Lead Pathways Study - Air

Health Risk Assessment of Contaminants to Mount Isa City



Report by:

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PREAMBLE

The Lead Pathway Study - Air report is one of several reports derived from a series of studies at Mount Isa City. The project team was tasked to carry out hazard assessment, exposure assessment and health risk assessment of lead (Pb) by utilising the enHealth risk assessment framework.

Within the National Environmental Protection Measures (NEPM) for soil contamination, there is allowance for higher tier and more refined risk assessment beyond the initial total concentration screening and tier-two steps. This provides a more refined site specific and evidence-based risk assessment that this research-based study aimed to deliver. The study included an extensive survey of various dust/soils samples of mining/smelting origins and residential area including a statistically based house-hold dust campaign. Several techniques were employed to provide physical and chemical characteristics of these samples. The rationale for choosing a particular technique or a set of related techniques is explained in relevant chapters of the report. Bioavailability/bioaccessibility measurement was performed for a more refined exposure assessment instead of using the default of 100% bioavailability assumption.

Amongst the chosen techniques, Synchrotron-based X-ray absorption spectroscopy method is an important one that affords Pb speciation/composition data and is the best cutting edge method to help with the interpretation of bioavailability/bioaccessibility data. The Pb isotope study is employed to understanding the complexity of a particular sample matrix. It has demonstrated that soil contamination could have come from multiple sources including past and present, natural and anthropogenic inputs.

Bioaccessibility (BAc) data were obtained as a surrogate estimate for the absolute bioavailability (ABA). A correction factor between BAc and ABA was derived based on ABA data obtained from 12 selected, representative but diverse set of samples. It may be prudent to point out that while the correlation between BAc and ABA is not ideal the most conservative conversion factor is used for the calculation of estimated ABA values. This study also found that the mean of BAc obtained from four pH values over the whole gastrointestinal tract rather than a single acid pH for the stomach phase is the best predictor of blood lead in children. The predicted risk in terms of blood lead in children agrees with the ultimate 'gold standard' of human blood survey conducted by Queensland Health. This study also indirectly confirms that relative bioavailability (RBA) and BAc (gastric phase) could over estimate potential risk as already suggested in published studies. An important detail to recognise is that gastric-only bioaccessibility measurement will over-predict bioavailability of lead; this can be demonstrated by using the USEPA IEUBK model to predict blood lead increase from ingestion of only soil by children. Food in the stomach and intestine is a very important factor in lead absorption. Following solubilisation in the stomach lead is transferred with nutrients from food to the intestine whether absorption of lead occurs. Lead absorption occurs via the intestinal phase and not from the gastric/stomach phase where solubilisation occurs. An average pH representing the fast, semi-fed and full-fed states of the stomach and the near neutral pH of the intestine is selected to provide an intermediate pH for testing in the PBET and represents a nutritional status intermediate between fasting and fed states. This also represents a more realistic exposure scenario of a daily life rather than the most conservative assumption that exposure only occurs during the fast-state (hunger).

EXECUTIVE SUMMARY

CONTEXT

Glencore through its subsidiary Mount Isa Mines Limited ('MIM'), conducts copper and lead–zinc–silver mining and processing operations adjacent to the City of Mount Isa. These operations generate dust and metallurgical fumes that can contain heavy metals such as copper, lead, zinc and cadmium, as well as 'metalloids'¹ such as arsenic and silicon (NPI, 2012).

In addition, while the mining operations are conducted on and under the Mount Isa Mines lease, there are also areas of natural mineralisation within the boundaries of the City of Mount Isa that have elevated levels of these metals and metalloids. Indeed, parts of the city are built on land that is encompassed by the MIM mining lease (ML 8058).

MIM has for over 40 years operated an air-quality control ('AQC') system to limit the exposure of the population of Mount Isa to these airborne dusts and fumes. (Wrigley, 1992). The AQC system controllers shut down the smelters and curtail certain dusty operations, when necessary, to maintain the air quality in Mount Isa. This is normally done based on weather forecasting and measurements of atmospheric conditions. In addition, there is a system of 10 continuous real-time sulfur dioxide ('SO₂') monitors that warns the controllers if unexpected weather events are leading to an increase in the concentration of SO₂ in the community (MIM, 2012a). The system also includes 5 passive monitoring stations, 9 highvolume samplers and 10 dust depositional gauges for monitoring dust in the Mount Isa city air (MIM, 2012a). The data from these samplers show that the air quality in Mount Isa has met MIM's operating licence conditions (DEHP, 2013, MIM, 2012c). The control of fumes is only ancilliary to SO₂ control (MIM, 2012a).

