History of Lead Exposure in Children Revealed from Isotopic Analyses of Teeth

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ABSTRACT. A pilot study to evaluate the efficacy of using high precision lead isotopes as an indicator of previous lead exposure in children was undertaken on deciduous teeth from 10 children in a lead-mining city. The present study illustrates the applicability of the method and provides data from two subjects who had different exposure to lead during early childhood. Teeth were examined by slicing the crowns into upper and lower sections and/or by selective dissolution with different mineral acids. Different exposures to mine lead and other sources, such as food, water, air (gasoline), are readily detected in any tooth from an individual.

KNOWLEDGE of the skeletal burden of lead is of critical importance. This is especially true for females because it is a potential endogenous source of lead that may be released from the bones during pregnancy,[1,2] during lactation,[2] and during post menopause.[3] Chronic exposure to lead, such as from mouthing activity in early childhood, may be camouflaged by dilution during periods of rapid skeletal growth in the young and adolescents, and, therefore, may not be detected by the normal methods of blood lead analyses.

The potential for using lead in whole deciduous teeth, enamel, or dentin as an indicator of past exposure of children to lead, and as a proxy for skeletal lead, has been well documented in many studies.[4-20] The advantage of deciduous tooth lead measurement over blood lead analysis lies in the incorporation of lead into the tooth during several years from in utero to exfoliation, compared with blood, which has an approximate 30-d mean life.[21] Given the chronology of tooth development (for example, anterior deciduous teeth—enamel mainly forms in utero and dentin forms largely post-natally), authors such as Shapiro et al.[4,5] have suggested that the circumpulpal dentin offers the best indicator of (post natal) lead exposure.

To date, all investigations of lead in teeth have used total lead contents; these provide only circumstantial evidence for the source of lead. Analysis of lead isotope ratios can provide information that relates to environmental lead sources.[22-28] As part of a study to determine the source of lead in humans in a lead-mining city,[29] we have undertaken a pilot study of deciduous teeth, using high precision lead isotope methods to evaluate the history of lead exposure of children.

Broken Hill is a city of approximately 25 000 inhabitants and is located about 930 km west of Sydney, NSW, Australia; it is also centered about the world's largest currently mined lead (Pb)-zinc (Zn)-silver (Ag) deposit. Mining activities, including underground and open-pit operations, and smelters in the latter part of the past century, have been conducted for more than 100 y. This area is desert and subject to severe windstorms, and the dust from the mining activities is considered to be the

main point source of lead in children, i.e., inhalation and ingestion of contaminated soil and house dust. The isotope values discussed in this paper are the abundance of the ^{206}Pb to the abundance of ^{204}Pb, expressed as the ratio $^{206}Pb/^{204}Pb$. The $^{206}Pb/^{204}Pb$ value generally ranges from 16.0 to 16.2 for the mine lead and dust from ceilings, vacuum cleaners, and kitchen wipes. The other potential sources of lead are food, water, and air; food and water contain < 10 and < 3 ppb lead, respectively, and are considered to contribute insignificantly to the body burden. Apart from the mine dust, the other major source of lead in air is from gasoline; approximately 60% of automobiles in Broken Hill use leaded gasoline (> 0.4 g/l lead, with a $^{206}Pb/^{204}Pb$ of approximately 16.5). Gasoline is considered a major source of lead in adult females from Broken Hill.[29]

Methods

At this stage, deciduous teeth from 10 children who had experienced differing exposure to lead had been tested. Estimates of exposure were based on information obtained from parents (early childhood mouthing frequency, learning difficulties, and behavioral problems) and included residence in areas identified by a blood lead survey of 899 1- to 4-y-old children as "high risk."[30] Most of the teeth consisted only of the crowns. Fortunately, in one case, 16 teeth, including 4 canines (3 with roots), were available from 1 child.

Part of this study involved the evaluation of different analytical procedures to gain maximum information. Hence, two main approaches were tried. The first involved the use of whole teeth, whereas the second involved cutting < 2-mm-thick cross-sectional slices from the incisal end and cervical part of the crowns, or, in the case of the canines, 4 or 5 slices from the crowns and roots. Saw marks were removed by polishing on emery paper, and the samples were rinsed in clean water with ultrasonic agitation for 10 min. Thereafter, the whole teeth or slices were soaked in clean water overnight and then soaked in 6% H_2O_2 for 4 h. In order to further remove surface contamination, the teeth were dipped into either 1.5M HCl or 16M HNO_3 for 20 s and then were rinsed consecutively in three teflon beakers containing clean water with 10 min ultrasonic agitation for each step. The teeth were then soaked in distilled acetone for approximately 1 min, the acetone was then decanted, followed by drying in the teflon beaker on a hot plate at approximately 100 °C in a laminar flood clean hood. All washing and subsequent operations were carried out in a "clean" laboratory.

Teeth were initially dissolved in clean 16M HNO_3. However, upon further testing with HCl and HNO_3, it was obvious that the different tooth tissues dissolved differentially. The method now used (and which we employed) is to slice and clean the tooth, as described above. This is followed by soaking for about 4 h in 1.5M HCl, rinsing the residue with acid and clean water, rinsing in distilled acetone, drying for 1 h at 100 °C, soaking for about 1 h in 3.4M HCl and repeating the first step, and finally digesting the dominantly organic material in a few drops of 16M HNO_3. After each acid leach, a ^{202}Pb solution of known isotopic composition and concentr tion is add to obtain the isotopic composition and le contents on the same tooth sample (i.e., isotope dilutic method). The contamination level for the analyses (i.e blank) is routinely less than 300pg.

Two approaches were undertaken to test for signi cant contribution from elevated lead contents in circur pulpal dentin.[4,5] In the first case, the circumpulpal dent was reamed out of a cross-section of a canine. In t second case, Parafilm was partially melted into the pu pal cavity of three incisors to minimize access of HC which may have dissolved some or much of the lead the circumpulpal dentin.

Isotope ratios were measured on a VG 54E or VG Sector thermal ionization mass spectrometer in fully a tomatic mode. The external precision of the isotope tios, based on more than 1 500 analyses of the interr tional NBS Lead Standards 981 and 982 and natu samples, is ± 0.1% (2 sigma) for the 54E and better the 54 Sector. Accuracy of the measured isotope rat in the teeth samples is achieved by normalization of t ratios to those given by NBS. Validation of the laborato was a prerequisite for undertaking a project, "Biokinet of Lead in Human Pregnancy," funded for the most p by NIEHS.

Results and discussion

Data presented in the following sections are from t subjects who had five or more teeth available, and w were subjected to differing exposure to lead during ea childhood. The results for the other subjects are, ho ever, consistent with results presented and will be pu lished is detail at such time as the full study is complet

Lead contents of the crowns from either the slic method or 1.5M HCl leaches ranged from 0.7 to 8 pp we attributed the higher contents to a contribution fr coronal dentin. These values are low, compared with ranges found in some other studies of children who w exposed to potentially high doses of lead. For examp Delves et al.[8] measured lead contents ranging from to 340 ppm in deciduous incisors from children w lived near a lead-smelting works, and Stack et al.[31] attr uted mean tooth lead levels of 60 ppm to the preser of a large smelter. In other studies, however, no corre tion was obtained between tooth lead and envir ment.[32,33] The low lead contents of the crowns were c sistent with the low blood lead of mothers in Broken H (i.e., < 10 μg/dl).

There is uncertainty about the use of whole teeth certain parts of teeth in determining childhood lead posure. Delves et al.[8] found no significant difference tween crowns and roots in children who lived in proximity of a lead smelter, compared with a con group. Shapiro et al.[4,5] and Grandjean et al.,[13,14] ho ever, recommended the analysis of circumpulpal der because it represents the exposure of the body to l from eruption to exfoliation, and this analysis can h an order of magnitude more lead than enamel or coro dentin lead. The major drawback of circumpulpal der analysis is its relatively limited quantity in decidu teeth (especially naturally exfoliated teeth), difficulty

separation, and analysis on a routine basis. Shapiro et al.[5] and Hansen et al.[34] described elegant methods for separating the circumpulpal dentin, but the maximum amount of lead available for analysis (< 10 to 38 ng), shown in Shapiro et al.'s[5] Table 3, is a nontrivial task in all except "clean" laboratories.

Results from this study agree with those of Shapiro et al.[4,5] in that, from certain environments, analysis of whole teeth can disguise significant information about exposure. This is shown in Table 1 and in Figure 1, wherein a comparison of data is presented for equivalent teeth, which were sectioned in two cases (Fig. 1[b] and 1[c]), and for the other case, for the whole tooth was differentially acid-leached (Fig. 1[a]). The $^{206}Pb/^{204}Pb$ values of the incisal end of the crowns, especially when sectioned, are higher than the cervical parts of the crown (i.e., enamel plus coronal dentin) or root dentin, in the case of the canines. These higher values are consistent with those of mothers from Broken Hill ($^{206}Pb/^{204}Pb$ = 16.4–16.8), if it is assumed that the present day mothers' blood isotopic profiles are similar to those prevailing during pregnancy. These profiles, of course, depend on skeletal lead, which may be quite different from present day blood lead.

The results for the whole tooth in Subject 2 could be misinterpreted to indicate that in utero exposure to lead was significant. However, the selective acid leaches shown in Figure 1(a) probably reflect a mixing of lead from the enamel and dentin and indicate that even the coronal dentin in this individual has high amounts of mine-type lead. Shapiro et al.[4] observed similar lead contents in subsurface enamel and coronal dentin for deciduous and permanent teeth.

A more complete history of exposure can be obtained in the roots of deciduous teeth are available, although, because of resorption, this is recognized as being rare. Data for sections through upper and lower canines from Subject 2 are illustrated in Figure 1. The root dentin contains an order of magnitude more lead than the incisal crown, and the $^{206}Pb/^{204}Pb$ values approach those found in the mine dust (16.0–16.2); these results indicate that during early childhood the individual's intake of mine lead exceeded that from other sources.

The center of the middle section, shown in Figure 1(b) (20.6 ppm), was reamed out to determine if most of the lead was derived from the circumpulpal dentin. Because

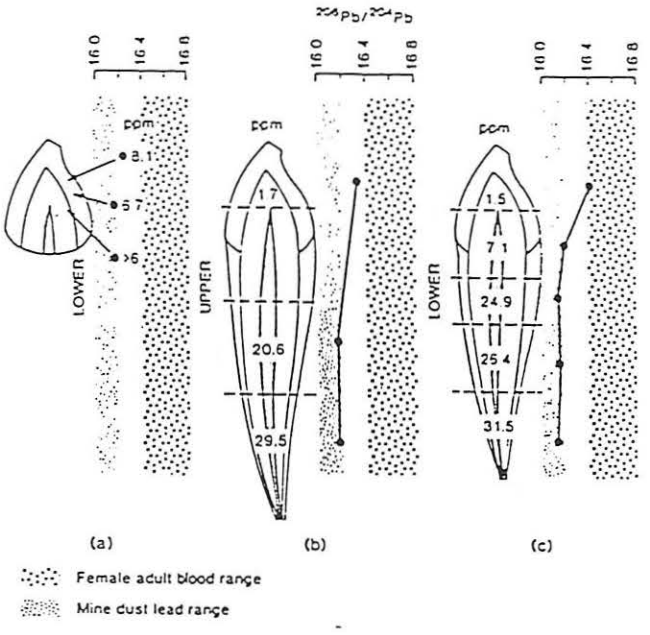

Fig. 1. Isotopic variations and lead contents in canine teeth from Subject 2. Figure 1(a) is a lower canine crown subjected to selective acid dissolution. Lower $^{206}Pb/^{204}Pb$ values indicate a larger exposure to mine lead during tooth development. Figure 1(b) and 1(c) are the upper and lower canine crown and roots, which have been sectioned and subjected to selective acid dissolution; the results are for 1.5M HCl leaches.

Table 1.—Comparisons of Equivalent Teeth from Individuals with Differing Lead Exposure

	Subject 1 (female) Upper incisors		Subject 2 (male) Lower canines	
	Left (Al)	Right (Sect)†	Crown (Al)	Crown root (Sect)
	1.5 M HCl	Incisal	1.5 M HCl	Incisal/crown
Pb ppm	1.7	1.1	8.1	1.5
$^{206}Pb/^{204}Pb$	16.49	16.62	16.22	16.39
	3.4 M HCl	Cervical	3.4 M HCl	Root
Pb ppm	2.9	1.1	16.7	24.9
$^{206}Pb/^{204}Pb$	16.56	16.48	16.16	16.13
	HNO_3		HNO_3	
Pb ppm	≥ 0.7		≥ 6	
$^{206}Pb/^{204}Pb$	16.63		16.17	

*Al = differential acid lead of whole tooth.
†Sect = section of tooth.

the lead contents and isotopic values are similar for both teeth, the contribution of lead from circumpulpal dentin for this individual seems minimal. It may be that the material being dissolved in the 1.5M HCl leach is cementum surrounding the root. Further investigation of the role of cementum in the lead budget of teeth is planned.

