual plumbing systems; a similar condition applies with the Sydney water supply. The close correlations of plumbing and water lead is also illustrated by the Epping and Turramurra houses in Sydney, where the isotopic composition of the first flush water reflects the solder with lead from geologically different sources which is used in the brass joints, whereas the running water is essentially characteristic of the mains supply.

This study, supported by the stable lead isotope results, confirms other observations of a higher lead content in the first flush samples. However, it shows that equilibrium is reached rapidly within the first minute or 10 l of water. Because of the large variability in lead content and isotopic composition for at least the first minute of flushing, the recommended collection time after only 30 s (e.g. see Refs. 2 and 5) would appear to be rather meaningless. Similarly, attempting to determine a global contribution of drinking water to PbB in a community is also rather meaningless; a true estimate can only be gauged from monitoring individual dwellings and subjects.

5. Acknowledgments

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Sources of lead in soil and dust and the use of dust fallout as a sampling medium

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Abstract

Pilot investigations using stable lead isotope and scanning electron microscopic analyses have been undertaken in different environments ranging from mining and smelting to urban in order to better understand the source of, and relationships between, soil and house dust. House dust is characterised by vacuum cleaner dust and/or surface wipes and compared with long-term dust (dust fall) accumulations over a > 3-month interval or with airborne particulates. Finer grain sizes of soils have lead concentrations from 2 to 9 times those measured in the bulk fractions. In Broken Hill isotopic ratios show that the major source of lead in soils is from the orebody, with rare examples containing lead from paint sources. In inner Sydney, soil lead value vary from 37 to 2660 ppm Pb in bulk samples and up to 3130 ppm in the finer fractions. The lead may be from diverse sources such as gasoline or paint. Finer fractions of vacuum cleaner dust from both Broken Hill and Sydney may contain up to three times the amount of lead measured in the bulk samples. In Broken Hill, the percentages by weight of total lead in the −250-μm fraction range from 11 to 51%. Bulk vacuum cleaner dusts from Broken Hill contain up to 4490 ppm Pb. Bulk vacuum cleaner dusts from inner Sydney contain up to 2950 ppm Pb. Isotopic variations in fractions of vacuum cleaner dust containing > 1000 ppm Pb from inner Sydney indicate that the lead in dust has come from different sources and such differences lessen the usefulness of analyses of bulk vacuum cleaner dust. Our results reinforce the importance of analysing the finer fraction of soil and house dust, especially those in the −150-μm (or even −100 μm) fraction for soils and the −100-μm fraction for vacuum cleaner dust. Dust-fall accumulations have many advantages over more conventional methods for estimating lead in house dust, such as vacuum cleaner dust or surface wipes. These advantages include: low cost; no power source required; can be set up by a technician; minimal inconvenience to householder (i.e., no power required, no noise, out of the way, a few minutes to set up and collect); integrates lead flux over a specific period; usually unbiased (in contrast to vacuuming or wipes where the householder may clean prior to a sampling visit); easy to 'control' by placement of other dishes in the same house. For Broken Hill, a strong correlation (r = 0.95) was obtained between the isotopic composition of lead in blood and dust-fall accumulation.

Keywords: Lead; Soil; Dust; Dust fall; Isotopes

1. Introduction

Lead from soil and dust can be a major contributor to blood lead in children because of ingestion by hand-to-mouth activity (e.g. Refs. [1–8]; detailed references in review documents such as Refs. [9–12]). The importance of soil as a predictor of blood lead has diminished in significance, however, because of the outcomes of the three urban Soil-Lead Abatement Demonstration Projects ('Three Cities Soil' projects). This program, carried out in Baltimore, Boston and Cincinnati, was designed to determine the effect on blood lead following the removal of lead-contaminated soil. The impact of soil removal on blood lead appeared to be negligible [13–15]. Thus on balance, dust assumes an even greater importance with respect to blood lead in children.

Another major problem is the poor understanding of the sources of lead in soil and dust. Most source investigations have employed statistical analyses of total lead concentrations (e.g., for reviews see Refs. 4, 12 and references therein) or multi-element analyses (e.g., Ref. 12 and references therein] or mineral and/or trace element speciation using scanning electron microscopy (S.E.M.), X-ray diffraction (XRD) and selective extractions (e.g., Ref. 12 and references therein). Investigations using these methods can only infer, rather than specify, the source of the lead.

Notwithstanding the above problems, lack of standardised sampling protocols for dust add to the uncertainty in applying dust lead to environmental health investigations. Nevertheless, apart from debate over lead bioavailability and its determination, the analytical protocols for lead determination in both soils and dusts are fairly well established [16].

In this paper, we will present results for dust and soil investigations in community settings ranging from mining and smelting to urban, in which we have employed a number of techniques including lead isotope and scanning electron microscope (S.E.M.) analyses, in order to understand more about the sources of lead and its impact on blood lead. One major advantage of the lead-isotope technique is the ability to evaluate individual subjects and their environmental impacts, an outcome which is usually subsumed in the statistical manipulation of large data sets. As these investigations have spanned an interval over 4 years, we have modified our techniques with time and this is reflected in the paper.

2. Methods

2.1. Study areas

Environmental sampling was performed in a number of Australian cities in which the sources of lead vary widely. Broken Hill is the site of the world's largest lead-zinc-silver mine, located about 930 km due west of Sydney. It is an isolated desert area previously subject to intense dust storms. It has operated for over 100 years, initially as shallow mining and associated smelting and later deep underground mining. During the past 20 years the tailings dumps and oxidised surface ore have been reprocessed resulting in an increased volume of fine-grained lead-rich dust (containing up to 3% Pb) available for wind dispersion. This recent activity is, however, possibly overshadowed by ancient weathering processes by which the primary sulfide orebody was oxidised, approximately 30 million years ago.

Sydney has lead derived mainly from gasoline and other point sources such as battery factories and secondary lead industry. Leaded paint as a significant contributor to blood lead in children has been largely ignored in urban Australian environments until recently [17], perhaps because of the misconception associated with the banning since the early 1970s of leaded paint for domestic purposes.

Other environmental sampling includes 40 houses from Port Pirie in South Australia (site of the world's largest lead smelter), Hobart in Tasmania (location of a zinc smelter with gasoline lead being an important source in some suburbs), and Adelaide in South Australia (lead derived mainly from gasoline and relatively minor lead industry). In each of these cities, suburbs were designated as high-risk and low-risk, based on proximity to point sources of lead, and five houses in each high- and low-risk site were sampled within an ~ 200-m radius. The sampling methods

and analytical results are described in Pisanielio et al. [18].