Of the metals and metalloids measured in these monitoring devices, lead has had the greatest focus due to its potential health effects. It is known to be toxic to humans and animals at sufficiently high doses (Donovan, 1996). In recent decades, the focus on lead toxicity has shifted from high-dose effects in people showing symptoms of lead poisoning to the effects of exposure to lower doses that cause no acute symptoms, particularly in the case of children and fetuses (Needleman, 2004).

As a result of studies that indicated that blood lead levels greater than 10– 15 micrograms per decilitre² of blood (' μ g/dL') can affect intellectual development, there has been a drive to lower blood lead levels in the population, and particularly in children (Donovan, 1996). This has led to a lowering of the threshold level at which steps should be taken to reduce exposure to lead from

¹ Elements that have properties intermediate between metals and non-metals.

² 1 decilitre is equal to 100 millilitres.

≥ 25 µg/dL³ for a member of the general population (OECD, 1993) to a level of ≥ 10 µg/dL for children (U.S. CDC, 2013). The Australian National Health and Medical Research Council ('NHMRC') in 1993 emphasised its concern over exposure to lead, especially in young children, and recommended that a blood lead level of less than 10 µg/dL, the level currently recommended⁴ (NHMRC, 2009), should be achieved for all Australians and set the following targets for reductions in blood lead levels by the end of 1998:

- 15 µg/dL for all Australians who are not occupationally exposed
- 90 per cent of all children aged from 1–4 years having blood lead levels below 10 μg/dL (Donovan, 1996).

This recommended lead level, however, should be considered as the level at which sources of exposure should be investigated, rather than a simple interpretation of a 'safe' level or a 'level of concern'.

As a result of these concerns and other trends, lead exposures of the general populations in developed countries have been reduced by the elimination of lead from such things as fruit pesticides, lead water pipes, paint, petrol and solder in food and drink cans (OECD, 1993). There has been a corresponding reduction in the blood lead levels in these populations. For example, the second national health and nutrition examination survey ('NHANES II' 1976 - 1980) conducted in the United States found that average blood lead levels in children aged 6 months to 2 years was 16.3 µg/dL (Goyer, 1991). For children aged 1-5 years, 88.2 per cent had blood lead levels $\geq 10 \,\mu g/dL$, 53 per cent had blood lead levels \geq 15 µg/dL and 9.3 per cent had blood lead levels \geq 25 µg/dL (U.S. CDC, 1994). By the time of the first phase (1988–1991) of the third US national health and nutrition examination survey ('NHANES III' 1988 - 1994), there had been a 78 per cent decline in the estimated geometric mean blood lead level for the US population as a whole, and only 8.9 per cent of children aged 1-5 years had blood lead levels \geq 10 µg/dL (U.S. CDC, 1994). By the 2007–2010 NHANES cycle, only 2.6 per cent of 1–5 year olds had blood lead levels \geq 5 µg/dL and the geometric mean was 1.3 µg/dL (U.S. CDC, 2013).

There has also been a decline in the blood lead levels in children in Mount Isa. In 2007, Queensland Health, a Queensland government department, surveyed 400 children aged 1–4 years who were volunteered by parents or guardians and found that their geometric mean blood lead level was 4.97 µg/dL, and that 11.3 per cent had blood lead levels $\geq 10 \mu g/dL$, with two (0.5 per cent) having blood lead levels exceeding 20 µg/dL (Queensland Health, 2011). A follow-up survey of 167 children aged 1–4 years and based on a whole of community response, conducted in 2010, found that their geometric mean blood lead level was 4.27 µg/dL, with 4.8 per cent $\geq 10 \mu g/dL$, and one child at 22.4 µg/dL (Queensland Health, 2011). The decline in both the geometric mean and the

³ ' \geq ' means 'greater than or equal to'.