The small increase in lead content towards the apices of the deciduous canine roots, the last part of the tooth to develop from about 9 mo of age onwards, is consistent with an increased exposure during childhood and is likely associated with hand-to-mouth activity.

The organic residue from the HCl leaches amounts to less than 1.4–2% dry weight of the total tooth that was dissolved in nitric acid. Even though this more tightly bound lead is insignificant in terms of the total lead budget in the teeth, it nevertheless retains a realistic estimation of the lead isotope profile (Table 1). It would, therefore, appear unnecessary to analyze the organic residue and, because of the extremely small amounts of total lead available for analysis, is not a trivial analytical exercise.

Variations between teeth and indications of exposure. The results of this aspect of the pilot study are complicated by the evolving analytical methods of slicing and selective dissolutions. It is still possible, however, to evaluate the effectiveness of the lead isotope approach.

The data for the 1.5M HCl leaches from different teeth in Subjects 1 and 2, given in Table 2, indicate that almost any tooth can give an estimate of childhood exposure in such an environment under consideration. Furthermore, both lead concentration and isotopic data clearly illustrate the difference of exposure in the subjects; data for Subject 2 were consistent with a higher exposure to mine lead than for Subject 1, probably arising from gasoline, water, and food.

The correlation between $^{206}Pb/^{204}Pb$ value and tooth lead content is moderate, but not always consistent. Similarly, although based on limited data at this stage, the correlation between $^{206}Pb/^{204}Pb$ and blood lead content is fairly strong but with anomalies.

Summary

The lead isotope method clearly indicates the extent of exposure of children to differing sources of lead, especially in the mining city of Broken Hill, where the major point source—the mine—has a large contrast in isotopic composition to the other potential sources of food, water, and gasoline.

As a result of this pilot study, it appears that analyses of slices of the incisal part of deciduous teeth give the clearest indications of the in utero environment, and the cervical sections provide indications of exposure from birth to exfoliation. Enhanced information can be gained from root dentin, but roots are not always available in deciduous teeth. Further investigation of the role of cementum in the lead budget of teeth is planned.

Table 2.—Comparisons of Isotopic Data for Different Teeth (1.5 M HCl Leach)

Tooth	Pb ppm	$^{206}Pb/^{204}Pb$
Subject 1		
Upper central incisor	1.8	16.52
Upper central incisor	−1.8	16.54
Upper cervical incisor	1.7	16.49
Low incisor	2.2	16.56
Subject 2		
Upper central incisor	7.5	16.20
Lower canine	8.1	16.22
Molar	4.3	16.26

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Source and Pathways of Lead in Humans from the Broken Hill Mining Community—An Alternative Use of Exploration Methods

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Abstract

To assist in recommendations for the most suitable lead abatement policies in Broken Hill, New South Wales, Australia, knowledge of the sources and pathways of the lead into humans is critical. We have approached these problems using the lead isotope fingerprinting method, combined with mineral speciation and "bioavailability" tests, approaches which have in the past been largely applied to mineral exploration.

High precision lead isotope ratio measurements and lead contents were determined by thermal ionization mass spectrometry on biological samples (blood, urine) and environmental samples from 27 families, encompassing 60 children, 41 female adults, and 17 male adults. Environmental samples analyzed (not from every household) included soils, gutter sweepings, ceiling dust, vacuum cleaner dust, long-term dust, surface dust wipes, external and internal air, food, water, and gasoline.

Sources of lead have been identified in the blood of children, using lead isotopes, with dominant contributions from the Broken Hill orebody, but with individual cases having a dominant source of lead from gasoline or paint. Nevertheless, of 28 children with a blood lead level (Pb_B) > 15 μg/dl, ~30 percent have more than 50 percent of their Pb_B from sources other than orebody lead. Female adults generally have a low Pb_B, <10 μg/dl, and the source of their lead is attributed to air (gasoline, orebody), food, and water. The source of lead in male adults can usually be correlated with their occupation, depending on whether it is related to high risk activities, such as mining (dominantly orebody lead) or service stations (gasoline lead), or "nonexposed." Knowledge of the occupation and lead isotope composition in the father's blood is an important indicator of lead pathways. Other potential sources of lead, such as food and water, have lead contents too low to be significant contributors to lead levels in most children.

Scanning electron microscopy (energy dispersive X-ray analyses) identified the most common lead species in soils and dusts to be composed of a complex Pb,Fe,Mn,Ca,Al,Si,O material with rare galena in houses close to the central mining activity. These lead complexes are quite different from ones found in other mining communities, such as those found in the United States, where the lead may be in less soluble forms such as pyromorphite or encapsulated in less soluble anglesite, pyrite, or quartz. Approximations of bioavailability (more correctly, solubility) were made by leaching, with 0.1 *M* HCl for 2 hr at 37°C, bulk (unsized) and a critical size fraction of −53+38 μm. The 0.1M HCl extracts 33 to 61 percent (mean = 47 ± 10%, n = 7) of the total leachable lead from gutter sweepings, from 41 to 84 percent (mean = 60 ± 10%, n = 10) from soils, and 17 to >100 percent (mean = 47 ± 38%, n = 5) from vacuum cleaner dusts. Thus the currently suggested amounts of ~100 mg/d ingested soil (dirt) and dust for a Broken Hill child can readily account for the elevated lead levels compared with the amounts for children in many other mining communities. Based on these investigations it is possible to construct a flow sheet of sources and pathways for the lead into humans at Broken Hill on which to base correct remedial actions.

Introduction

WITH the increased awareness of environmental matters, many exploration geologists and geochemists have turned their skills to the environment (e.g., Society of Economic Geologists *Newsletter*, Nos. 11, 12, 1992, 1993; Association of Exploration Geochemists, *Explore*, No. 78, 1993). Likewise, sophisticated methods originally developed for exploration are now finding application in environmental fields, such as electromagnetic methods for detecting salinity problems. In this paper, we demonstrate the application of lead isotopes in determining the source and pathways of lead in families from the Broken Hill community, New South Wales, Australia, the site of one of the largest Pb-Zn-Ag mines in the world. In using

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the fingerprinting method for determining the source of lead in, for example, people, the lead isotope profiles in blood and/or urine are compared with those found in the potential environmental sources such as air, food, water, gasoline, and dust. In simple terms, a close similarity in isotopic profiles between blood and an environmental source(s) indicates that the environmental source may be a significant contributor to the lead in blood. In practice, the isotopic profiles show mixtures of lead from a number of sources.

Most investigations of correlations between blood lead and environmental lead have focused on urban environments and point to sources such as lead smelters (see references in, for example, the Agency for Toxic Substances and Disease Registry report to Congress, 1988). Few studies have addressed the problem around lead mining centers (e.g., Barltrop et al., 1974, 1975; Heyworth et al., 1981; Gallacher et al., 1984; Bornschein et al., 1988; Moffat, 1989; Cotter-Howells and Thornton, 1991). In many of these investigations, the lead level was low (<10 μg/dl) and was attributed to the low bioavailability of the lead species (e.g., Steele et al., 1990). Bioavailability is the proportion of a substance taken up by the gastrointestinal tract compared with the total amount available; Davis et al., 1992). However, in most cases, there was no investigation of the lead species or its bioavailability, and Mushak (1991) has criticized the scientific arguments and sampling protocols of many of the above studies. Thus, in addition to the lead isotopes, we have used optical microscopy, scanning electron microscopy, X-ray diffraction, and solubility tests to understand more about the source and pathways of lead to the body. The impact of such investigations is to establish the source and pathways as a guide for remediation. For example, if a child has a high blood lead level and there are high levels of lead in the house soil, it may be incorrectly assumed that the cause of the high Pb_B is the soil and hence it is removed. In fact, the lead in this child may have come from gasoline or paint. Thus, replacement of the soil does not solve the problem.

Broken Hill is a city of about 25,000 people located about 930 km due west of Sydney. A 1992 survey by the New South Wales Health Department showed that ~20 percent of children aged 1 to 4 years have $Pb_B > 25$ μg/dl; until recently the level of concern set by the Australian National Health and Medical Research Council (this level compares with that of 10 μg/dl set by the U.S. Centers for Disease Control). Broken Hill 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 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 by which the primary sulfide orebody was oxidized, approximately 30 million years ago. It has been estimated by geologists familiar with the Broken Hill orebody that possibly as much as 40 million metric tons of oxidized ore has been removed by erosion (G. McIlveen, pers. commun., 1993) and may 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 orebody lead).

Materials and Methods

Sample collection

A brief description of sampling methods is given below; more details are given in Gulson et al. (1993) and Davis (1993). Venous blood samples (1–5 ml) from family members were usually collected in a medical surgery into precleaned and preweighed teflon containers without anticoagulants. To minimize sample heterogeneity, the total blood sample was predigested in concentrated nitric acid. Cold water from kitchen taps was collected in cleaned 125 ml polyethylene bottles after a 30-s flush. Early samples were not acidified. However, acidification of these samples with 1 percent nitric acid after >6 mo showed them to have the same lead isotope compositions, but the lead content had doubled, probably due to accumulation of the lead in bacteria on the walls of the containers (M. Florence, pers. commun., 1993). At the low levels measured in the waters, these changes do not affect the conclusions. Reticulated water samples from three of the four tanks supplying the community were collected by the Broken Hill Water Board. Ceiling dust was scraped into plastic bags; note that "dust" is a generic term covering material transported into the houses via airborne and mechanical means and it has no size connotation. Subsampling of the upper and lower parts of the dust accumulations up to 10 cm thick, to evaluate any historical changes showed there to be no isotopic variation with time.

Vacuum cleaner dust from the householder's cleaner was an integration of material removed from the floor over periods from days to weeks. Part of the contents was shaken into plastic bags or removed with disposable gloves. Selected vacuum dust (and soil) samples were sized according to the method outlined below. Kitchen counter dust was collected onto a ~75 × 75-mm acid-washed polyethylene sheet from counter tops, window ledges, refrigerator tops

or anywhere dust fallout had taken place in the kitchen. Long-term dust was collected into petri dishes over a 3-mo period in selected houses.

Systematic sampling of soils was not undertaken because of the recognized widespread contamination of the Broken Hill area over millions of years and >100 years of mining activities. However, in selected gardens, the top 1 to 2 cm of soil was scooped with a stainless steel spatula into a plastic bag. These samples were obtained from areas where the children spent most time playing outdoors (e.g., under swings). Other soil samples included sand-pit and "cracker dust" materials; the latter is a fine residue (<5 mm) from quarrying operations and is found in the city. Footpath soil and gutter sweepings were collected from some heavily trafficked areas to determine if it was possible to detect gasoline lead in a matrix dominated by orebody lead.

Air-borne particulate matter, collected over a 24-h period, was that retained on high-volume air filters (70 m^3/min), supplied by the Pasminco mining company. Filters were measured for two periods approximately 12 mo apart. On the first occasion in August-September 1991, filters from the northern (Proprietary Square) and southern areas (Westside Drive) of the central mining activity were compared with those from the central business district (Mining Managers Association building [MMA]; Fig. 1). On the second occasion in August-October 1992, filters were available from Westside Drive and MMA. House air was measured over an 8-h period in five houses selected for comprehensive sampling (Fig. 1) on the basis of geographic location, and in four of the five houses, a child with a blood lead level >20 μg/dl. The particulates were collected using SKC Inc. pumps operating at 2 l/min, the air being drawn through a 32-mm 0.45-μm Millipore cellulose acetate filter. To estimate the contribution of food to the body burden, a 6-day duplicate diet was collected from the five households. Samples of leaded gasoline (~0.8 g/l Pb)