2.2. Sampling

2.2.1. Soil sampling. In Broken Hill, samples were collected from the top, ~ 15 mm, with a stainless steel scraper over an area of ~ 1 m² and placed in a polyethylene bag. In Sydney, where soil was available usually only in garden beds, the top 25 mm was collected from several locations and composited into a polyethylene bag. For Broken Hill and Sydney samples, the material smaller than 2 mm was analysed as a random 'grab' sample ('bulk' sample). Approximately 7–100 g of selected samples were fractionated further into various size fractions using nylon sieves and the finest fractions of $-53 + 38$ μm were prepared using a Sonic Sifter to obtain better liberation of the fine particles. Size ranges were: $+1000$ μm, $-1000 + 500$ μm, $-500 + 250$ μm, $-250 + 150$ μm, $-150 + 75$ μm, $-75 + 53$ μm, $-53 + 38$ μm, $-38 + 10$ μm, $-10 + 5$ μm, -5 μm.

To achieve further concentration of the heavier materials, ~ 100–150 mg of different fractions, especially the $-53 + 38$-μm fraction, was weighed and transferred to a separation funnel containing methylene iodide (SG 3.2), or more recently, this separation is achieved in test tubes with centrifugation. The $-53 + 38$-μm fraction was chosen because the -10-μm fraction of dusts and soils is known to be extremely difficult to remove from the hands [3], recent 'bioavailability' experiments in the U.S. have been performed on material with a mean size of about 50 μm [19], and lead isotope studies on vacuum cleaner dust from houses in Port Pirie, Hobart and Adelaide used a -60-μm fraction [18].

2.2.2. Gutter sweepings. Roadside gutter sweepings at Broken Hill were sampled with a stainless steel scraper and brush by sweeping the dusts into a labelled self-sealing plastic bag.

2.2.3. Vacuum cleaner dust. For Broken Hill and Sydney, the householders vacuum cleaner bag was sampled in the same way as for soils; i.e. with a bulk 'grab' sample, and commonly a bulk sample

was fractionated further using the Sonic Sifter. In future, a bulk and -100-μm fraction will be analysed. Bulk samples of dust (and soil) will be analysed until such time as sufficient data become available in the literature for comparisons between the finer fractions (i.e., standardisation on the finer fractions).

2.2.4. Surface wipes. Surface dust was obtained from tops of refrigerators and/or kitchen cupboards using an acid-washed polyethylene sheet ~ 60 mm², moistened with clean water. These were then stored in acid-washed polyethylene bags. Samples were prepared for analysis in a similar manner, using 1 M HNO₃, to that employed for the interior dust-fall samples.

2.2.5. Interior dust-fall accumulations. Lead loading or flux can also be measured by deposition of airborne particulates into a fixed receptacle over a specific time interval. This very simple method has received little attention in the literature but offers considerable advantages over other methods. In a pilot study, we have collected house dust over periods ranging from 3 to 6 months in petri dishes in the Broken Hill mining community and in the urban Sydney environment.

Prior to use, polycarbonate petri dishes 50 and 85 mm diameter were soaked overnight in an alkaline detergent, rinsed with clean water, soaked overnight in 6 M HCl, rinsed with clean water and air-dried in a laminar flow workbench station.

A piece of 'Blutak' (plasticine) was placed on the exterior base of the dish to ensure that it was not easily disturbed. To obtain an estimate of spatial variation within some residences, bases of the dishes were placed in two separate locations (e.g. different rooms) at heights varying from floor level to ~ 2 m for periods ranging from 3 to 6 months. In other cases to obtain an estimate of reproducibility, two petri dishes were placed side-by-side. For sampling at Broken Hill, Whatman filter paper was placed inside the dish. This practice was discontinued for later sampling in Sydney because of the difficulty in removing dust from the paper for analysis. To remove the dust, the petri dish was approximately half-filled with 7 M HNO₃ and the solution decanted with rinsing into an acid-cleaned teflon beaker.

The amount of dust in the urban environments was usually too small to allow accurate weighing so only lead loading (flux) was measured [20].

2.3. Analysis

2.3.1. Scanning electron microscopy. Deposits in the petri dishes were examined under a binocular microscope, then sub-sampled using double-sided tape, as spot increments over the filter paper or interior base of the dish. The tape was coated with carbon. Particles from the heavy liquid concentrate were mounted on adhesive tape and coated with carbon. Analyses were performed with a Cambridge Stereoscan 240 S.E.M. with EDS.

2.3.2. X-ray diffraction. XRD analyses were able to identify the main minerals in the −53 + 38-μm fraction but were little use when used for the bulk fractions because of the small amount of lead minerals present and their non-crystalline form.

2.3.3. Lead isotope analyses. Soils, gutter sweepings and vacuum cleaner dusts were digested in a 7 M HNO$_3$/7 M HCl mixture overnight or heated to ~ 80°C in a covered teflon beaker for ~ 4 h. A solution of ^{202}Pb, whose isotopic composition and lead concentration were known, was added to the sample prior to digestion to enable the lead concentration to be measured at the same time as the isotope ratios. After centrifuging, the solution was evaporated to dryness and dissolved in 1 M HBr. Lead was separated from interfering elements using standard anion exchange chromatographic methods in HBr medium. Further purification of the lead was achieved using anodic electrodeposition. Similar methods were used to separate the lead from the interior dust-fall accumulations and surface wipes.

Isotopic ratios, measured as ^{206}Pb:^{206}Pb, ^{207}Pb:^{206}Pb and ^{206}Pb:^{204}Pb, were determined on an Isomass 54E thermal ionisation mass spectrometer run in fully automatic mode. With each batch of 15 samples, ~ 100 ng of NBS Common Lead Standard 981, was measured as a control of accuracy and precision. A correction of + 0.08% amu was applied to the measured ratios. The precision on the ^{206}Pb:^{204}Pb ratio is ± 0.1% (2 sigma) based on over 1700 measurements of 981 and natural samples.