⁴ The NH&MRC blood lead level for investigation is currently 5 μg/dL NHMRC (2016) 'Managing individual exposure to lead in Australia – a guide for health practitioners'. National Health and Medical Research Council, Commonwealth of Australia. Canberra. April 2016.

number of children $\ge 10 \ \mu g/dL$ for the 2010 survey compared with 2007 was statistically significant.⁵

For comparison, the last national blood lead survey of children's blood lead level, conducted in 1995, found that the geometric mean for 1575 Australian children aged 1–4 years was 5.05 μ g/dL and that 7.3 per cent of them had blood lead levels \geq 10 μ g/dL (Donovan, 1996). Four of the children (0.25 per cent) had blood lead levels \geq 25 μ g/dL (Donovan, 1996). This study did not include children from Mount Isa and would still have included exposure from lead in petrol.

In late 2006, Mount Isa Mines commissioned a *Lead Pathways Study* to investigate the natural and industrial pathways of lead and other heavy metals into the Mount Isa community, and assessing the potential human and ecological health risk⁶. The evaluation addressed all exposure pathways that could be affected by air dispersion (i.e., ingestion, inhalation and dermal exposures from airborne materials). This study is headed by The University of Queensland's Centre for Mined Land Rehabilitation, in collaboration with the National Research Centre for Environmental Toxicology.

PURPOSE

This report is the third of the three reports that comprise the *Lead Pathways Study*. The other two reports were the *Lead Pathways Study – Land* (published in July 2009) and the *Lead Pathways Study – Water* (published in September 2012).

The risk assessment process used in the study followed the recognised Australian Government risk assessment framework as laid out by enHealth, a part of the Australian Government's Department of Health and Ageing.

The purpose of these reports is to provide Glencore, members of the Mount Isa community and other stakeholders (such as the Queensland Government) with a better understanding of sources of lead and other metals and metalloids, and the exposure of members of the public to them, so that the risks are understood and action can be taken if necessary to maintain public health.

⁵ The Queensland Health report used the definition of statistical significance that is commonly used in science, i.e. that there is less than a one-in-twenty probability that the observed decline was due to random variation rather than being a real result.

⁶ The Lead Pathways Air Report dates from December 2012 and refers to guidelines that may have changed. These are identified where appropriate.

The specific purpose of this report, the *Lead Pathways Study – Air* is to provide the findings of investigations designed to:

- 1. determine contributions of lead-containing particles and fumes from sources in the mining and processing operations to blood lead levels in the community, particularly of children less than five years' old⁷
- 2. estimate air particulates as a potentially significant lead exposure source for inhalation and ingestion by members of the community and, particularly, children.
- 3. determine appropriate actions and follow up works to manage the risks

FOCUSSING QUESTIONS

The focussing questions for this study were:

- 1. What are the potential pathways of lead and other heavy metals and metalloids from mining and mineral processing activities, and natural mineralisation?
- 2. How does the form of lead in the environment affect its ability to affect human health?
- 3. What is the risk to the health of the Mount Isa population, particularly to young children, from exposure to heavy metals and metalloids in air and dust found in the City's environment?
- 4. What procedure was used to determine the risk to the health of the Mount Isa population?
- 5. What measures can be taken to reduce the risk?
- 6. What would benefit from further examination?

CONCLUSIONS

Potential Exposure Pathways

The potential exposure pathways of lead into the human body are:

- ingestion through the mouth and, subsequently, the digestive system
- inhalation through the mouth and nose into the lungs
- absorption through the skin.

⁷ The Queensland Health blood lead surveys at Mount Isa surveyed children 1-4 years of age. The USEPA (2010) Integrated Exposure Uptake Biokinetic (IEUBK) model for blood lead prediction uses an age range of 0.5-7 years as default.

Of these three pathways, the two major routes of lead absorption by the human body are through ingestion and inhalation pathways, whereas absorption through the skin is considered to be insignificant (IPCS, 1995).

Ingestion through the mouth into the digestive system can be through food and drink, or through non-nutritive substances such as dirt and paint. Babies and small children often put their thumbs or fingers in their mouths, which can result in transferring lead-contaminated dust into their mouths.