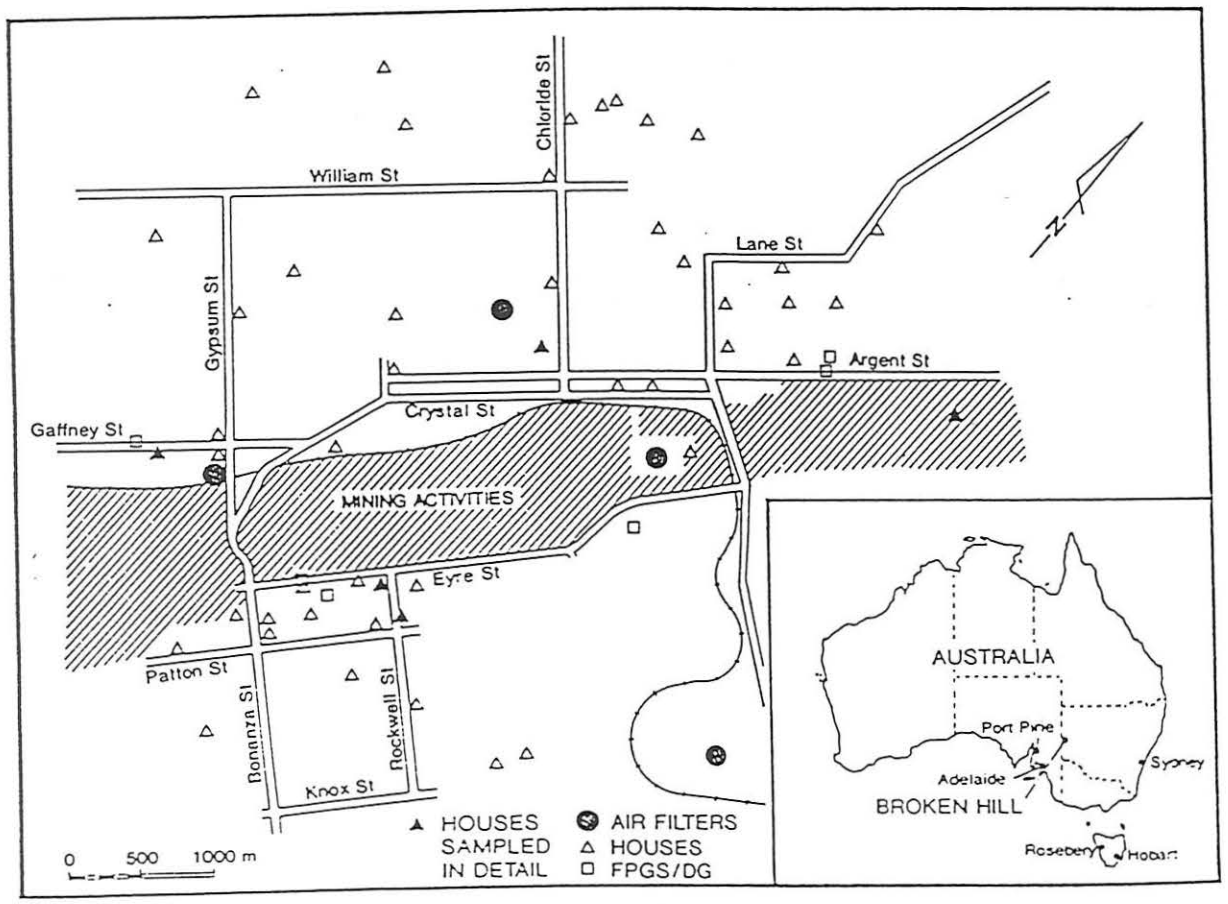


FIG. 1. Sketch of Broken Hill city showing locations of houses and subjects sampled with respect to the mining activities in the center of the city. Air sampling sites: 1, Westside Drive; 2, MMA building; 3, Proprietary Square. "FPCS/DC" denotes footpath and gutter sweepings/directional gauge locations. The high risk areas identified by the 1991/92 New South Wales Health Department blood lead survey of 899 children generally are those within 300 to 500 m of the mining activities and specifically are in the south between Eyre and Patton Streets, and in the southwest, around Gaffney Street.

were collected on three occasions; over 60 percent of cars in Australia still used leaded gasoline as of December 1993. One collection in September 1992 included all major brands sold in Broken Hill.

Sample preparation

The majority of soils and vacuum cleaner dusts (house dusts) were analyzed as bulk fractions. In selected cases, the samples were sieved through nylon sieves and the −53+38-μm fraction passed through methylene iodide (density 3.2) to obtain a concentrate for lead isotope and SEM analysis. The −53+38-μm fraction was chosen because the −100-μm fraction of dusts and soils is known to be extremely difficult to remove from hands (e.g., Duggan and Inskip, 1985), recent bioavailability experiments in the United States have been performed on material with a mean size of about 50 μm (Davis et al., 1992), and lead isotope studies on vacuum cleaner dust from houses in Port Pirie, Hobart, and Adelaide used an approx −60-μm fraction (Pisaniello et al., in press).

Sample digestion

Biological samples (blood, urine, food) were digested in a "clean" laboratory in Class 100 laminar-flow workbench stations using double quartz-distilled nitric acid in a microwave oven. After digestion, the lead was separated on a 0.5-cc AG1-X4 anion exchange resin bed in an HBr medium. Further purification was achieved using the same acid in a 0.1-cc bed volume of AG1-X8 anion exchange resin. Approximately 50 ml of water was evaporated to dryness under a clean nitrogen flow and then treated in the same manner as for the biological samples. Vacuum cleaner dust, ceiling dust, soil, and gutter sweepings were leached with clean 7 *M* HNO_3-7 *M* HCl for ~1 h using an approach similar to that employed for gossan and soil evaluation in mineral exploration (e.g., Gulson, 1986). Kitchen wipes and air filters were leached with the same acid in an ultrasonic bath for ~15 min. Because only isotopic ratios were determined for the wipes and air filters, more recent samples were treated with 1 percent HNO_3. Lead was separated using a 0.5-cc resin bed as for the biological samples. Further purification of the lead was achieved using anodic electrodeposition (e.g., Gulson, 1986).

To ascertain whether the elevated blood lead levels in Broken Hill children, compared with levels from other mining communities, were due to the difference in solubility of the lead species, selected bulk and sized fractions of vacuum dust and soils were subjected to 0.1 *M* HCl leaches for 2 h at 37°C. The lead content was measured by isotope dilution mass spectrometry for all samples except the ceiling dusts, air filters, and kitchen wipes. A 46 percent pure ^{202}Pb solution, whose isotopic composition and concentration were accurately known, was added to the samples prior to digestion. Selected bulk samples and sized fractions were analyzed for a variety of major and trace elements using inductively coupled plasma-atomic emission spectrometry and -mass spectrometry (ICP-AES and ICP-MS); these data will be reported elsewhere.

Lead isotope ratios were measured on a solid source thermal ionization mass spectrometer (Isomass 54E) in fully automatic mode. To allow interlaboratory comparisons, the data have been normalized to National Bureau of Standards SRM 981 common lead standard and SRM 982 equal atom standard by applying a correction of +0.08 percent per mass unit. Quality control was maintained through a number of approaches including replicate analyses of blood samples, isotopic analyses of blood and urine pairs from the same subjects, serial testing of one subject—e.g., 21 weekly urine measurements gave a mean and standard deviation of the $^{206}Pb/^{204}Pb$ ratio of 16.745 ± 0.022 (1σ), and participation in a quality assurance program based on doped pig's blood. Bulk samples of soils, vacuum cleaner, and ceiling dusts were analyzed by X-ray diffraction and the bulk and −53+38 μm fraction of the same samples was inspected by optical and scanning electron microscopy for morphology. Lead-bearing phases were analyzed by EDX in a Cambridge stereoscan.

Results and Discussion

Lead sources

The major source of lead in Broken Hill has been attributed by the media, especially, over several years to the mining operations, particularly the mine ("skimp") dumps. The lead isotope compositions of the Broken Hill mines and mineral occurrences in the surrounding areas are well documented (e.g., Reynolds, 1971; Gulson, 1984; Gulson et al., 1985). Analyses of sulfide minerals from different parts (lodes) of the Broken Hill deposit show the lead to have a uniform isotopic composition with a $^{206}Pb/^{204}Pb$ value of 16.00 ± 0.02 (2σ). Since the oxidized surface material has the same isotopic composition as the primary sulfide ore (Gulson and Mizon, 1979), material which may have been subjected to weathering for over 3 m.y. has the same isotopic composition as the primary sulfide ore. Although lead-rich ore of a different geologic origin and isotopic compositions from elsewhere in the Broken Hill area (Thackaringa ore, Reynolds, 1971) was processed in the early history of the city, its contribution to the lead budget is insignificant (e.g., estimated hundreds of thousands of metric tons of Thackaringa was processed compared with >120 Mt from the main Broken Hill lodes). The limited contribution of the Thackaringa ore to the lead budget is confirmed from the analyses of ceiling dust

which, in many cases, provide a historical record of lead production in the city; however, the lead isotope compositions of the dusts show them to come overwhelmingly from the main Broken Hill orebody lead, as discussed in a following section.

Other possible major lead sources were envisaged to be from gasoline and paint. Although generally disregarded as a potential source because of the isolation of, and relatively small automobile numbers in, Broken Hill, gasoline lead could contribute significantly to blood leads via inhalation and ingestion because: (1) the city has many old automobiles burning leaded gasoline; (2) the lead content of Broken Hill gasoline is about 0.85 g/l; and (3) there are numerous storm water depressions at major intersections, out of which automobiles accelerate—it is under such circumstances of acceleration that the highest amounts of unburned fuel and lead are generated (e.g., Chamberlain et al., 1978).

Paint has been largely ignored as a potential contributor to Pb_B levels 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 European mines whose $^{206}Pb/^{204}Pb$ ratios are ~18 or greater (e.g., Moorbath, 1962). Later, the lead in Australian manufactured paint could have come from the Broken Hill orebody 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 orebody lead.

Environmental samples

Household soils—"old" soils: Because of the ubiquitous surface soil contamination around Broken Hill, only limited sampling was carried out; the data are given in Table 1 and illustrated in Figure 2. The −53+38 μm fraction generally contains more lead than the bulk sample by a factor of 1 to 2 (Table 1). The amounts of lead and the isotopic composition, similar to that in the orebody, in soils from houses 526, 556, 557, 558, 560, 561, and 563 are consistent with their geographic location, expected source of lead, and isotopic composition of the blood lead in children. The remaining samples were analyzed because of isotopic peculiarities in the children whose Pb_B level was >15 μg/dl. Many of these old soils with lead contents below 1,000 ppm are from houses located at least 1 km from current or recent mining activities. Several of these soils contain between 500 and 1,000 ppm Pb, considerably above the current New South Wales Environment Protection Authority levels of 300 ppm for intervention; in fact, the contours for the 300-ppm level extend to the edges of the city (New South Wales Health Department, pers. commun., 1993). Isotopic values of these, and furthermore of most soils, indicate that the lead is mainly derived from an orebody source but also that the soils include varying proportions of lead from gasoline and/or paint, or both. Another possible source may be lead originating from the host rocks to the orebody, but the low lead contents (<30 ppm) of the host rocks (e.g., Reynolds, 1971; Gulson, 1984) would contribute insignificantly to the old soils.

TABLE 1. Isotopic Ratios and Pb Contents for "Old" Soils from Broken Hill

Sample no.	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Pb (ppm)
526 bulk	35.64	15.38	16.02	2,660
526 bulk	35.67	15.39	16.02	1,700
541 bulk	35.77	15.39	16.12	850
541 bulk	35.79	15.40	16.13	1,350
552 bulk	35.70	15.38	16.08	1,480
552 bulk	36.09	15.43	16.35	110
552 bulk	36.31	15.45	16.53	190
552 bulk	35.68	15.38	16.06	7,270
553 bulk	35.93	15.41	16.31	425
553 bulk	36.01	15.44	16.27	210
553 bulk	36.01	15.42	16.32	1,220
553 bulk	35.83	15.39	16.17	1,800
556 bulk	35.73	15.41	16.05	500
556 bulk	35.66	15.38	16.03	3,260
557 bulk	35.76	15.41	16.06	2,330
557 bulk	35.66	15.37	16.03	650
558 bulk	35.65	15.38	16.02	4,490
559 bulk	35.96	15.40	16.30	325
559 bulk	35.98	15.42	16.28	695
559 bulk	36.21	15.45	16.44	335
559 bulk	35.85	15.40	16.21	230
560 bulk	35.70	15.39	16.04	1,860
561 bulk	35.71	15.40	16.03	1,390
562 bulk	35.90	15.40	16.19	345
562 bulk	35.79	15.39	16.14	290
562 bulk	35.85	15.41	16.17	2,070
563 bulk	35.76	15.40	16.10	1,130
563 bulk	35.72	15.38	16.09	3,190
563 bulk	35.74	15.41	16.04	1,740
563 bulk	35.63	15.37	16.03	2,230
563 bulk	35.74	15.41	16.03	2,850
563 bulk	35.70	15.39	16.03	2,670
564 bulk	35.86	15.39	16.21	125
565 bulk	35.79	15.40	16.12	255
565 bulk	35.89	15.42	16.17	150
PS bulk OLD	35.68	15.40	16.01	39,000

Household soils—"new" soils: This category includes soil brought in from west of Broken Hill to replace old contaminated soil containing ~0.5 to 1 percent Pb, sandpit material, and cracker dust used as a pavement material. The lead contents in these materials are generally low (Table 2). The isotopic ratios in five of the eight samples (Fig. 2) are totally different from those of the orebody lead and are consistent with those observed in the unmineralized host rocks to the Broken Hill orebody (e.g., Reynolds, 1971; Gulson, 1984).