3. Results and discussion

3.1. Soils

Lead isotopic ratios and lead concentrations were measured for bulk and −53 + 38-μm fractions of soils from the Broken Hill mining community and from some urban soils. The particle size distributions for the Broken Hill soils are summarised in Table 1. Considerable variation may be found in the weight percentages for the various fractions. For example, in House 526, the percentage in the −53 + 38-μm fraction in two samples varies from 1.7 to 5.5%. As found in other surveys, the finer fractions contain 2–9 times higher concentrations than the bulk fractions (Table 2). Thus in the −53 + 38-μm fraction, the amount of lead may vary from 22 to 537 μg, and the −150-μm fraction contains from 12 to 69% of the weight. A comprehensive survey of 1038 samples by the NSW Health Department and the NSW Department of Mines has shown the same trends (Brooks, K., pers. commun., 1994).

There is little or no difference in lead isotope ratios for the bulk samples and −53 + 38-μm fractions of the Broken Hill soils (Table 2) because the major source of lead in the soils is from the orebody. The major sources of lead in Broken Hill are from the orebody, which has a ^{206}Pb:^{204}Pb ratio of 16.00 ± 0.02 (2 sigma), from gasoline which has a ^{206}Pb:^{204}Pb ratio of 16.56 ± 0.16 (2 sigma), and from leaded-paint which can have isotope ratios of 16.0 or > 17 [21]. Thus any sample with a ^{206}Pb:^{204}Pb ratio of < 16.05 have > 95% of their lead derived from an orebody source, if leaded paint is absent from the house or neighbouring areas. The higher ratios in House 553 are from a mixture of ~ 60–70% orebody lead and 30–40% paint lead (~ 17.1); lead paint flakes were separated and analysed from this soil. The ratios of ~ 16.1 for soils from House 541 are a mixture of orebody lead (~ 90%) and lead from petrol and paint.

S.E.M. analyses have identified a variety of lead-bearing phases in the soils, the majority of which are complex and contain PbFeMnCaPAl-SiO. Minor amounts of minerals formed during weathering and oxidation processes, such as anglesite, pyromorphite and coronardite are dis-

Table 1
Particle size distributions in weight percent for soil and dust samples

Broken Hill Size (μm)	Soils (n = 13)			Gutter sweepings (n = 5)			Vacuum dust (n = 5)		
	Range			Range			Range		
	Min	Max	Median	Min	Max	Median	Min	Max	Median
+1000	3.0	30.8	11.2	4.9	21.3	6.8	21.8	48.3	27.4
−1000 + 500	1.9	33.9	20.2	13.5	20.0	14.1	10.7	27.2	13.6
−500 + 250	9.0	39.6	33.8	27.6	33.9	29.0	10.5	20.0	13.6
−250 + 150	11.5	19.2	14.9	16.2	24.7	24.2	6.5	14.2	8.3
−150 + 75	8.7	45.6	12.4	14.3	22.7	18.4	2.6	25.7	19.0
−75 + 53	0.2	9.6	1.2	0.6	1.7	0.8	0.0	9.0	0.9
−53 + 38	0.8	12.0	2.1	1.1	2.1	1.9	0.0	15.3	4.5
−38 + 10	0.3	5.8	1.4	0.3	1.0	0.7	0.0	4.3	0.3
−10	0.0	0.55	0.03	0.00	0.11	0.01	0.0	0.06	0.01

Inner Sydney Size (μm)	Vacuum dust (n = 5)			Soils (n = 2)	
	Range			Range	
	Min	Max	Median	Min	Max
+1000	45.0	83.9	58.8	17.6	30.9
−1000 + 500	1.3	11.4	9.8	19.9	20.3
−500 + 250	2.9	16.4	14.9	12.1	43.0
−250 + 150	2.1	6.7	6.0	10.4	26.3
−150 + 75	2.9	8.3	4.4	3.4	7.0
−75 + 53	0.8	1.6	1.1	0.3	0.8
−53 + 38	1.5	5.0	4.6	0.3	1.2
−38 + 10	2.1	5.5	2.5	0.2	0.9
−10	0.05	0.8	0.6	0.0	0.2

cernible. Rare galena may also be found from houses within the grounds of the central mining activities.

Analyses of soils from Sydney are limited because, in many cases, there was no soil. Data for several bulk samples from different sites within two inner city houses (701, 702), exhibit considerable variation in lead concentration (Table 3). These data compare with other data from inner Sydney which show a mean lead concentration of 627 ppm (range 5-2840) in soil from areas where children play and 1944 ppm (range 123–5407) in 'sink' areas [17]. Lead isotopic ratios are relatively uniform in one case (701), suggesting a single source of lead or that the lead from different sources is well-mixed. In the other case (702), there appear to be at least two sources of lead, the lower $^{206}Pb:^{204}Pb$ ratios probably derived from gasoline. Lead concentrations and isotopic ratios

in sized fractions of soils from two other houses (Table 3, 704, 707) are variable indicating that there is lead from different sources in each fraction.

3.2. Gutter sweepings

The data for gutter sweepings from Broken Hill are presented in Table 2. As with the soils, the lead concentrations are from 2–4 times higher in the finer fraction compared with the bulk sample. The lower lead concentrations in the gutter sweepings compared with pavement gravel (< 0.5 cm^3 sized material) from the same location may be a function of weather conditions. Wet conditions prevailed at the time of sampling and these conditions could have dissolved much of the lead bromides and chlorides derived from automobile exhaust and partially flushed the gutters of lead [3]. This may have resulted in an effective concen-

Table 2
Lead isotopic and concentration data for soil and dust samples from Broken Hill

Sample	$^{206}Pb/^{204}Pb$	Pb (ppm)
Household soils		
526 1 BULK	16.02	2660
526 1 −53 + 38	16.01	3815
526 2 BULK	16.02	1700
526 2 −53 + 38	16.03	3165
541 1 BULK	16.12	850
541 1 −53 + 38	16.11	2415
541 2 BULK	16.13	1350
541 2 −53 + 38	16.10	3225
553 1 BULK	16.32	1220
553 1 −53 + 38	16.28	2910
553 2 BULK	16.17	1800
553 2 −53 + 38	16.13	3150
556 1 BULK	16.05	500
556 1 −53 + 38	16.02	4540
556 2 BULK	16.03	3260
556 2 −53 + 38	16.01	8500
557 1 BULK	16.06	2330
557 1 −53 + 38	16.02	4475
557 2 BULK	16.03	650
557 2 −53 + 38	16.00	4735
Soil around depositional gauges		
DG 1 BULK	16.02	7200
DG 1 −53 + 38 7M	16.01	10000
DG 2 BULK	16.01	11600
DG 2 −53 + 38 7M	16.02	9700
Pavement 'gravel'		
PG 1 BULK	16.27	460
PG 1 −53 + 38	16.11	1020
PG 2 BULK	16.08	440
PG 2 −53 + 38	16.07	605
PG 3 BULK	16.08	1750
Gutter sweepings		
GS 1 BULK	16.05	7100
GS 1 −53 + 38	16.02	22500
GS 2 BULK	16.15	560
GS 2 −53 + 38	16.09	1620
GS 3 BULK	16.13	960
GS 3 −53 + 38	16.07	4080
GS 4 BULK	16.14	1180
GS 4 −53 + 38	16.08	3750
Lead sources		
Orebody	16.00	
Petrol	16.46–16.67	
Paint	16.0, > 17	