Particles less than $250 \,\mu\text{m}$ in size are the most likely to enter through the ingestion route because coarser particles are less likely to adhere to hands and be transferred to the mouth.

Food in the stomach and intestine is an important factor in lead absorption. Previous studies evaluated lead isotope absorption by volunteers who were fed lead with meals or specific foods, or while fasting. For the volunteers who were fasting, as much as 71 per cent of soluble lead was absorbed (Heard et al., 1983). However, when the lead was ingested with a meal, absorption fell to a range of 3–7 per cent of the dose (Heard et al., 1983, James et al., 1985, Maddaloni et al., 1998).

Age is a significant variable for lead absorption and metabolism. The portion of ingested lead taken up by the body is typically less than 5 per cent for adults, but as high as 50 per cent for children (Zeigler et al., 1978). Infants and toddlers are at greater risk due to increased exposure (through hand-to-mouth behaviour), increased ability to absorb lead, the susceptibility of their rapidly developing central nervous systems, and their less-developed gastrointestinal tract (Maynard et al., 2005).

The inhalation pathway consists of breathing in solid particles or liquid droplets found in air. Particles and droplets that are less than 10 micrometres ('µm') in diameter (known as 'PM₁₀' particles) and those less than 2.5 µm ('PM_{2.5}' particles) pose the greatest problems for human health, because they can penetrate deep into the lungs and get into the bloodstream (IPCS, 1995). Particles larger than about 7 µm tend to deposit on the walls of the airways (the thoracic region) and become part of the mucus that is moved up to the mouth and then swallowed (IPCS, 1995). PM_{2.5} gives an approximation for fine mode particles, and therefore alveolar deposition, while PM₁₀ indicates the thoracic aerosol component (Raunemaa, 2002).

Lead absorbed through ingestion or inhalation moves into the body's circulatory system and from there can move into various organs or the bones. Lead is gradually excreted from the body. Two important routes of lead excretion from the body are urine and faeces (IPCS, 1995).

A lead uptake study indicated that 20 per cent of dosed lead was bound to the skeleton after three weeks (Heard and Chamberlain, 1984). The half-life of lead in the human body is approximately 30 days in blood stream and 10–30 years in bone (JECFA, 2011).

Measuring the effect of Form of Lead in the Environment on Human Health

Simply analysing the concentration of lead or other contaminants in soils, dusts or other materials is usually not an accurate measure of the potential health effect of the contamination (Ng et al., 2010). The health effects depend, in part, on the body's ability to absorb the contaminating substance.

The ability of the human body to absorb lead depends on the form of the lead. Lead can exist as metal or as a chemical compound. Minerals are naturallyoccurring chemical compounds.

The solubility of lead minerals and other compounds relate to their uptake or absorption in the human body via ingestion exposure and is described as bioaccessibility. The bioaccessibility of lead as a free ionic species such as lead acetate is higher than less soluble mineral forms (Ruby et al., 1999). Lead sulfate (PbSO₄, known as 'anglesite' in its mineral form) is less soluble than lead acetate but more soluble than highly insoluble lead sulfide, and lead carbonate (PbCO₃ – 'cerussite' in its mineral form) is 1.3 times more soluble (IPCS, 1995). Cerussite, however, is soluble in hydrochloric acid (Read, 1970) (a component of stomach digestive juices (Burtis et al., 1988)). It is much more easily absorbed into the circulatory system via ingestion exposure than galena or anglesite (U.S. EPA, 2007b, Dieter et al., 1993, Ruby et al., 1999).

Lead mineral type, and the matrix in which it resides, affect its *bioavailability*. The bioavailability of lead is the fraction of the lead ingested and/or inhaled that reaches the circulatory system in the body and can thus be measured in the blood.

Bioavailability is the fraction of dose that reaches the systemic circulation of a receptor (e.g. humans) and is determined using living organisms. Because of the ethical issues associated with using people, most of the tests to determine bioavailability of samples of lead-containing materials (such as dirt and dusts) are carried out using animal test subjects, usually rats or mice, but also pigs (U.S. EPA, 2007b) rabbits (Freeman et al., 1993) and monkeys (Freeman et al., 1995).