Gutter (curbside) sweepings and pavement material (gravel): Sweepings from the curbside gutter and

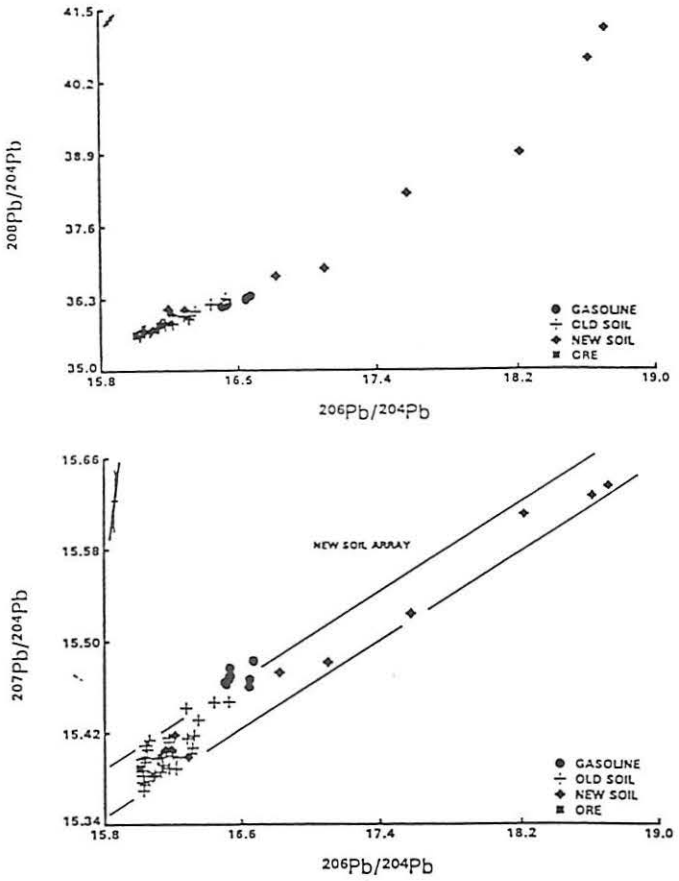


FIG. 2. Isotope ratio plots for bulk (or unsized) samples of "old" and "new" soils from the Broken Hill area compared with plots for orebody and gasoline samples.

pavement gravel were collected to assess the ability of lead isotopes to detect the contribution from gasoline lead. Some samples were sized to −53+38 μm. Samples from the main thoroughfare, Argent Street, are on the northern outskirts of the town and Eyre Street, on the southern section of the main mining activities, experiences considerable heavy traffic from ore trucks. 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 percent of the lead in the Argent Street samples is derived from gasoline (Table 3, Fig. 3). The lower lead contents in the gutter sweepings compared with gravels may be a function of the sampling 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 (Duggan and Inskip, 1985). This may have resulted in an effective concentration of, for example, orebody lead. In contrast, gasoline-derived lead would penetrate the soils, be converted to less soluble lead oxides and sulfates (Harrison et al., 1981), 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 gravel and gutter sweepings from the sample at 666 Argent Street. The finer fractions contain more lead than the bulk samples (Table 3), usually by a factor of two or three and have a higher proportion of orebody lead (Fig. 3). The apparently greater contribution of orebody lead in the finer fractions may also be a solubility function resulting from the moist conditions.

Vacuum cleaner dusts: Bulk samples of vacuum cleaner dust exhibit variable lead contents and isotopic ratios (Table 4, Fig. 4), which may partly arise from the sampling method. The isotopic composition of lead from dusts in 21 of the 27 houses indicates that at least 80 percent is orebody lead assuming that the orebody end member has a $^{206}Pb/^{204}Pb$ ratio of 16.0, and gasoline lead, 16.5. Except for two samples, those with <1,000 ppm Pb and $^{206}Pb/^{204}Pb$ ratios > 16.15 are more than 1 km distant from the central mining activities. One of the houses (543) within 1 km of the central mining activities has dust with a $^{206}Pb/^{204}Pb$ of 16.48 and ~2,500 ppm Pb. The owners operate a service station and the isotopic results are consistent with entrainment of gasoline lead via clothes from the service station to the home. In contrast, the soils from this house contain >2,000 ppm Pb in the −60-μm fraction and have isotopic ratios indicating that >80 percent of the lead comes from the orebody source. We have observed considerable variation in lead isotope composition and lead contents in different size fractions of vacuum cleaner dust, with generally higher lead contents in the finer fractions (Gulson et al., 1993). Higher lead contents in the finer fractions of vacuum cleaner dust (and soils) have also been measured by the New South Wales Health Department (K. Brooks, pers. commun., 1992) and in comprehensive studies at Port Pirie (Body et al., 1988). Because of the variability in isotopic composition and lead content within a single vacuum cleaner bag, the potential variability for dif-

TABLE 2. Isotopic Ratios and Pb Contents for "New" Soils from Broken Hill

Sample no.	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb (ppm)
553 bulk	38.92	15.61	18.22	1(
558 bulk	36.85	15.48	17.10	3(
558 bulk	36.71	15.47	16.82	3[illegible]
558 bulk	36.13	15.41	16.19	6[illegible]
558 bulk	41.16	15.64	18.70	1[illegible]
564 bulk	36.11	15.40	16.28	4[illegible]
564 bulk	35.87	15.41	16.15	1(
560 bulk	36.03	15.42	16.21	47[illegible]
561 bulk	35.69	15.39	16.04	1,23[illegible]
PS-bulk	38.20	15.52	17.58	
532 bulk	40.61	15.63	18.60	[illegible]

TABLE 3. Isotopic Ratios and Pb Contents for Pavement Gravels and Gutter Sweeping from Selected Streets in Broken Hill

Sample[1]	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb (ppm)	Location
Pavement gravel					
PG bulk	35.74	15.41	16.03	22,000	Cnr White and Eyre
PG bulk	35.67	15.39	16.02	6,400	145 Eyre St
PG bulk	35.64	15.38	16.01	4,400	St Annes and Eyre St
PG bulk	36.03	15.43	16.27	460	108 Gaffney St
PG −53+38, 7 *M*	35.77	15.39	16.11	1,020	108 Gaffney St
PG −53+38, 0.1 *M*	35.72	15.38	16.08	520	108 Gaffney St
PG bulk	35.82	15.43	16.08	1,470	670 Argent St
PG bulk	35.74	15.39	16.08	1,750	666 Argent St
PG bulk	36.05	15.43	16.26	80	18 Lawton St
PG bulk	35.80	15.41	16.08	440	Jabez St
PG −53+38, 7 *M*	35.73	15.39	16.07	605	Jabez St
PG −53+38, 0.1 *M*	35.67	15.38	16.04	420	Jabez St
Gutter sweepings					
GS bulk	35.70	15.39	16.05	7,100	145 Eyre St
GS −53+38, 7 *M*	35.70	15.40	16.02	20,500	145 Eyre St
GS −53+38, 0.1 *M*	35.66	15.39	16.02	6,600	145 Eyre St
GS bulk	35.79	15.42	16.07	3,290	Eyre St opp St Annes
GS bulk	35.78	15.39	16.15	560	Cnr Harris and Gaffney
GS −53+38, 7 *M*	35.73	15.38	16.09	1,620	Cnr Harris and Gaffney
GS −53+38, 0.1 *M*	35.73	15.40	16.09	610	Cnr Harris and Gaffney
GS bulk	35.84	15.42	16.13	960	666 Argent St
GS −53+38, 7 *M*	35.74	15.39	16.07	4,080	666 Argent St
GS −53+38, 0.1 *M*	35.72	15.38	16.08	1,410	666 Argent St
GS bulk	35.86	15.43	16.14	1,180	Jabez St
GS −53+38, 7 *M*	35.73	15.39	16.08	3,750	Jabez St
GS −53+38, 0.1 *M*	35.77	15.40	16.11	1,510	Jabez St

[1] 7 *M* = 7 *M* HNO_3-7 *M* HCl leach, 0.1 *M* = 0.1 *M* HCl leach

ferent sampling times, and the necessary frequency of vacuuming in this community (i.e., vacuum cleaner dust is a short-term integrator), the efficacy of using lead contents especially from vacuum cleaner dust sampling remains unconvincing. Certainly, lead contents of bulk vacuum cleaner dust are probably meaningless.

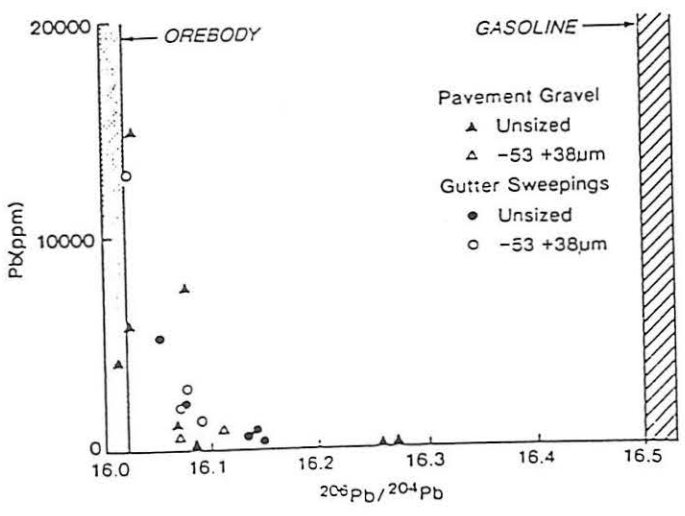


FIG. 3. $^{206}Pb/^{204}Pb$ ratio vs. Pb (ppm) in bulk (or unsized) and some of the −53+38-μm fractions for pavement gravel and gutter sweepings from selected streets in Broken Hill compared with orebody and gasoline values.

Ceiling dust: Ceiling dust may be a potential major source of contamination because of the age of the houses and the potential for easy disturbance of the dust during renovations. The lead isotope compositions of the dust were measured for ten randomly located houses (Table 5). Because the dust sampling was undertaken prior to the major study, only one of these houses coincides with the biological samples. The lead isotope compositions of eight of the ten 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 can be attributed solely to the orebody as the source of lead. The other two houses are located within 2 km of the central mining activity and, although their $^{206}Pb/^{204}Pb$ values are slightly higher at 16.08 and 16.16, the dominant proportion (>80%) of the lead is attributed to orebody lead.

Gasoline: The isotopic compositions for leaded gasoline obtained at the time of high volume air sampling are shown in Table 6. There is little isotopic variation in gasoline for the September 1992 sampling with a small change of ~0.5 percent in the isotopic composition when one brand was resampled ~3 mo later. Likewise, there is a ~0.8 percent change in isotopic ratios from 1991 to 1992. These

TABLE 4. Isotopic Ratios and Pb Contents For Bulk Vacuum Cleaner Dust

Sample no.	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb (ppm)	
504	36.08	15.41	16.41	400	
508	35.86	15.39	16.20	230	
510	35.72	15.37	16.12	360	
513	35.71	15.40	16.04	1,470	
514	35.67	15.37	16.07	535	
515	35.78	15.40	16.12	125	
516	35.99	15.42	16.30	905	
519	35.74	15.38	16.11	3,290	
520	35.71	15.38	16.08	105	
522	35.63	15.36	16.05	20	VC water
522	35.69	15.38	16.07	70	VC sludge
525	35.74	15.39	16.12	1,220	
526	35.61	15.37	16.02	705	
530	35.80	15.38	16.17	220	
531	35.79	15.40	16.12	675	
532	35.68	15.37	16.08	765	
533	35.74	15.36	16.15	340	
534	35.68	15.38	16.04	1,700	
536	35.72	15.39	16.08	270	
538	35.88	15.41	16.19	405	
542	35.77	15.41	16.09	1,570	
543	36.20	15.46	16.48	2,510	

changes, however, have a negligible effect on the conclusions.

External air: In 1991, the lead contents of the filters analyzed varied from 0.08 to 0.67 $\mu g/m^3$ (with one of 1.23) at Proprietary Square (Fig. 1 for location), similar to those from the MMA site in the city

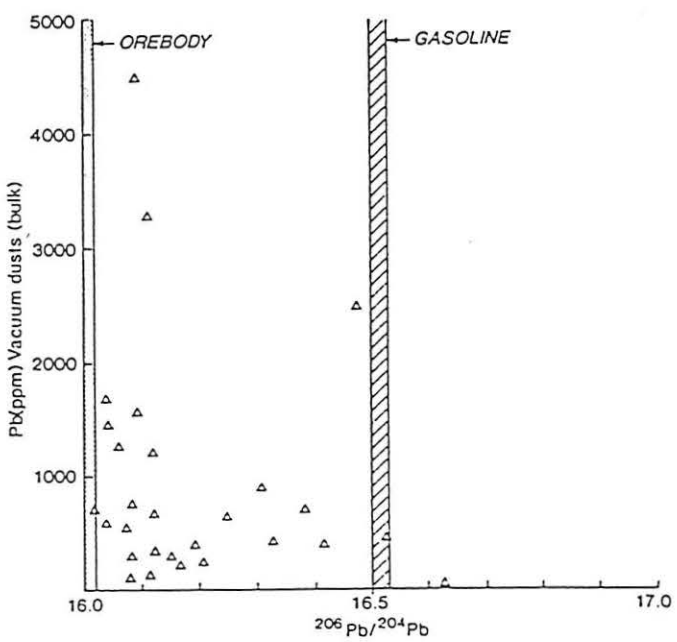


FIG. 4. $^{206}Pb/^{204}Pb$ ratio vs. Pb (ppm) for bulk vacuum cleaner dust from residences in Broken Hill compared with orebody and gasoline values.