tration of, for example, orebody lead. In contrast, gasoline-derived lead would penetrate the soils, be converted to less-soluble lead oxides and sulphates [22], or be absorbed directly onto Fe and Mn oxide particulates, or both, and remain essentially in situ. Such a mechanism may explain the difference in pavement gravel (PG 3 in Table 2) and gutter sweepings (GS 3 Bulk in Table 2) from the sample at 666 Argent Street, the main thoroughfare.

Assuming that there are only two major sources of lead in these materials, viz. orebody lead and gasoline lead, the isotopic ratios indicate that almost 20% of the sample from 666 Argent Street is derived from gasoline. The finer fractions contain a greater contribution of orebody lead than the bulk sample and this may also be a function of the ease of solubility of gasoline-derived lead in moist conditions, suggested above.

3.3. Vacuum cleaner dust

3.3.1. Broken Hill. Particle size distributions and lead concentrations for vacuum dust from residences in Broken Hill are summarised in Tables 1 and 4. The percentages by weight of total lead in the −250-μm fraction are lower (11–51%) than the ~ 83% measured by Que Hee et al. [23] for the Cincinnati urban study. This may be a function of the lead species and weather(ing) conditions. Lead concentrations in the finer fractions, especially the −53 + 38-μm fraction, are up to three times that found in the bulk sample. These data confirm other published data that show the highest concentration of lead is found in the finest fractions because of the increased lead concentration/unit volume. A more comprehensive survey by NSW Health/Department of Mines on several hundred samples has shown the same types of patterns (Brooks, K., pers. commun., 1993).

Lead isotopic results from vacuum dust and from surface wipes show that the majority of dust in Broken Hill is derived from an orebody source (Fig. 1). However, there are a number of houses in which the lead in vacuum and surface dust comes from other sources. It was thought that

Table 3
Lead isotope ratios and concentrations for bulk and sized soils from Inner Sydney House

House	$^{206}Pb/^{204}Pb$	Pb (ppm)
701 1	17.22	2660
701 2	17.06	765
701 3	17.20	1500
701 4	17.23	1310
702 1	17.07	160
702 2	16.76	290
702 3	17.02	1660
702 4	16.58	37
703	17.26	
704 −75 + 53	17.63	650
704 −53 + 38	17.00	1490
707 −53 + 38	17.65	960
707 −75 + 53	17.01	3130

−75 + 53, −53 + 38 denote size fractions in μm. 1, 2, 3, 4 denote different samples.

Table 4
Lead isotope ratios and concentration data for vacuum cleaner dust from Broken Hill

House	$^{206}Pb/^{204}Pb$	Pb (ppm)
523 BULK	16.01	4090
526 −53 + 38	16.00	8300
536 BULK	16.06	1285
536 −53 + 38	16.05	6000
541 BULK	16.25	615
541 −53 + 38	16.20	3750
541 −125	16.23	2320
556 BULK	16.09	4490
556 −53 + 38	16.06	12100
556 -125	16.08	8570
557 BULK	16.04	590
557 −53 + 38	16.03	2600
511 BULK	16.65	43
511 −75	16.29	1980
511 −150	16.53	1390
511 −250	16.25	825
511 −500	16.12	760
517 BULK	16.38	715
517 −75	16.25	3250
517 −150	16.30	1260
517 −250	16.35	780
517 −500	16.29	755
523 BULK	16.53	475
523 −75	16.26	4820
523 −150	16.38	
523 −250	16.53	
523 −500	16.48	60

−500 denotes −500 − 250-μm fraction.
−250 denotes −250 + 150-μm fraction.
−150 denotes −150 − 75-μm fraction.
−75 denotes −75 + 53-μm fraction.

analysis of different size fractions of the dust may provide a better understanding of the different sources. The data for three of these 'anomalous' houses (511, 517, 523) are listed in Table 4 and the data for House 517 are plotted in Fig. 2. Given the isotopic variations in fractions containing relatively elevated lead concentrations (> 1000 ppm), it is clear that the lead in some of these fractions is derived from sources other than the orebody. For example, in House 511, the lead in the −150-μm fraction could be derived from gasoline.

Data for House 517 are very complex and illustrate the frustrations one can face in carrying out investigations directed at correct remedial actions. This house is located < 300 m from the central mining activities. Lead in dust wipes from kitchen surfaces were solely derived from an orebody source. The bulk vacuum cleaner dust had a $^{206}Pb:^{204}Pb$ ratio of 17.0 and 2350 ppm Pb [21], too high for gasoline and it was attributed to paint. Lead concentrations in the teeth of the male and female sibling were some of the highest measured in children from Broken Hill [24] and the isotope ratios in the teeth also indicated a non-orebody source. Two follow-up samplings of vacuum cleaner dust at approximately 6 and 12 months after the initial sampling showed a de-

crease in the bulk $^{206}Pb:^{204}Pb$ ratio to 16.38 (615 ppm Pb) and 16.25, illustrating an increasing component of orebody lead. The different size fractions for the second collection, illustrated in Fig. 2, could not, however, explain the isotope ratios in the first vacuum cleaner dust sample or the teeth. Close inspection of the initial sample of dust showed there to be fine lead paint flakes which had a $^{206}Pb:^{204}Pb$ ratio of 18.3 and thus provided an explanation for the high 'anomalous' value in the first sampling. Despite statements from the parents during numerous visits that the renovations were carried out several years prior to our first sampling, upon seeing the isotope

Fig. 1. Histogram of isotope ratios expressed as the ^{206}Pb:^{204}Pb ratio for vacuum cleaner dust and surface wipes from houses in Broken Hill showing that for the overwhelming majority of samples, the source of lead in house dust is from an orebody source (solid square). P1, P2 and C1, C2 and M denote samplings at different times. An incomplete 'square' indicates isotopic differences in vacuum cleaner and surface dust. Hatching is for vacuum cleaner dust.

results, they recalled that the siblings were crawling around at the time of paint renovations!