Recent studies using animals have demonstrated that the bioavailability of lead from some soils and mine waste materials may be considerably lower than some have previously assumed (Bruce et al., 2007, Diacomanolis et al., 2007), due to the type of minerals present.

Bioavailability is considered the 'gold standard' for measuring uptake of lead by the body, but the cost of the tests and the ethical issues associated with animal testing mean that it often cannot be applied.

A report by the United States' Environmental Protection Agency ('US EPA') (2007b) showed bioavailability by mineral type, as general guide, with galena having a relatively low value compared to lead oxide and with cerrusite having the highest bioavailability.

The concept of *bioaccessibility* was developed as a proxy for bioavailability to reduce the need to use living animals in the assays. Bioaccessibility is the soluble fraction under laboratory-simulated conditions, i.e. an indicator of bioavailability to

the receptor (e.g. humans). The bioaccessibility of ingested lead is determined using a simulated digestive system, mimicking the chemical environment in the stomach and intestines. Such tests include the one used in this report that is known as the 'physiologically-based extraction test' ('PBET'). Bioaccessibility tests also include those that use simulations of the fluids found in lungs to mimic absorption of contaminants through the lungs.

Bioaccessibility gives a prediction of bioavailability. Results from these bioaccessibility tests tend to be higher for lead than from bioavailability tests (Bruce et al., 2007, Diacomanolis et al., 2007).

Bioavailability tests, using Sprague Dawley[®] rats, were conducted for this study at the Queensland Health and Forensic Scientific Services Biological Research Facility, Coopers Plains (Animal Ethics approval number 07P05) on ten representative samples obtained from the mine site and the residential areas of Mount Isa. These samples were:

- a composite sample of community soils
- a composite sample of roof gutter dusts
- a composite sample of carpet dusts
- dust collected from the lead smelter
- dust collected from the surface of the Number 5 tailings dam
- sediment from the Leichhardt River
- material collected from a naturally mineralised outcrop of the Urquhart Shale (on the Barkley Highway, adjacent to the RSL Club's main gate)
- a sample of lead concentrate
- dust collected from the copper smelter
- a slurry prepared from particulates dislodged from 50 high-volume air samples, the number necessary to generate sufficient sample for the tests.

The samples were analysed at Entox, a centre of The University of Queensland within the Queensland Health facility. The bioavailabilities were determined from measurements of the lead content of the rats' blood and urine after they were dosed orally with the lead-bearing samples. All the composite samples had bioavailability results less than 10 per cent, with the highest being 6.2 per cent determined from lead measured in blood samples from rats dosed orally with the slurry of composite air particulates collected by the high-volume samplers from 50 air-PM₁₀ filters collected at Mount Isa city from 2008 to 2010 (HVA slurry; see Table 115, page 273).

Bioaccessibility tests were conducted on the same samples to allow a relationship between bioavailability and bioaccessibility to be determined. This meant that the bioavailability of samples could be calculated from bioaccessibility tests and no further tests using live animals were necessary.

The results of work conducted for this study indicated that bioavailability can be calculated from the bioaccessibility of a representative data set using the equation, which was derived from Table 117 (page 276) and based on the upper 95 per cent confidence interval level for slope (0.17) of the line fitted through zero:

This equation shows that the bioavailability of a sample is less than 20 per cent of its bioaccessibility when calculated from an individual measurement of bioaccessibility.

It is thus important to identify the various forms of lead from different sources and to assess the quantities potentially available for ingestion and/or inhalation exposure by the Mount Isa community.

Health Risks from Airborne Lead

Based on the results of this study, the risk to young children from inhalation of airborne lead in Mount Isa is very low. The contribution of airborne sources of lead via the inhalation pathway to blood lead levels ranges from 0.2 to 2.1 per cent of the total blood lead. On the other hand, the contribution from dust and soil via the ingestion route ranges from 37 to 93 per cent (with a median value of 74 per cent). Dietary intake of lead makes up most of the balance of lead intake via the digestion route (Walker and Griffin, 1998). Thus, inhalation is shown to be less than 5 per cent of the total exposure for people living in Mount Isa, while total ingestion is greater than 95 per cent.