TABLE 5. Isotopic Ratios for Ceiling Dusts from Broken Hill

Sample no.	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
BH 5A old top	35.62	15.37	16.00
BH 5B old bot	35.65	15.39	16.01
BH 5C new	35.58	15.36	15.99
BH 12A	35.64	15.38	16.01
BH 13A	35.80	15.39	16.15
BH 15B	35.65	15.39	16.01
BH 16	35.69	15.37	16.08
BH 18	35.62	15.38	16.00
BH 19	35.63	15.38	16.01
BH 22B	35.61	15.36	16.03
BH 26A	35.62	15.38	16.00
BH 28B	35.60	15.37	16.01
558	35.67	15.39	16.03

(0.06–0.39 $\mu g/m^3$); data are given in Table 7 and plotted in Figure 5. The lead isotope ratios exhibit considerable variation at the Proprietary Square and Westside Drive sites ranging from almost wholly orebody lead to ~90 percent gasoline lead. At the MMA site, the values are reasonably consistent and the contribution from gasoline lead varies from ~60 to 85 percent. There is a poor correlation of lead content and $^{206}Pb/^{204}Pb$ with the best correlation for data when the wind was blowing predominantly from westerly to northerly directions. Any deviation from this correlation probably derives from the change in wind direction estimated at 0900 and 1500 hours daily. In the period August-October 1992, the isotopic data (Table 7) for the Westside Drive filters exhibit a dominance of orebody lead from 70 to 90 percent. Over the same period, the isotopic composition at the MMA site exhibited a contribution of gasoline lead from 30 to 85 percent, but on any given day, the $^{206}Pb/^{204}Pb$ ratio for the MMA site is greater than those for the Proprietary Square and Westside Drive

TABLE 6. Isotopic Ratios for Gasoline from Different Collection at Broken Hill

Sample no.	$^{205}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
BH 1991	36.35	15.48	16.4
BH 1991	36.31	15.47	16.4
BH Sept 1992	36.22	15.47	16.4
BH Sept 1992	36.20	15.47	16.4
BH Sept 1992-1	36.23	15.48	16.4
BH Sept 1992-2	36.19	15.47	16.4
BH Sept 1992	36.18	15.46	16.4
BH Sept 1992	36.17	15.46	16.4
BH Sept 1992	36.29	15.46	16.4
BH Dec 1992*	36.25	15.51	16.4

* Denotes low-temperature mass spectometer run, possible fractionation

TABLE 7. Isotopic Ratios and Pb Contents for High-Volume (HV) Air Filters from Different Sites at Different Sampling Times

Sample no.	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb ($\mu g/m^3$)
HV air filters 1991				
Proprietary Square 8/22	35.62	15.36	16.04	0.67
Proprietary Square 8/24	36.01	15.43	16.35	0.11
Proprietary Square 8/26	35.83	15.40	16.17	1.23
Proprietary Square 8/28	35.95	15.41	16.35	0.45
Proprietary Square 8/29	35.90	15.42	16.25	0.21
Proprietary Square 8/31	35.95	15.42	16.33	0.08
Proprietary Square 9/1	36.24	15.47	16.57	0.14
Proprietary Square 9/2	36.14	15.44	16.53	0.26
Proprietary Square 9/3	36.28	15.48	16.54	0.24
Proprietary Square 9/4	36.06	15.43	16.42	0.33
MMA 8/21	36.11	15.43	16.49	0.24
MMA 8/22	36.13	15.45	16.43	0.28
MMA 8/26	36.29	15.48	16.57	0.20
MMA 8/27	35.99	15.40	16.41	0.39
MMA 8/28	36.23	15.46	16.57	0.15
MMA 8/29	36.18	15.45	16.53	0.06
Westside 9/2	36.22	15.46	16.53	0.11
Westside 9/8	35.89	15.42	16.22	0.09
HV air filters 1992				
MMA 8/27	35.87	15.41	16.22	0.22
MMA 8/27	35.89	15.42	16.22	
MMA 9/14	36.09	15.42	16.44	0.22
MMA 9/14	36.12	15.43	16.45	
MMA 9/26	36.04	15.43	16.42	0.23
MMA 10/8	36.03	15.44	16.34	0.12
MMA 10/20	35.80	15.40	16.16	0.24
Westside 8/27	35.70	15.39	16.05	0.17
Westside 9/14	35.82	15.40	16.16	0.15
Westside 9/26	35.73	15.39	16.10	0.24
Westside 10/8	35.68	15.37	16.07	0.19
Westside 10/20	35.67	15.38	16.04	0.42

Lead contents supplied by Pasminco

sites (Fig. 5). Also, lead concentrations are always higher at the Proprietary Square site compared with those at the MMA site. If wind direction is a significant contributing factor to the city of Broken Hill, there should be a positive correlation in lead isotope composition for the sampling locations. Although based on few analyses, there does appear to be a positive correlation in such data (not shown). These differences may be a reflection of differing meteorological conditions at the sampling times. For example, moist conditions prevailed in the 1992 period and this may have reduced the gasoline aerosols relative to the orebody dust by solubilization of the lead bromides and chlorides whereas the dry conditions in 1991 enhanced the gasoline contribution. The high-volume air data thus show that the amounts of lead in the air near the central mining operations and in the city are similar but that the isotopic composition is dependent largely on wind direction. Needless to say, there is a considerable amount of lead in Broken Hill air derived from gasoline.

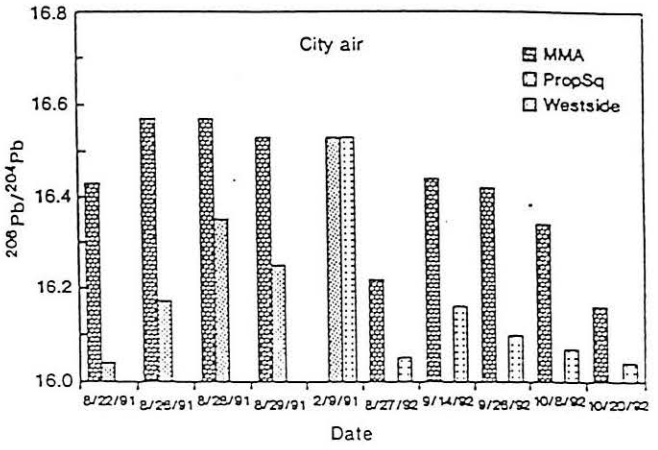


FIG. 5. Plot of $^{206}Pb/^{204}Pb$ ratio vs. time in high-volume air filters from three sites in Broken Hill.

House air: Lead contents for an 8-h period in the air from five houses selected for detailed investigation are low and vary from 0.04 to 0.15 $\mu g/m^3$ (Table 8), approximately half the levels measured in external air from the high-volume filters over the same period. All levels fall, however, well within the 3-mo average of 1.5 $\mu g/m^3$ recommended by the Australian National Health and Medical Research Council. The $^{206}Pb/^{204}Pb$ values for the Community Health Centre and the house from the North Mine site (526) have a dominant contribution of orebody lead but with at least 30 percent gasoline, paint, or tobacco lead. (The $^{206}Pb/^{204}Pb$ ratios in cigarettes sold in Australia range from 18.1–18.6 and lead contents, ~1–10 μg/cigarette; Gulson, unpub. data.) Smokers occupy the remaining four houses and the isotopic compositions could derive from this source, along with gasoline and/or paint lead. The latter is unlikely, however, because internal and external paintwork was in good condition except for house 556. The highest $^{206}Pb/^{204}Pb$ is found in house 541, located in the city center and is considered to represent a dominant contribution from gasoline lead.

Paint: Because of the antiquity of many houses and their dilapidated condition, paint samples were collected from selected residences, especially where the

TABLE 8. Isotopic Ratios and Pb Contents for Broken Hill House Air

Sample no.	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb ($\mu g/m^3$)
Community Health	35.73	15.37	16.14	0.124
526	35.78	15.37	16.18	0.055
536	36.11	15.38	16.48	0.153
541	36.24	15.43	16.60	0.085
556	36.04	15.42	16.38	0.040
559	35.94	15.41	16.30	0.077

children had elevated Pb_B levels. The isotopic compositions of most samples of leaded paint lie at two extremes (Table 9). One extreme is close to the orebody lead (viz., $^{206}Pb/^{204}Pb$ of 16.02–16.05) and the other has a $^{206}Pb/^{204}Pb$ of ~17.0. Two samples have $^{206}Pb/^{204}Pb$ values in between these two extremes. Thus mixtures of leaded paints with the isotopic compositions of the two end members of 16.0 and 17.0 can give a spectrum of isotopic values and this needs to be considered when designating the sources of lead in soils, dust, and humans.

Water: Drinking water is another possible source of lead in blood. Cold waters from 27 of 28 houses have lead contents < 0.5 ppb (μg/l; Table 10); one house had a lead level of 3 ppb when first sampled but this was collected while house renovations were in progress. Repeat collection 5 mo later gave a level of 0.4 ppb. These lead contents are low and are consistent with low values found in 25 houses each from Adelaide, Port Pirie, and Hobart (Pisaniello et al., in press). They are consistently lower than the current "action level" of the U.S. Environmental Protection Agency (1991) of 15 μg/l for "lead in pipes." The lead isotope compositions of the waters exhibit considerable variation between houses (Table 10) as we have found in the other three cities mentioned above. Waters drawn from three of the four storage tanks in Broken Hill also have low lead contents and the isotopic ratios are uniform compared with results for the houses (Table 10). The low lead contents in the reticulated supply contrast with the higher values of 5 to 69 μg/l measured in the Stephens Creek reservoir (Coggins et al., 1979), one of the supplies for the city. The isotopic uniformity of the reticulated water supply supports the hypothesis that the variability in houses reflects lead input from the individual plumbing systems. This has also been shown for some Sydney houses (Gulson et al., 1994).

TABLE 9. Isotopic Ratios for Lead-Bearing Paints in Broken Hill

Sample no.	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Location
553	35.72	15.39	16.05	Under eaves
553	36.77	15.46	17.01	Cobalt St bargeboard
553	36.92	15.48	17.13	Cobalt St veranda posts
553	37.84	15.57	17.90	Cobalt St gutter
559	35.63	15.36	16.04	Front veranda posts
560	36.08	15.41	16.41	Left side house
563	35.64	15.37	16.03	Right side house
563	35.75	15.40	16.07	Left side house
St Road	35.71	15.41	16.02	Station Rd
4 Chloride St	36.72	15.48	16.97	Chloride St windows
540	35.93	15.39	16.27	Chloride St walls
541	35.63	15.37	16.03	Chloride St walls
541	35.64	15.36	16.04	Chloride St walls
541	35.64	15.38	16.01	Chloride St walls
541	35.67	15.37	16.06	Red paint on swing
541	36.82	15.49	16.95	Front post
541	37.04	15.50	17.23	Bargeboard next door
541	36.25	15.43	16.53	Under verandah
541	36.75	15.51	16.84	Under window sill
523	35.66	15.38	16.02	Door and wall
534	37.60	15.56	17.65	Moorish St wall

Biological samples

Blood in male adults: As a father's occupation may be a potential pathway for lead in a child and there are limited data for child-parent relationships (e.g. Barltrop and Strehlow, 1989), lead isotopes were measured for male adults wherever possible (n = 17; Table 11). On isotope ratio plots (Fig. 6), the male adult data scatter slightly (just outside the 2σ error) below the orebody-gasoline array. Results are generally consistent with the father's occupation. For example, in two cases (515, 543) the father had Pb_B > 25 μg/dl (Table 11) and operated a service station. The isotopic ratios of the blood in the father were almost identical to those in gasoline (Figs. 6 and 7). In one case (543), the elevated Pb_B level in the child indicated >70 percent from gasoline lead, whereas in the other, ~40 percent of the contribution of orebody lead probably resulted from extensive renovations of the house during pregnancy (this child was born with delayed visual maturation of the optic nerve). Where the father was exposed to lead from mining activities for over 10 yr, especially underground mining (e.g. houses 514, 526, 534, 536, 560, 561?), the lead level is variable and the blood contains a higher proportion of orebody lead than that of the spouse (Fig. 7). For male adults in nonexposed or limited lead exposure environments (e.g., houses 513, 516, 523, 559, 584), Pb_B is generally <10 μg/dl and the isotopic compositions are variable.