House 541 also has 'anomalous' lead isotope data with the ^{206}Pb:^{204}Pb ratio of ~16.2, compared with an orebody value of 16.0. Although located in the centre of the town, and the elevated blood lead of the child and lead from the vacuum cleaner dust was initially attributed to a mixture of gasoline and orebody lead, further investigation showed that deteriorating paint on the front of the house was a more likely source.

S.E.M. investigations of vacuum dusts showed that, apart from houses located in close proximity to mining operations which contained galena and rare sphalerite, the most common lead-bearing material was similar to the complex oxidised material found in the soils, i.e. phases containing PbFeMnCaPAlSiO and rarely S.

3.3.2. *Urban environments.* Bulk samples of dust from the householder's vacuum cleaner in Inner Sydney contained from 760 to 2950 ppm Pb (Ta-

ble 5), the highest concentration coming from a house [707] in which the major source of lead is attributed, on the basis of lead isotopes, to paint. Repeat sampling of two houses approximately 6 months apart, showed good agreement in the bulk sample for one house (500 and 460 ppm Pb) but more than twice the difference in the other (825 and 1750 ppm Pb). These values are lower than the mean value of 2255 ppm Pb (range 100–23 000, median value 1000 ppm) reported for 22 inner Sydney houses by Fett et al. (1992). Results for different size fractions, shown in Table 5, are consistent with other studies in that the finer fractions have higher lead concentrations than the bulk sample by up to a factor of 3. In House 708 located on a highly-trafficked thoroughfare, the lead concentrations in the bulk vacuum cleaner dust are no higher than for the other houses in low-traffic areas. However, all lead compounds except one containing antimony, were identified by S.E.M. and lead isotope analyses as gasoline-derived.

In contrast to the majority of houses in Broken Hill, the lead isotope ratios for different fractions from the inner Sydney vacuum dust can exhibit considerable variations (Table 5), such as was observed in the 'anomalous' houses from Broken Hill discussed above. These differences in the fractions containing >1000 ppm Pb mean that the lead in the dusts has come from different sources and reinforces the point that a lead concentration measurement on a bulk vacuum cleaner dust is meaningless for source identification.

S.E.M. investigations of the 'heavy density' fraction of vacuum cleaner dusts were able to identify lead-bearing materials, some of which were paint and others gasoline-derived compounds. In a number of cases, the particles were large enough (10–50 μm) to separate by hand-picking, and thence to be measured for their lead isotope ratios (Gulson et al., in prep.). For the house located on the heavily-trafficked thoroughfare, lead compounds were gasoline-derived PbBrCl.

One disturbing aspect of the investigation of the inner Sydney houses pertains to the presence

Fig. 2. Lead isotope data expressed as the $^{206}Pb:^{204}Pb$ ratio and lead concentration data for different size fractions of vacuum cleaner dust from House 517 in Broken Hill, in which there is another major source of lead besides that from the orebody, the $^{206}Pb:^{204}Pb$ ratio of which is 16.00 ± 0.02. The other source of lead is from paint.

or absence of lead phases in the different size fractions. For example, S.E.M. analyses of several hundred grains from the coarse $-500 + 250-\mu m$ fraction of the vacuum cleaner dust from Houses 704–707 showed there to be no lead phases present. In contrast, numerous lead phases were identified in the finer fractions which had been concentrated using methylene iodide.

3.4. Interior dust-fall accumulations

Lead loading or flux can also be measured by deposition of airborne particulates into a fixed receptacle over a specific time interval. This very simple method has received little attention in the literature but offers considerable advantages over other methods. The results have been calculated for a 1-month period for comparison with the data from Cincinnati [4].

3.4.1. Urban environment — background houses. Data were obtained from four houses in different geographic locations in Sydney which were occupied only by adults. Lead flux expressed as $\mu g/m^2/month$ and the $^{206}Pb/^{204}Pb$ ratios are

tabulated in Table 6. In the four houses (709–712) sampled during a 3-month period in the second half of 1993, there is reasonable agreement in lead flux for the 50- and 85-mm dishes, which were placed side-by-side. The lower flux in the 85-mm dish from House 709 is because a sample was removed prior to analysis for S.E.M. investigation. The lead flux data for the four houses are consistent with respect to geographic and traffic density. For example, House 710 is located in a low density housing estate, adjacent to bushland, more than 2 km distant from any major traffic thoroughfare. There is good isotopic agreement between dishes except for House 710. Differences in this house are attributed to placement of the dishes in a main thoroughfare of the house, whereby particulates from clothes could be dislodged and fall into the dish.

Isotopic ratios measured in these dusts are relatively uniform considering the differences in geographic locality, traffic density and age of houses. The data plot within the range measured for lead in air from high-volume filters and gaso-

Table 5
Lead isotope ratios and concentrations for bulk and sized fractions of vacuum cleaner dust from inner Sydney houses

House	$^{206}Pb/^{204}Pb$	Pb (ppm)
701	17.64	1060
702	17.03	755
703	16.97	500
704 BULK	16.73	1580
704 − 500	16.49	1240
704 − 150	16.45	7950
704 − 100	17.03	2140
704 − 75 + 53 conc	16.96	12800
704 − 53	16.98	2150
705 BULK	17.51	500
705 2 BULK	17.46	460
705 − 150 + 75 conc	18.32	11680
705 − 100	17.65	1360
705 − 75 conc	18.02	14910
705 − 53	17.61	870
706 BULK	17.09	825
706 2 BULK	17.01	1750
706 − 150 + 75 conc	17.89	28500
706 − 75	17.26	2210
706 − 75	17.26	2200
706 − 53	17.29	2400
706 − 53	16.77	8800
707 BULK	17.87	2950
707 − 100 + 75 conc	18.00	45300
707 − 75	17.73	2100
707 − 75 conc	17.81	31280
707 − 53	17.69	2660
708 − 75	16.59	800
708 sill	16.67	1400

− 500, − 150, − 100, − 75, − 53 denote size fractions in microns for the ranges − 500 − 250, − 250 − 150, − 150 + 75, − 75 + 53, − 53 + 38, respectively.

1/2 denote collection up to 6 months apart.

Concentration denotes methylene iodide concentrate.

line over the same period (Fig. 3) and hence would be consistent with an origin of lead from gasoline.