Only a few studies of urban environments have previously reported the contribution of inhalation of lead to be less than 6 per cent of the contribution to blood lead level (Davies et al., 1990, Dong and Hu, 2012). The relatively low contribution of exposure to lead via inhalation arises because the maximum weight of air particulate matter which can be inhaled by a child or adult is quite small. This current study confirms that inhalation exposure is less significant compared to ingestion.

High-volume samplers capturing total particulates suspended in the air at five different locations in Mount Isa show that the air concentrations at these sites are lower than the maximum level of < $0.5 \ \mu g/m^3$ (measured as air-PM₁₀, averaged over a year) set in the Australian government's *National Environmental Protection Measure for Air* and the *Queensland Environmental Protection Policy (Air)*. The latter is collected as total suspended particulates (TSP) with a size cut-off of 50 μ m which includes air-PM₁₀ as a subset. None of the monitoring sites has had an annual average exceeding the NEPM for air since 2009. Although a size difference exists between TSP and air-PM₁₀, there is unlikely to be any variation in exposure of lead between TSP and air-PM10 to the population as the bioaccessibility of lead for the HVA slurry (20.5%; Table 118) prepared from air-PM₁₀ filters collected at Mount Isa city was almost the same as the median for soil <250 μ m fraction (22%) (Table 103). The HVA slurry has lead composition and %BAc that shows it to be soil-derived material (Section 3.10).

The mean bioaccessibility (BAc) of lead in natural mineralisation in Mount Isa city was 2% compared with 24% in garden soil samples tested in this study and about an order of magnitude lower than the often-adopted default value of 100%. The actual individual % BAc value obtained from each house specific dust sampling program was used in the IEUBK modelling of blood lead level.

The results of tests to determine the bioavailability and bioaccessibility of lead in air and dusts in the Mount Isa city environment were inputted to the Integrated Exposure Uptake Biokinetic ('IEUBK') model developed by the US EPA. This model is used to predict blood lead levels in children from a child's exposure to

lead and the bioavailability of the lead to which it has been exposed (U.S. EPA, 2010). The IEUBK model has been in use for about 20 years and has been widely used by regulators for children's health risk assessments to guide decision making (Díaz-Barriga et al., 1997, Dong and Hu, 2012).

The actual individual BAc value and predicted ABA obtained from each house specific dust and soil sample set was used in the IEUBK modelling of blood lead level. Since local house specific dietary Pb intake was not determined, the national average dietary Pb intake was assumed for the Mount Isa children and used for the IEUBK modelling together with other default values such as maternal blood Pb, soil ingestion rate etc. Despite these limitations, the IEUBK model affords a means for identifying potential Pb exposure risk of children who might be living in a specific house. The discrepancy between blood survey and predicted blood Pb level by the model may be due to several factors including sampling/survey period, different population (residency of children), and default input parameters for the model not being representative of Mount Isa children.

Method Used to Determine the Health Risk in Mount Isa

These conclusions about the health risk to children in Mount Isa are based on an investigation that followed the Australian human health risk assessment procedure from enHealth.

EnHealth has developed a method for assessing the health risks of contaminants and potentially toxic substances on the population. The LPS-Air study followed EnHealth's method to try to understand the possible exposure of the Mount Isa community to lead and other associated metals and metalloids. The research followed the EnHealth risk assessment approach of:

- issue identification
- hazard assessment
- exposure assessment
- risk characterisation.

The project assessed the concentrations of heavy metals and metalloids in source materials, air particulates, garden soil and dust accumulation around Mount Isa City, and in areas of the mine leases and background sites. As far as possible, all potential sources of lead that could contribute to dispersion and exposure pathways of heavy metals and metalloids were identified. The study thus included historical mining sediments and natural mineralisation as potential sources, and assessed if the effects were of significance to the air–dust pathway in Mount Isa.

Issue identification

Potential sources of the lead to which the community could be exposed via the air-particulate pathway were identified. The origin of lead to this pathway is primarily the Urquhart Shale, which is the geological formation that contains the lead and copper minerals that are mined in Mount Isa. The Urquhart Shale includes natural outcrops of mineralised material, some of which occur in the residential areas that are close to the mining operations.