Blood in female adults: The majority of female adults are domestic managers and hence are nonexposed. Blood lead levels for 40 of the 41 subjects ranged from 2.8 to 10.4 μg/dl (Table 11) with an arithmetic mean and standard deviation of 5.8 ± 1.9 μg/dl. Isotopic ratios for long-term (>10 yr) female residents were usually in the range 16.4 to 16.7 and other circumstances prevailed for those whose values lay outside this range. For example, the female adult from house 560 with a $^{206}Pb/^{204}Pb$ ratio of 16.21 resides in a very high risk area close to the mining activities and is of lower socioeconomic status. The subject from house 538 with a higher isotope ratio lived for several years away from Broken Hill. On isotope ratio plots (Fig. 8), the data for female adults lie significantly below the orebody-gasoline array.

Blood in children: There are insufficient isotope data to draw substantive conclusions about children's blood with respect to geographic location, although those identified specifically for us with elevated Pb_B levels by the Health Department are generally from South Broken Hill. Four examples which illustrate

TABLE 10. Isotopic Ratios and Pb Contents for Cold Water from Households and the Reticulated Water Supply at Broken Hill

Sample no.	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb (ppb)	Location
504	36.13	15.45	16.41	0.3	
504*	36.04	15.41	16.37	1.2	
508	37.37	15.61	17.13	0.1	
510	36.30	15.44	16.61	0.3	
510*	36.07	15.42	16.40	0.6	
511-1	36.18	15.41	16.54	3.0	
511-2	36.21	15.42	16.55	3.1	
511*	36.16	15.39	16.52	2.7	
511 NS	36.42	15.45	16.69	0.4	
513	36.99	15.48	17.20	0.1	
513*	36.81	15.43	17.14	9.9	
514	36.64	15.47	16.85	0.3	
515	37.07	15.54	17.46	0.8	
515 NS	37.05	15.55	17.37	0.2	
515*	36.96	15.52	17.33	0.4	
517	36.23	15.43	16.56	0.3	
517 NS	36.68	15.48	16.95	0.1	
518	36.38	15.42	16.66	0.0	
518*	36.74	15.49	16.71	0.2	
519	36.01	15.41	16.37	0.2	
519*	35.74	15.38	16.12	2.4	
520	36.41	15.46	16.71	0.1	
520*	36.66	15.56	16.65	0.7	
521	36.19	15.42	16.54	0.6	
522*	36.26	15.42	16.60	0.4	
523	36.34	15.41	16.70	0.3	
523 NS	36.10	15.27	16.60	0.1	
524	36.57	15.49	16.77	0.1	
525	35.93	15.40	16.30	0.4	
526	36.43	15.43	16.74	1.7	
530	36.21	15.43	16.48	0.1	
530*	36.13	15.42	16.45	0.3	
531	35.89	15.41	16.22	0.2	
531 NS	36.05	15.42	16.37	0.1	
532	36.37	15.49	16.50	0.0	
532 NS	36.14	15.45	16.43	0.1	
533	36.41	15.45	16.78	0.2	
534	36.15	15.43	16.44	0.1	
534*	36.07	15.42	16.38	0.4	
536	36.21	15.43	16.46	0.1	
538	36.22	15.44	16.50	0.2	
541	36.09	15.41	16.42	0.4	
542	35.72	15.37	16.11	0.9	
542 NS	35.83	15.40	16.19	0.3	
543	36.19	15.42	16.52	0.5	
543 NS	36.13	15.42	16.44	0.1	
Reticulated tank	36.09	15.42	16.41	1.1	4 block 10
Reticulated tank	36.26	15.44	16.52	0.3	Hebbard St
Reticulated tank	36.15	15.43	16.46	0.5	Wyman St

NS = new sample
* = water sample acidified > 6 mo after collection

differences in isotopic compositions and lead contents, and geographic locality are shown in Figure 9. The children from South Broken Hill usually have a dominant proportion of orebody lead in their blood, but there are children from other areas who also have elevated Pb_B levels.

On isotope ratio plots (Fig. 10), the data for children's blood are similar to those from male adults but less than 50 percent of the children's blood analyses lie within the orebody-gasoline array. Clearly, there is a third, or possibly more, significant source of lead. The most logical source of lead in the children's blood is leaded paint. The analyzed paint samples with higher isotope ratios than the orebody have a nonore component which forms a mixing array on isotope ratio plots (not shown) with a lower slope

TABLE 11. Isotopic Ratios and Pb Contents for Subjects from Broken Hill

Sample no.[1]	$\frac{^{208}Pb}{^{204}Pb}$	$\frac{^{207}Pb}{^{204}Pb}$	$\frac{^{206}Pb}{^{204}Pb}$	Pb (μg/dl)	Subject[2]
50S mother	36.31	15.44	16.64	2.7	LR
50S child 1	36.25	15.42	16.59	5.9	
50S child 2	36.25	15.44	16.57	4.8	
510 mother	36.36	15.47	16.63	4.9	LR
510 child 1	36.13	15.41	16.47	14.7	
510 child 2	36.10	15.41	16.45	11.7	
514 father	35.97	15.41	16.36	16.4	M, MR
514 mother	36.26	15.44	16.62	10.3	
514 child 1	36.25	15.43	16.60	5.3	
514 child 2	35.88	15.38	16.30	7.7	
515 father	36.19	15.44	16.56	23.3	SS, HR
515 child	35.90	15.39	16.31	18.8	
516 father	36.55	15.48	16.83	2.8	LR, SM
516 mother	36.32	15.43	16.70	5.3	
516 child 1	36.10	15.42	16.48	8.7	
516 child 2	35.97	15.38	16.40	13.2	
517-1 mother	36.19	15.41	16.57	4.7	HR
517-2 mother	36.22	15.43	16.57	4.4	
517 child 1	36.01	15.38	16.40	13.5	
517 child 2	36.00	15.39	16.39	14.4	
518-1 child 1	36.19	15.44	16.52	5.1	HR
518-2 child 1	36.11	15.41	16.49	5.0	
518 child 2	36.01	15.40	16.40	5.9	
519 mother	36.13	15.39	16.57	7.2	M, HR
519 child	35.90	15.40	16.29	11.6	
521 father	36.01	15.41	16.38	16.6	MR, SM+
521 mother	36.03	15.39	16.43	8.4	
521 child	36.14	15.42	16.50	14.7	
521-1 NS child	35.99	15.41	16.34	9.7	
521-2 NS child	35.95	15.39	16.33	9.7	
523 father	36.18	15.42	16.53	8.7	LR
523 mother	36.34	15.45	16.61	5.5	
523 child 1	36.06	15.42	16.42	15.2	
523 child 2	35.98	15.39	16.35	23.2	
524-1 mother	36.13	15.42	16.48	7.8	HR
524-2 mother	36.07	15.40	16.45	7.8	
524 child 1	35.87	15.39	16.25	21.1	
524 child 2	35.87	15.38	16.28	15.0	
525 mother	36.08	15.40	16.47	4.6	LR
525 child 1	36.20	15.41	16.60	12.5	
525 child 2	35.99	15.40	16.38	13.1	
525 child 3	35.95	15.40	16.32	23.1	
525 NS child 3	35.83	15.39	16.24	22.4	
526-1 father	35.84	15.40	16.22	14.4	M, HR, SM
526-2 father	35.88	15.40	16.23	14.5	
526 mother	36.18	15.41	16.59	4.2	
526 child 1	35.90	15.40	16.26	9.4	
526 child 2	35.87	15.40	16.22	16.2	
526 child 3	35.80	15.40	16.13	20.7	
526 NS1 child 3	35.93	15.40	16.28	21.0	
526 NS2 child 3	35.79	15.37	16.21	16.9	
530-1 father	35.76	15.35	16.20	12.6	M, O, LR
530-2 father	35.85	15.39	16.23	12.6	
530 mother	36.34	15.47	16.61	4.1	
530 child 1	35.99	15.40	16.35	12.6	
530 child 2	35.86	15.38	16.24	17.7	
530 child 3	35.86	15.38	16.25	15.5	
534 father	35.86	15.38	16.27	16.1	M, HR, SM
534 mother	36.08	15.40	16.48	6.7	
534 child 1	35.85	15.41	16.19	19.9	
534 child 2	35.83	15.38	16.24	19.3	
534 child 3	35.93	15.40	16.29	16.6	

TABLE 11. (*Cont.*)

Sample no.[1]	$\frac{^{208}Pb}{^{204}Pb}$	$\frac{^{207}Pb}{^{204}Pb}$	$\frac{^{206}Pb}{^{204}Pb}$	Pb (μg/dl)	Subject[2]
536 father	35.76	15.37	16.17	18.2	M, HR, SM
536 mother	36.15	15.43	16.52	6.5	
536 child 1	35.94	15.40	16.31	9.2	
536 child 2	35.83	15.36	16.26	10.3	
538 mother	36.56	15.46	16.86	6.3	MR, SM
538-1 child	35.90	15.42	16.18	40.7	
538-2 child	35.86	15.41	16.17	40.4	
538 NS child	35.84	15.39	16.18	27.6	
541 father	36.31	15.44	16.64	7.4	M, MR, SM
541-1 mother	36.59	15.47	16.92	4.1	
541-2 mother	36.56	15.46	16.91	4.1	
541 child 1	36.12	15.41	16.47	10.5	
541 child 2	36.22	15.44	16.51	21.9	
541 NS child 2	36.14	15.42	16.48	15.5	
542 father	36.11	15.42	16.48	15.9	HR, SM
542 mother	36.21	15.42	16.58	5.8	
542 child 1	35.97	15.42	16.33	26.0	
542 child 2	35.82	15.38	16.22	35.4	
543 father	36.35	15.48	16.65	21.1	SS, MR, SM
543 mother	36.36	15.43	16.73	3.3	
543 NS1 mother	36.43	15.46	16.75	2.7	
543 NS2 mother	36.26	15.47	16.79	5.9	
543 child	36.08	15.43	16.42	25.3	
544 child 1	36.06	15.40	16.47	4.3	LR
544 child 2	36.15	15.40	16.55	7.3	
553 child 1	36.11	15.42	16.43	16.5	P, MR, SM
553 child 2	36.08	15.44	16.35	47.1	
553-1 NS child 2	35.87	15.37	16.29	39.8	
553-2 NS child 2	35.98	15.40	16.32	40.0	
556 mother	35.99	15.40	16.39	13.6	HR, SM
556-1 child	35.79	15.38	16.18	27.5	
556-2 child	35.82	15.39	16.17	27.9	
557 father	36.04	15.41	16.40	10.3	E, MR, SM
557 mother	36.20	15.44	16.57	4.8	
557 child	35.72	15.37	16.14	30.5	
558 father	36.08	15.44	16.35	15.0	HR, +
558 mother	36.02	15.44	16.33	8.6	
558 child	35.89	15.41	16.25	21.9	
559 father	36.13	15.41	16.52	9.2	MR, SM
559 mother	36.26	15.44	16.61	4.7	
559-1 child	35.96	15.40	16.35	20.7	
559-2 child	35.01	15.41	16.35	20.5	
560 father	35.81	15.40	16.19	29.1	M, HR, SM
560 mother	35.84	15.40	16.21	10.4	
560-1 child 1	35.63	15.34	16.07	45.5	
560-2 child 1	35.73	15.38	16.10	43.2	
560-1 child 2	35.65	15.36	16.06	32.6	
560-2 child 2	35.64	15.36	16.04	33.9	
561 father	35.76	15.37	16.15	21.6	M, HR
561 child	35.77	15.37	16.20	14.5	
565 father	36.16	15.40	16.53	12.0	MR, SM
565 mother	36.24	15.44	16.58	6.3	
565 child	36.00	15.40	16.36	24.6	
501 female	36.50	15.46	16.86	5.4	
502 female	36.35	15.44	16.71	3.4	
503 female	36.40	15.44	16.78	5.2	
504 female	36.10	15.40	16.51	10.4	
505 female	36.25	15.43	16.62	6.7	
506 female	36.29	15.41	16.67	3.7	
507 female	36.26	15.42	16.65	4.6	
509 female	36.41	15.45	16.75	9.0	
511 female	36.21	15.43	16.58	7.1	

TABLE 11. (*Cont.*)

Sample no.[1]	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb (μg/dl)	Subject[2]
512 female	36.44	15.44	16.78	6.8	
513 female	36.25	15.38	16.67	7.7	
513-1 male	36.08	15.40	16.47	6.8	
513-2 male	36.09	15.40	16.48	6.9	
520 female	36.11	15.40	16.50	7.8	
522 female	36.35	15.44	16.67	5.3	
527 child	35.91	15.39	16.29	9.4	
528 child	36.27	15.44	16.57	12.5	
529 child	36.21	15.44	16.55	14.8	
532 child	35.86	15.39	16.23	17.1	
539 child	35.92	15.41	16.28	21.3	
540 child	36.86	15.50	17.08	8.0	
546 child	36.22	15.42	16.57	4.1	
546 NS child	36.22	15.43	16.57	4.5	
551 male	36.03	15.41	16.37	8.8	
552-1 child	35.94	15.42	16.35	7.2	
552-2 child	35.98	15.41	16.35	8.1	
554 male	35.87	15.38	16.28	13.7	
556 child	36.13	15.42	16.48	19.1	
562 child	35.90	15.40	16.26	25.3	
563 child	35.81	15.37	16.24	15.0	

[1] 5 = house designation, NS = new sample at different time, -1,-2 = separate analyses of same sample

[2] M = mining activity of male adult, SS = service station activity of male adult, P = painter, E = electrician, SM = smoker, LR = low ris (with respect to proximity to mining activity), MR = moderate risk, HR = high risk, + = elevated Pb_B from renovations, O = worke underground in nonactive area for 2 yr

than that of the orebody-gasoline mixing array. This may partly explain why much of the isotopic data from the blood of male adults and children, and from some of the female adults, lies below the orebody-gasoline array.