3.4.2. Urban environment — 'contaminated' houses. Lead flux was measured over a 6-month period in four inner city houses in which children were identified with elevated blood lead, originally attributed to gasoline lead (704–707 in Table 6). The other house (708) was located on a major traffic thoroughfare with > 27 009 cars/day. A detailed multi-visit environmental survey was undertaken in these houses. The dishes were placed

in separate rooms. Flux calculated for a 1-month interval, assuming an equal deposition rate over the 6-month period, was not as high as for House 711 (Table 6). Differences in flux between dishes from the same house are most likely due to the random removal of a sample for S.E.M. investigation. Isotopic ratios are similar for the two dishes from Houses 707 and 706 but there are measurable differences in the other two houses. One explanation for the differences may be preferential removal of lead particle(s) for the S.E.M. investigations but the other explanation may be that there are slightly different sources of lead for the particles. For example, in House 705, the higher $^{206}Pb{:}^{204}Pb$ ratio in the kitchen may reflect a larger input from lead paint dust from an adjoining wall, transported to the kitchen when large sliding doors are open. The lower ratio in the lounge-room in which the door opens out onto a busy road, may reflect a component of gasoline lead. A similar explanation may account for the differences in House 704, and gasoline lead has been identified in the vacuum cleaner dust from this house. The slightly higher $^{206}Pb{:}^{204}Pb$ ratios in these houses compared with the 'background' houses are attributed to another source as well as gasoline lead, and this is suggested to be paint. The dust from House 708 contains many particles of PbBr and PbCl from a gasoline source and this is confirmed by the similarity in isotopic ratios for the dust and external air and gasoline (Fig. 3).

3.4.3. Broken Hill mining community. Dust loading is considerably higher in Broken Hill compared with Sydney although houses which are > 1.5 km from the central mining activities (538, 564, 565 in Table 7) have loadings similar to those in Sydney. Loadings for sampling locations at heights > 1.5 m (e.g. on top of cupboards) are usually less than half those at floor level (such as behind a TV). There is negligible difference in isotopic composition of dusts from the two sampling locations within the one house, consistent with a uniform source(s) of lead.

For Houses 526, 556, 557, 558, 560 and 561, over 80% of the lead in the dust is from an orebody source, assuming that the main end

Table 6
Lead isotope ratios and lead loading data for dust-fall collection in urban Sydney houses

House number	Dust Size (mm)	Pb ($\mu g/m^2$/ month)	$^{206}Pb/^{204}Pb$	
Background houses (July–Sep: 1993)				
710	50	14	16.74	
	85	11	16.62	
712	85	47	16.57	
709	50	96	16.56	
	85	50	16.55	
711	50	176	16.50	
	85	176	16.49	
Contaminated houses (Jan. 5–June 23 1993)				
705	85	42	17.18	Lounge
	85	58	17.31	Kitchen
704	85	230	16.92	Family Room
	85	170	16.50	Kitchen
707[a]	85	135	17.19	Lounge
	85	53	17.14	Upstairs bedroom
706	85	38	16.78	Kitchen
	85	65	16.82	Kitch./Family Room

[a] Sampled during ground floor renovations.

Fig. 3. Fig. 3. Lead isotope data, expressed as the $^{206}Pb:^{204}Pb$ ratio, for dust-fall accumulation from houses in Sydney compared with the range measured for high-volume air filters (HV Air Range) and gasoline over a 2-year period (12/91 to 5/93). ▲ 'Background' houses; ●, House 708 in major traffic thoroughfare; Other symbols, 'Contaminated' houses in which a child has elevated blood-lead, probably arising dominantly from paint.

Table 7

Lead isotope ratios and lead loading data for dust fall collection in broken hill houses (3 months, Sept–Nov 1992)

House Number	Location of House[a]	Pb(μg/m^2/ month)	^{206}Pb/ ^{204}Pb	Location of dish[c]
517	Close	980	16.15	Kitchen cupb
526	Within	850	16.05	Fridge
		1033	16.07	TV/floor
536	Close	138	16.13	Fridge
538	Distant	80	16.27	Kitchen cupb
541	CBD	460	16.25	TV/floor
		263	16.21	Passageway
556	Close	2067	16.05	Kitchen cupb
557	Close	367	16.08	Loungecupb
		1130	16.06	Lounge TV/fl
558	Close[b]	8670	16.03	Dining/shelf
560	Close	5290	16.04	Kitchen cupb
561	Close	763	16.04	Kitchen cupb
564	Distant	177	16.15	Kitchen cupb
565	V. Distant	57	16.16	Kitchen cupb

[a]With respect to central mining activities.

[b]Residence with unsealed cornices.

[c]Dish placed on top of unit Dish diam 85 mm.

Abbreviations: CBD, high traffic density; cupb, cupboard.

members are an orebody source and gasoline. Dust from houses located >1.5 km from the mining activities (538, 564, 565) have higher ^{206}Pb:^{204}Pb ratios (>16.15) interpreted to have a slightly higher component of lead from a petrol or cigarette source. (All cigarettes analysed from the above houses have a ^{206}Pb:^{204}Pb ratio between 18.1 and18.6 and lead contents of ~1 μg/cigarette; Gulson, unpublished data). The ^{206}Pb:^{204}Pb ratios of 16.21–16.25 in House 541 from the Central Business District can be attributed to petrol, cigarette and paint, besides orebody lead. The front of this house, where the female sibling spends most of her day, has flaking lead paint and exposure to gasoline. Sweepings from the front steps have a ^{206}Pb:^{204}Pb ratio of 16.19 and hand wipes 16.29, similar to the 3-month dust. Houses 517 and 536 are both in the same street, and although within 300 m of mining activities, have similar and slightly higher ^{206}Pb:^{204}Pb ratios than the other houses close to the mine. The source of the slightly higher ^{206}Pb:^{204}Pb may be gasoline as the houses are near to garages/repair workshops or paint from earlier renovations.

There are too few data to draw substantive correlations between dust-fall accumulations and blood lead although children in houses 558 and 560 with the highest dust loading and lowest ^{206}Pb:^{204}Pb ratios have some of the highest blood leads we have measured in Broken Hill. The ^{206}Pb:^{204}Pb ratio in the blood of the child from House 541 is similar to the dust-fall accumulation and identical to the dust removed from her hands. There is a good correlation of isotope ratios in blood lead in children and dust (Fig. 4); the most disparate data may have lead derived from paint.