The mobilisation of deposited airborne particulates from mine-related sources and/or from local surface soils derived from lead-enriched bedrock creates the direct source to community, if these particulates are present in and around the residences of Mount Isa.

To assess the concentrations of lead (and other heavy metals and the metalloid, arsenic) in material at and related to these sources, samples were collected from areas of:

- 1. natural outcrops of the Urquhart Shale containing the lead mineralisation and several other geological formations (mainly shale and referred to as 'background rock' or 'BGR'), without lead mineralisation, occurring adjacent to the Urquhart Shale and up to approximately 30 km from the city centre.
- 2. the Mt Isa mine site including:
 - i. waste rock dumps
 - ii. run-of-mine ('ROM') ore stockpiles
 - iii. lead smelter
 - iv. lead slag piles
 - v. copper crusher
 - vi. copper smelter
 - vii. copper slag piles
 - viii. tailings storage facility
 - ix. historical tailings removed from the Leichhardt River in 2008
 - x. fallout on the mine site
 - xi. dust from the haul roads associated with the Black Star open cut mine
- 3. the Mt Isa residential area at locations inside and outside of houses, including:
 - i. garden soil
 - ii. the fraction of soil particles less than 10 μm in size (the 'PM_{10} fraction'), which relate to soil particles dispersed by wind
 - iii. fallout dust in gardens
 - iv. dust on verandas
 - v. dust on roofs
 - vi. dust from roof gutters
 - vii. outdoor air particulates
 - viii. dust from carpets
 - ix. dust from other floor surfaces (such as timber floors or tiles)
 - x. dust from interior window sills
 - xi. dust from window troughs
 - xii. indoor air particulates.

Sixty-seven houses were used to examine the spatial distribution of lead and other heavy metal and the metalloid concentrations across the city. This was a statistically-representative number for Mount Isa city that was calculated using a sample size equation (Equation 4) from the geometric standard deviation (1.8 μ g/dL) of the Mount Isa blood lead survey (Queensland Health, 2008) with a minimum analytical difference of 1.2 μ g/dL and corrected for confounding factors (Kupper and Hafner, 1989).

Total concentration data of metals and the metalloid were examined by Q-Q plots and the Shapiro-Wilk Test to determine whether the data were normally distributed (i.e. whether they fall on a bell-shaped curve). These results indicated that the data for most elements in the samples were not normally distributed, and thus statistical tests used for normal distributions could not be used to determine the associations between various data sets. Instead, non-parametric tests were used for the statistical analyses (see Section 2.6 page 157 and Section 3.1.1 page 160). Most environmental data sets are not normal with random outliers.

Median values and geometric means were used because arithmetic means cannot be used for data that are not normally distributed.

The samples were analysed using the following analytical techniques:

- analytical chemistry techniques to determine the total concentrations of metals and the metalloid in the samples, primarily through NATAregistered analytical laboratories, but samples of air particulates, fallout dust and background rock were analysed by the Earth Science Geochemistry and Centre for Mined Land Rehabilitation ('CMLR') laboratories at the University of Queensland
- lead isotope concentration measurements, undertaken in the Radiogenic Isotope Facility ('RIF') at the University of Queensland, using highresolution, multi-collector inductively-charged plasma mass spectroscopy ('MC-ICP-MS'). These had a higher level of accuracy, by a factor of 100 times, than all previous measurements of lead isotopes in Mount Isa
- lead L_{III} edge x-ray absorption near-edge spectroscopy ('XANES'), undertaken at the Australian National Beamline Facility, which was located at the Photon Factory in Tsukuba, Japan, with the resulting spectra being analysed using a series of steps, as part of a well-defined statistical procedure, to determine the composition of the lead minerals present, including principal component analysis ('PCA') followed by target transformation to select the set of model compounds for linear combination fitting (Section 2.4.3.1.1)
- x-ray diffraction, undertaken at the Centre for Microscopy and Microanalysis ('CMM') at the University of Queensland, to identify the mineral forms of lead present in samples, as a complement to the XANES analysis
- particle size analysis using a Malvern Mastersizer 2000 located in the School of Chemical Engineering at the University of Queensland
- scanning electron microscopy ('SEM'), undertaken at the CMM to understand the physical characteristics (such as shape and surface roughness) of the particles present in the samples
- bioavailability testing on 10 samples of different types of lead-bearing Mount Isa material, using Sprague Dawley[®] rats at the Queensland Health and Forensic Scientific Services Biological Research Facility, Coopers Plains (as described above)
- bioaccessibility using the PBET (see Measuring the effect of Form of Lead in the Environment on Human Health, page 9, for more detail) to simulate the human digestive tract (see Section 2.4.5.2, page 149).