If only data for children with $Pb_B > 15$ μg/dl are considered (Fig. 11, Table 11), they appear to be rather confusing. In detail, however, they can be assessed in conjunction with other information obtained during home visits, replies to a questionnaire, and environmental samples. For example, the children whose data plot on the left-hand side of Figure 11 are those with the highest Pb_B levels (>40 μg/dl), live in South Broken Hill, and have a low socioeconomic status. Their blood also contains the greatest amount of orebody lead and this is one end member of the mixing relationship defined by the dashed curve in Figure 11. In other children whose data plot to the right-hand side of Figure 11, it is possible to equate the isotopic values with a known history of pica (garden soil with paint) or exposure to gasoline. It is possible to estimate the approximate contributions of orebody lead and gasoline lead by simple proportionality. For example, the orebody lead has a $^{206}Pb/^{204}Pb$ of 16.0 and gasoline, ~16.5. Thus, blood with a $^{206}Pb/^{204}Pb$ of 16.25 would have 50 percent from each source. Lead from paint is somewhat more complex. If it has the same isotopic composition as the orebody lead—as does some paint we have ana-

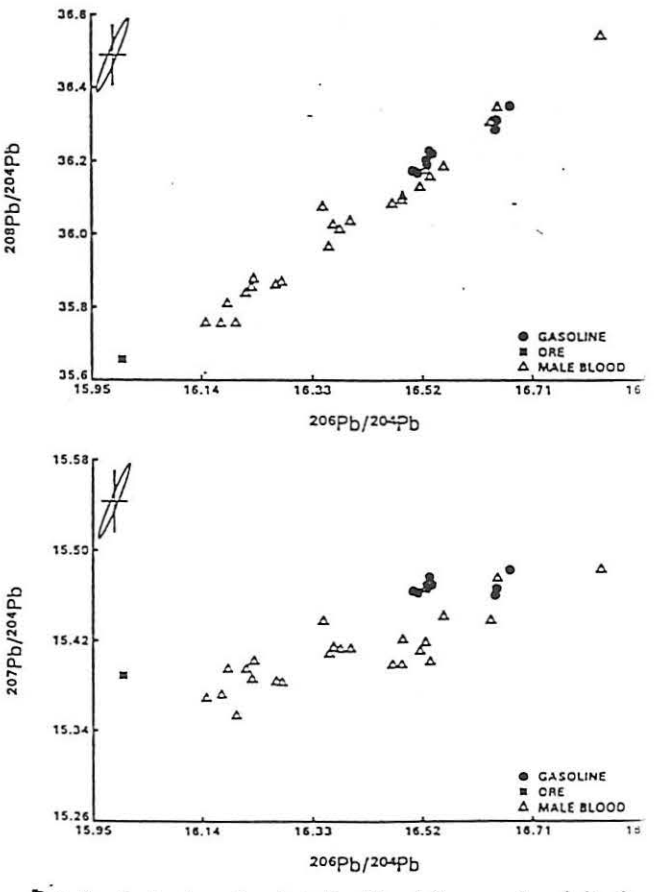


FIG. 6. Isotopic ratio plots for blood from male adults fr Broken Hill compared with orebody and gasoline values.

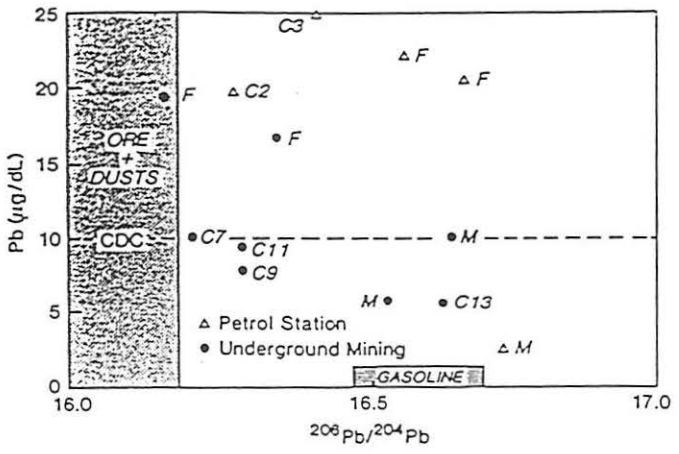
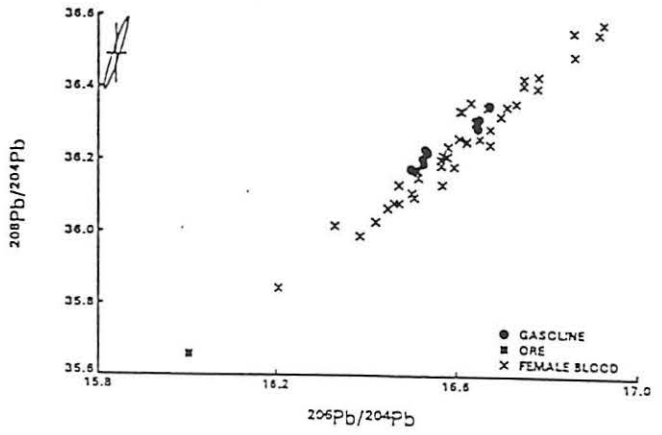


FIG. 7. $^{206}Pb/^{204}Pb$ vs. Pb_B levels for families in which the male adult was engaged in underground lead mining activities or operated a service station. Numbers following "C" refer to the age of the child in years; M = mother; F = father. The isotopic values measured in the orebody lead and household dusts are shown by the open area. The dashed line at 10 µg/dl is "level of concern" of the U.S. Centers for Disease Control (CDC). The range of isotopic values for gasoline lead is shown.

lyzed—it is not possible to determine if the elevated Pb_B is from paint or orebody lead using lead isotopes. If, however, paint has a $^{206}Pb/^{204}Pb$ value > 17.0, isotopic ratios measured in blood will represent a mixture of those from paint and soil which in turn, may contain orebody lead and/or gasoline lead, and depending on the relative proportions, may have a range of isotopic values. It is thus necessary to analyze the appropriate samples of soil and paint mixtures that the children ingested. Accepting orebody lead, gasoline, and paint as the dominant sources of Pb_B, it is obvious from Figure 11 that the majority of Broken Hill children with Pb_B > 15 µg/dl derive varying amounts of lead from different sources and that ~30 percent of the children have a greater proportion of gasoline and paint lead than orebody lead in their blood.

Thus, even though the dominant amount of lead in the soil and dust in many of these houses has an orebody source and would be targets for remediation, in fact, the source in the children's blood is demonstrated by lead isotope fingerprinting to be substantially from other than the orebody source. For example, the child from house 543 (Table 11) has a Pb_B of 25 µg/dl and vacuum cleaner dust (Table 4) and back and front yard soils (Table 1) contain >2,000 ppm Pb. Without isotopic analyses, there is no way to determine the source of the lead in the blood. The father operates a service station and his isotopic ratios indicate that the 21-µg/dl Pb in his blood is almost wholly from gasoline. The lead in the vacuum cleaner dust is also almost solely gasoline-derived lead. Lead in the child's blood is estimated to be ~80/20 from gasoline/orebody lead; the child also occasionally helps



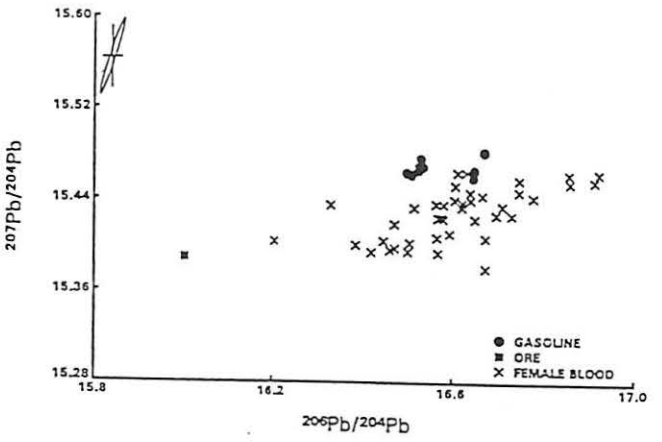


FIG. 8. Isotopic ratio plots for blood from female adults from Broken Hill compared with orebody and gasoline values.

the father at the station. There is thus a pathway from the service station to father to house dust to child as well as a potential direct pathway from gasoline to child. The isotopic ratios in the soils show that > 80 percent of the lead is derived from an orebody source and is only a minor contributor to the Pb_B level.

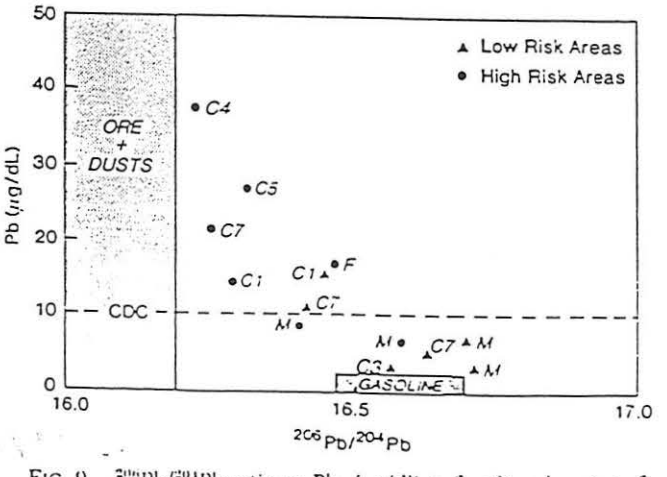


FIG. 9. $^{206}Pb/^{204}Pb$ ratio vs. Pb_B (µg/dl) in families showing effect of geographic locality on results. Letters and numbers are as for Figure 7.

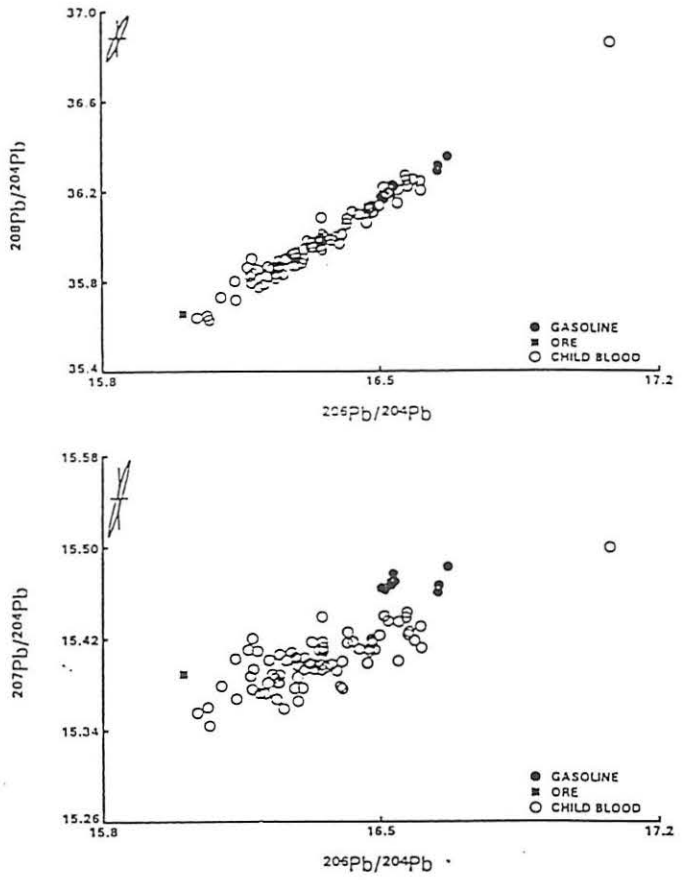


FIG. 10. Isotopic ratio plots for blood from children of varying ages at Broken Hill compared with orebody and gasoline values.

Hence, remediation by soil removal would have only partially solved the problem of elevated Pb_B levels in this child.