3.4.4. Comparison with other sampling media. The isotopic data for the dust-fall accumulation (long-term dust) in inner Sydney can be compared with dust obtained by other methods. Much of the data for the long-term dust suggest that the largest contribution of lead is gasoline-derived as the data plot closer to the field for gasoline lead (Fig. 3). The vacuum dust from the 'contaminated' houses can contain a variety of lead-bearing phases, especially paint flakes of varying sizes. As the majority of the gasoline-derived particles are extremely fine (<20 μm), they are probably not retained in the vacuum cleaner bag but are recycled through the exhaust. Body et al.

DUST FALL VS PbB

Fig. 4. Plot of ^{206}Pb:^{204}Pb ratios in blood of children from Broken Hill versus ^{206}Pb:^{204}Pb ratios in dust-fall accumulation in their house.

(written communication, 1993) has shown that up to 30% of particles in house dust can be < 5 μm, and that most cleaners will not trap such dust, resulting in recontamination of the house. As these fine particles are of a critical size and can be redeposited on the surface of carpets, floor, and furnishings, they are a greater potential hazard than can be ascertained from bulk vacuum cleaner dust. Ewers et al. [25] observed increases in surface loading (i.e., recontamination) by up to almost 4-fold, especially after the first cleaning, in 14% of the houses investigated.

Airborne particulates retained on 0.45-μm filters give a clearer indication of gasoline-derived lead as the isotopic ratios plot either within or very close to the field for gasoline lead. Disadvantages of airborne sampling include short sampling interval, inconvenience to householder, and the cost of the pump and ancillary equipment.

3.4.5. Comparison with other studies. The only other published study using flux from dust-fall accumulators is that of Clark et al. [4], although Body et al. (personal communication, 1993) have used this approach for environmental monitoring of house dust in Port Pirie.

The lead flux reported by Clark et al. [4] for Cincinnati varies in mean values from 0.035 μg Pb/m^2 for post 2nd World War housing to 0.199 μg Pb/m^2 for 19th century dilapidated housing measured over a 30-day period. These values are

up to 100 times lower than those observed in Sydney. At this stage, no explanation can be given for the difference in these results but it is unlikely to be attributable to gasoline lead in Australia, even though ~ 50% of automobiles in Sydney still use gasoline containing ~ 0.4 g/l Pb. Monitoring of the air in Sydney by the NSW EPA with high-volume air samplers showed that over the period of sampling, the monthly lead contents in Sydney city and suburban total suspended particulates varied from 0.1 to 1.0 μg/m^3 (Johnson, D., pers. commun., 1993). The highest monthly averages are for Sydney city whereas those in the suburbs are usually less than 0.5 μg/m^3. These Sydney suburban values are not markedly higher than the average of between 0.1 and 0.3 μg Pb/m^3 in most U.S. cities without lead point sources [26].

Interior lead loadings measured for Sydney are not inconsistent with some other studies which employed vacuuming methods. For example, Solomon and Hartford [27] measured mean values of 680 μg/m^2 for Illinios in the U.S. ($N = 12$) in the 1970s when gasoline lead use was very high, Diemal et al. [28] found values of 123 μg/m^2 in their Arnhem (Holland) study, Fergusson and Schroeder [29] measured values of 636 μg/m^2 for 65 houses in Christchurch (New Zealand), and Laxen et al. [30] found values ranging from 10 to 473 μg/m^2 in 10 houses from Edinburgh (Scotland).

3.4.6. Advantages and disadvantages of dust-fall accumulations. Rinehart et al. [20] summarised the advantages and disadvantages of various methods for collecting house dust and concluded that none of the present methods satisfies all requirements. However, dust-fall accumulations have received little attention and the following are advantages and disadvantages of this method. The advantages are:

(1) low cost;
(2) no power source required;
(3) can be set up by a technician;
(4) minimal inconvenience to householder (i.e., no power required, no noise, out of the way, a few minutes to set up and collect);

(5) integrates lead flux over a specific period;

(6) usually unbiased (in contrast to vacuuming or wipes where the householder may clean prior to a sampling visit);

(7) easy to 'control' by placement of other dishes in the same house.

The disadvantages are:

(1) inadvertent contamination by householder or children;

(2) lead concentration measurements difficult because of small amount of dust;

(3) time delay (e.g. > 1 month) for sampling.

We consider the advantages far outweigh the disadvantages and would encourage trials of this approach to establish its efficacy or otherwise in environmental surveys. Ongoing trials in the Sydney houses have produced encouraging results, especially with respect to reproducibility in different seasons.

3.5. Sampling and particle size distribution for soil and dust analyses

Most studies have considered soil and dust together but this can lead to erroneous conclusions, especially with respect to their impact on blood lead. Grouping of soil with dust is inappropriate for the following reasons: (1) the source of lead in residential soil may not be the same as in house dust and soil may only contribute a relatively small amount (20–30%) to house dust [12]. In some locations even where there is a point lead source such as a smelter, the source relationship between soil and house dust may not be valid [18]. (2) It is unlikely that there is a robust soil/dust relationship where there is a barrier such as grass or paving between the soil and the exterior environment. (3) There is a further problem of the 'integration time' of the media. Lead in soil may represent accumulation over decades and, unless transported from its protolithology (i.e., the original rock from which it weathered), may have a relatively simple source. In contrast, house dust can in some environments, such as in an arid mining community, accumulate in one day and be derived from multiple sources. (4) The formation of soils and dusts may be entirely different and they may have different particle size distributions. Soil is generally compact and its particle size substantially sorted (graded) by geological processes over generations. In contrast, house dust accumulates either by airborne transport or mechanical transport on items such as clothes and footwear. Hence, its particle size may be more uniform and finer than soil.

Because soil sampling and analysis have been a major tool in the earth sciences (mineral exploration) for several decades, and then later, in environmental investigations, the sampling and analytical protocols are fairly well-defined. There is a convergence towards sampling the first 25 or 50 mm of the soil horizon as this is the most easily disturbed and available for ingestion by children or for wind-born transport. The problem of grassed areas can be overcome by removing the grass during sieving. The major area of disagreement is the particle size fraction to be analysed. In soil surveys for land-use management or mineral exploration, the -2-mm or -80-mesh (180 μm) has been historically the preferred fraction. However, such surveys are of little relevance to health problems where the important, interrelated factors are: grain size, potential to adhere to children's hands, and 'bioavailability' [31]. These factors are inter-related because, for example, a finer particle size will adhere more strongly to a child's hand than a coarser size [1,3].