Bioavailability of lead: In a summary of lead in mining waste environments, Steele et al. (1990) suggest that Pb_B levels are not elevated compared with those of areas occupied by active or past smelting because of the low bioavailability of lead in soils and house dusts in these environments. This is in spite of the extremely high amounts of lead that may be present in the soils and dusts. However, Mushak (1991) has reevaluated this paper and other data from mining communities and shown there to be deficiencies in scientific argument and sampling protocols (e.g., Barltrop et al., 1975). In the Derbyshire area, the low Pb_B levels were attributed by Cotter-Howells and Thornton (1991) to the presence in the soil of the relatively insoluble lead species, pyromorphite $[Pb_5(PO_4)_3Cl]$, a weathering-oxidation product of galena. In Telluride, Colorado, Bornschein et al. (1988) measured a geometric mean Pb_B of 6.1 μg/dl in 94 children aged 6 yr and younger. In this mining community, galena is encapsulated in quartz, pyrite, or relatively insoluble weathering products of the sulfides. In contrast to most of the cited literature o mining communities, the mean lead in 899 childre from Broken Hill is 15.9 μg/dl (New South Wal Health Department Survey, 1992: unpub. data).

To assess whether or not these elevated Pb_B leve were the result of greater solubility of lead-bearin phases in Broken Hill, 0.1 *M* HCl solubility tests wer performed on selected bulk samples and th −53+38-μm fractions of vacuum cleaner dust an soils (Gulson et al., 1993). These fractions were als analyzed for a suite of elements using ICP-AES an ICP-MS and the composition of the lead-bearin phases was established from SEM and XRD. It shou be noted that the 0.1 *M* HCl leaches only approx mate stomach conditions and thus merely give indic tions of the gross relative solubility of the lead-bea ing phases. Over 90 percent of the ceiling dust, va uum cleaner dust, and soils consists of commo rock-forming minerals such as quartz, muscovit feldspar, rare spessartine garnet and sillimanite, an iron oxides which contain negligible lead or nonlabi lead. Furthermore, except in rare cases, the majorit of the lead-bearing phases are very complex Pb, F Mn, P, Si, Al, O + Ca + P materials (Davis, 1993) an so the solubility for different materials may be rath similar, depending on grainsize. There is a negligib isotopic difference between HNO_3-HCl leaches the bulk material, total leachable lead (HNO_3-H(

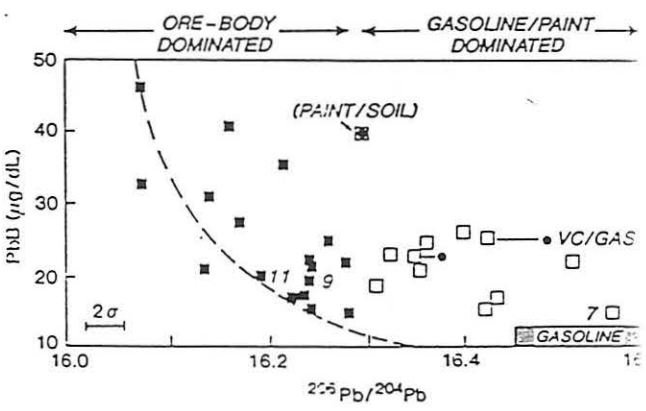


FIG. 11. $^{206}Pb/^{204}Pb$ ratio vs. Pb_B (μg/dl) in children whose P > 15 μg/dl. Samples whose lead isotope composition is dominan orebody are shown by solid squares and those with dominan gasoline and paint are indicated by the open squares. The circ are vacuum dust (vc) and are joined by a thin line to the Pb_B for t child from that house. The isotopic composition for paint can either ~16.0 or >17.0 (Table 5). Given that there is evidence some children deriving most of their lead from one of the ma sources, the other data imply their Pb_B coming from gasoline a or paint or both. The dashed line represents the mixing relati between the child with the highest proportion of orebody lead a the female adults with the lowest Pb_B (~3 μg/dl) representing a gasoline, food, and water lead. The numbers 7, 9, and 11 are ag of these children.

leach) of the −53+38-μm fraction, or the 0.1 *M* HCl leach of the −53+38-μm fraction for gutter sweepings, soils, or vacuum cleaner dust (Gulson et al., 1993). For example, the 0.1 *M* HCl leach extracts 33 to 61 percent (mean = 47 ± 10%, $n = 7$) of the total leachable lead from gutter sweepings, from 41 to 84 percent (mean = 60 ± 10%, $n = 10$) of the soils, and 17 to >100 percent (mean = 47 ± 38%, $n = 5$) of the vacuum cleaner dusts. The >100 percent probably arises from sample heterogeneity, even though the sample is the −53+38-μm fraction. These results are similar to the ~65 percent available lead obtained for urban and house surface dusts by Duggan and Williams (1977) and Harrison (1979).

Even though there are widely varying percentages of bioavailable lead within the one sample, the amounts of lead which can be potentially absorbed under simulated stomach conditions are very high. It is not possible to estimate precisely the amount of lead absorbed by the gastrointestinal tract of an infant at Broken Hill because of the widely varying estimates of the amount of "dirt" ingested. For example, parental anecdotes vary from "eats no dirt" to "handfuls every day" (then obvious from the stool). Nevertheless, if a child does eat dirt, or ingests it via soil or house dust which is attached to the hands, the solubility of the lead-bearing phase(s) in Broken Hill can easily explain the elevated Pb_B levels in children compared with children in other mining communities.

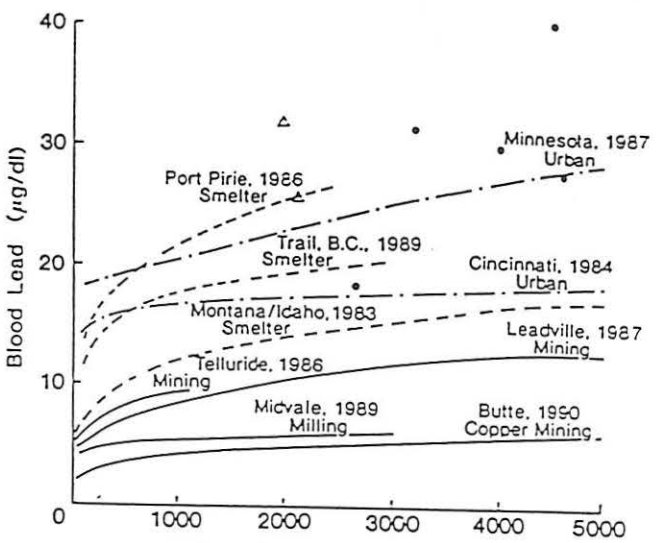


FIG. 12. Pb_B/soil dose ratios at Broken Hill compared with those from mining, smelter, and urban sites in the United States (redrawn from Davis et al., 1992). Data for the United States are for children. Solid lines are for mining communities, finely dashed lines are for smelter communities, coarsely dashed lines are for urban environments. Triangles denote children whose blood lead is attributed to paint or gasoline and solid circles those whose lead is from an orebody source.

Comparisons with Other Studies and Relevance to Remedial Actions

The most comprehensive studies carried out in mining communities are, for example, those in North America at Telluride (Bornschein et al., 1988) and Aspen (R.L.Bornschein, pers. commun., 1992) and in the U.K. (Barltrop et al., 1975; Cotters-Howells and Thornton, 1991). In the Telluride study, Bornschein et al. (1988) used structural regression equations to infer the source and pathways of the lead in the children and attributed a significant contribution to lead from paint. Other studies in the U.K. have employed multivariate analyses to infer sources and pathways of lead into the children, but in these cases, the low Pb_B levels were attributed to the low-solubility lead-bearing phases (e.g., Steele et al., 1990; Cotter-Howells and Thornton, 1991). The high Pb_B levels and bioavailability of the orebody lead at Broken Hill means that it is quite different from many other mining communities, especially those in the United States, and any remedial actions that are implemented have to be specific for Broken Hill. The difference in Pb_B levels in relation to soil lead for Broken Hill compared with those for other mining communities is shown in Figure 12. There is clearly no simple correlation between soil lead and blood lead.

In a discussion of the U.S. Environmental Protection Agency's integrated uptake/biokinetic model (IU/BK) as it applies to mining communities, Karam and Beck (1991) use a value of 0.33 for the lead transfer coefficient, a parameter which describes the transfer of lead from soil to house dust. Calculations using their formula to estimate house dust lead contents for Broken Hill give quite erroneous underestimates of the contribution of soil to house dust. Furthermore, except for studies performed by Bornschein and his colleagues, other investigators have not sized the soils or house dust, even though in many of these studies, samples were pulverized. Karam and Beck (1991) further suggest that, using the transfer coefficient of 0.33, the gastrointestinal absorption of lead for children 0 to 6 years old in mining communities is ~12 percent and not the 30 percent applied in the IU/BK model for urban and smelter communities. The low figure is based on mining sites where there is good encapsulation of galena by anglesite ($PbSO_4$), pyrite, or quartz, or even the presence of so-called "insoluble" galena. Bioavailability tests described above show that the lead species from Broken Hill are highly soluble and similar to those in urban environments. Thus the global conclusions of Steele et al. (1990) of a lower impact of mine waste-derived lead

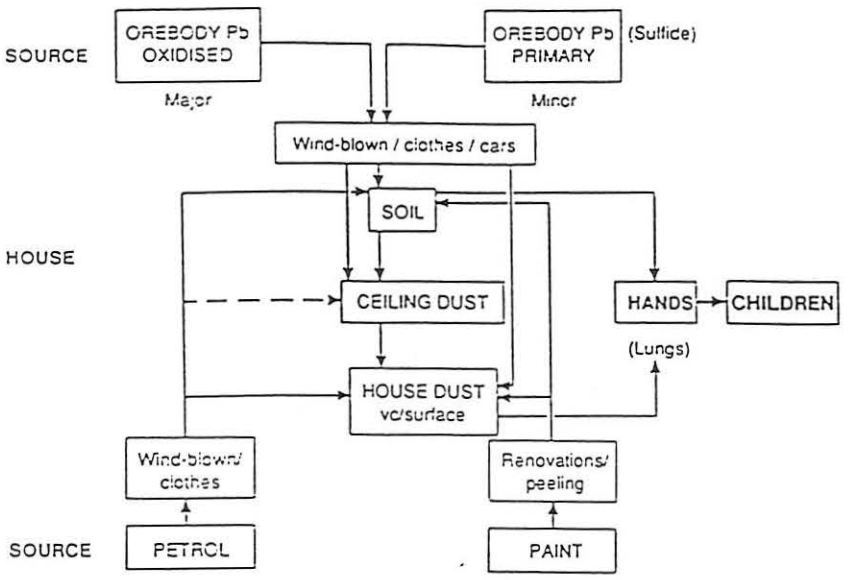


FIG. 13. Provisional flow sheet for sources and pathways of Pb into children from Broken Hill.

in soils (or dusts) on Pb_B levels are not valid and each mining community needs to be assessed individually.

Sources and Pathways

A provisional flow sheet for sources and pathways of lead into children in Broken Hill is shown in Figure 13. This summation is based on the lead isotope results and lead contents, mineral speciation, solubility data, observation, and discussions with parents. The lead isotope fingerprinting approach is the only method which can assign, with any degree of certainty, sources to lead—any other method can only infer the source of lead from total lead contents and/or with other elements or observations. Considering the degree of variability in lead contents and isotopic compositions from, for example, vacuum cleaner dusts, it is necessary to utilize a very large data base for statistical manipulation from which to draw inferences using conventional methods.

If it is accepted that the lead isotope data demonstrate that the orebody lead is a major contributor to Pb_B levels via soil and dust in many Broken Hill children, then the other potential contributors are food, water, air (including gasoline), and paint. Even though the isotopic compositions for food and water would allow them to be contributors to Pb_B level, the amounts of lead in these substances are relatively low and so their contribution to the Pb_B level is small (Gulson et al., in press). Isotopic data for the high-volume air filters indicate that the lead is derived from either gasoline, orebody lead, or both, depending on prevailing wind directions. However, the contribution from inhalation to lead body burden is reco nized to be small, even in children (<5%). When t isotopic data are considered for the children, cas exist where the overwhelming proportion of lead derived from orebody lead but in other cases it can derived from gasoline lead or paint. In addition, it estimated that at least 30 percent of children in Br ken Hill with $Pb_B > 15$ μg/dl investigated in this stu have a significant proportion of gasoline or paint le in their blood. In view of the antiquity of ma houses in Broken Hill, paint is probably a significa source of lead in some children, especially throu pica. Paint lead is definitely implicated as a maj source in at least one case, and there may be a nu ber of others.

Conclusions

Calls to close the underground mining operatio are ill founded because the microscopic investig tions demonstrate that galena is only a minor comp nent in soils and house dusts, except in a house clo to the concentrator and rail-loading facilities. The m jority of lead is found in oxidized ore, but it is n possible to determine if this material is from ancie weathering or recent mining activity. However, it possible, using approaches commonly in practice exploration and the earth sciences, to assign sour and pathways of lead in children and adults and t allows for correct remedial procedures to be ins gated. Earth scientists have an increasingly import role to play in resolving environmental problems b cause many of these are centered on earth scien

media. Furthermore, the approaches used in mineral exploration are directly applicable to environmental problems.

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August 25, December 9, 1993

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