The 'stickability' will also partly depend on the mineral species in so far as platey minerals will adhere more easily than granular minerals. Mineral species and particle size also impact on 'bioavailability'. For example, coarse lead sulfide (galena) is essentially insoluble under simulated gastrointestinal tract conditions, but -60 μm galena dissolves readily [32]. Likewise, silicates from smelter processing may produce 'soils' with up to several thousand ppm Pb but have very low 'bioavailability', not only because of the relative insolubility of the mineral species but their overall large particle size [33].

In contrast to soils, the sampling and analytical protocols for dust are the subject of considerable debate, especially currently in the U.S. and Aus-

tralia, where guidelines for regulatory purposes are being established. In fact, even the definition of dust is equivocal.

Many of the more recent investigations of mining communities have been carried out by the University of Cincinnati in which they have analysed a −250-μm soil fraction and the −149-μm house dust fraction. The choice of the −149-μm fraction appears to be based on trials with a reference house dust, in which ~75% of the weight and ~77% of the lead was in this fraction [23]. Unfortunately, the reference house dust contained approximately the same amount of lead (~1000 μg Pb/g dust fraction) in each size fraction, a condition not usually found in natural samples. This reference dust was also used to determine adherence of dust to the hands of one small adult (Table 6 in [23]). Their results show significant adherence for the −833 + 392-μm fraction, only twice that adhering for the −149-μm fraction. These data differ from those of Duggan and Inskip [3] in which they found, in four subjects, that the adherence was highest in the fractions <150 μm. The differences in the two studies are probably due to differences in protocol.

Duggan et al. [34] found that over 90% of playground dust removed from children's hands (*N* = 29) comprised particles <10 μm in diameter and the maximum diameter was 80–100 μm.

Given the three factors of grainsize, 'stickability' and 'bioavailability' most likely to impact on blood lead, it is suggested that the most meaningful particle size fraction to analyse, from a toxicological aspect, is the −150 μm in soils, or preferably the −100 μm (Mushak, written communication, 1993).

Furthermore, the unexpected results of the 'Three Cities' Soil study [13–15] imply that dust is the most critical medium impacting on blood lead. Unfortunately, there is no consensus on sampling protocols, including particle size for dust analysis. Rinehart et al. [20] summarised the methods for dust collection as:

(1) passive wipe methods (Vostal, preweighed wipes, OSHA, NIOSH, Lioy's wipes, dislodgeable dust, dust fall); and

(2) battery-powered/AC-powered vacuum methods (commercial vacuum cleaners, High Volume Surface Samplers, University of Cincinnati method using a low volume portable air sampler, Sirchee-Spittler modified dust buster, Blue Nozzle method, Prpic-Majic method, Lioy's vacuum method).

Once again, Rinehart et al. [20] emphasised that the critical material to be collected is that which will adhere to children's hands.

Rinehart et al. [20] recommended that, at the present time, there is no single 'best' method for sampling dust. Preweighed wipe methods are impractical and analytically difficult. The OSHA wipe method is not at all reliable and none of the wipe methods are acceptable if lead concentration measurements are required. With respect to vacuum cleaners, if AC power is not available, only the University of Cincinnati and dust buster systems are applicable.

3.6. Relationship of soil and interior lead

From their investigations of mining communities and urban Cincinnati, the University of Cincinnati researchers have suggested that there is a pathway of lead from soil → (air) → house dust → hands → blood [4,6]. However, the results of the Three Cities Soil Abatement program indicate that the relationship between soil and blood lead is not robust [13–15]. These conclusions were based on total lead concentrations and statistical correlations.

Fergusson and Kim [12] using a multi-element approach, have estimated that the contribution of soil/street dust to house dust is approximately 30–40%.

From the lead isotope results outlined above, it is possible to evaluate the relationship of soil and house dust (vacuum cleaner ± wipes ± dust fall). Isotopic results for the 40 houses in high-risk and low-risk sites in Adelaide, Hobart and Port Pirie indicate that only in about 10% of the houses is there a robust relationship between soil and house dust [18]. Some of these data are summarised in Fig. 5 for Port Pirie. If the source of the lead in the air or dust (surface or vacuum) was directly from soil, there should be a coincidence of the

Fig. 5. Isotopic variation for individual houses in Port Pirie (site 201, 202,...,), expressed as the ^{206}Pb:^{204}Pb ratio, in bulk soil samples (SS), the -60-μm fraction of vacuum cleaner dust (VC), house air measured with a 4-l/min pumping system for an 8-h period (AT), and surface dust wipes (WD). The results are for a high-risk suburb located, <2 km from the smelter and for a low-risk suburb located over 4 km from the smelter.

isotopic results for each house. As this is only present in about 10% of the houses, it is unlikely that soil is the major contributor to house dust. In some cases, such as the low-risk sites in Hobart, the vacuum dust appears to be a mixture of lead from air (probably gasoline-derived) and lead from soil, but this relationship does not necessarily hold in other locations.

In Sydney, there can be various sources of lead depending on the individual house. In some cases, lead isotope and the S.E.M. analyses have shown that lead from gasoline is dominant and in others lead from paint is the major contributor to house dust.

In contrast to the above cities, in the Broken Hill community where the major point source of

lead is from the orebody, over 80% of lead in vacuum and surface dust in the majority of houses, comes from an orebody source [21]. In some other houses from Broken Hill, a significant contribution is from gasoline or paint (Fig. 1).

4. Conclusions

A combination of the lead isotope and S.E.M. methods provide an extremely powerful approach for determining the sources of lead in soil and dust. More research is needed into sampling house dust and especially more detailed testing of dust-fall accumulation as a more appropriate indicator of lead exposure. To facilitate investigations of dust-fall accumulation using different methods,

we now employ petri dishes separated into halves by a thin partition. One hemisphere is used for lead flux analysis and the other hemisphere is retained for other investigations. The 'critical' finer fractions of soil and dust should be used in trying to establish relationships between soil and dust and blood lead in children. At this stage, to allow comparison between earlier studies, it will be necessary to analyse a 'bulk' fraction as well as the $-150-$ (or even better, the -100) μm fraction for soils and the -100-μm fraction for dust.

In our future studies, the bulk soil sample will be pulverised in a tungsten carbide mill prior to analysis, and another subsample of the bulk material passing through a 150-μm and perhaps 100-μm sieve will be prepared for analysis. These size fractions are the most meaningful toxicologically (Mushak, written communication, 1993). Until a better system of dust collection is introduced, a bulk and -100-μm fraction will be analysed. Bulk samples of dust (and soil) will be analysed until such time as sufficient data become available in the literature for comparisons between the finer fractions.

Acknowledgements

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