The XANES results were independently reviewed by Dr Jade Aitken, of the University of Sydney, to confirm and validate the findings.

Hazard assessment

The framework of hazard assessment for the Lead Pathways model is given in Figure 11 Lead pathways model (blue arrows indicate potentially significant lead pathways in Mount Isa)(page 118).

The two critical factors determining the likelihood of lead getting into the blood via the air–dust pathway, and from there into other organs of the body, are the size of the lead particles in the environment and the chemical form of the lead.

The critical particles are those that are less than about 250 μ m in size, which can enter the body via the ingestion pathway, and those less than about 10 μ m in size, which can enter via the inhalation pathway. The study found lead particles in these size ranges present in dirt, dust and air samples in Mount Isa. However, as already mentioned, lead in air in PM₁₀ particles is below the annual average of 0.5 μ g/m³ specified by the *National Environmental Protection Measure for Air*, so inhalation is unlikely to be a significant source of lead.

The bioavailability tests showed that the highest bioavailability of the samples tested was 6.2 per cent (for the high-volume PM_{10} particulate slurry) and that the bioavailabilities for the other samples were almost all less than 3 per cent (Section 3.5 and Table 117).

The same 10 samples were subjected to the PBET to determine bioaccessibility. The raw results indicated that the bioaccessibility results were about nine times higher than the bioavailability results, corresponding to a mean slope of 0.11 (Table 117). The poor relation between ABA and BAc, demonstrated by r^2 =0.0096, arises from the limited data set for representative samples having very low measured ABA.

This study used a more conservative conversion of bioaccessibility to bioavailability for the measured set of representative samples (Table 117) by calculating the 95 per cent confidence interval. The slope of the upper level of the 95 per cent confidence interval (0.17) was selected as being most conservative, which resulted in the use of the conversion equation on page 10 to convert from bioaccessibility to bioavailability. In statistics, the 95 per cent confidence interval is normally used. In this case, the 95 per cent confidence interval has a lower bound slope of 0.05 and an upper bound slope of 0.17. The basis of using a conservative approach is demonstrated in Australia by the NEPC (2013) using upper bound values, such as BMDL₀₅ for arsenic, following withdrawal of the PTWIs for arsenic and lead in 2010 (JECFA, 2010). As a result of using the conservative approach, the bioaccessibility was assumed to overestimate the bioavailability of the samples by a factor of 5.88 times rather than 9 times, meaning that the calculated bioavailabilities used in this study were higher than indicated by the raw results, which have a slope of 0.11. That is, the conversion factor used, which lies within the 95 per cent confidence interval, results in the conservative assumption of more lead being absorbed by the body than the actual bioavailability tests indicate.

The median bioaccessibility of sub-set of ten representative and/or composite samples for bioavailability measurement was 14.9% (cf. mean 14.8% Table 117) which was lower than all samples obtained from the mine site (%BAc = 29; Table 101) and the city samples (%BAc = 21; Table 114).

Exposure assessment

The US EPA's IEUBK model has default values for the various sources of lead to which a child might be exposed. These default values include, but are not limited to: lead in food, maternal blood lead level, the bioavailabilities of lead in dusts that might be ingested or inhaled, and lead in water. The accuracy of the predictions produced by the model will depend on correction of these default values for site-specific values. These site-specific values included measured levels of lead in dust, soil and high-volume PM_{10} air sampling in a sample set of 67 houses in Mount Isa.

Risk characterisation

Risk characterisation brings together the previous three steps of the risk assessment and enables the risk to be assessed, in this case the potential effects of lead on the population of Mount Isa, and provides a way to consider what decision or management processes may be needed to deal with identified risks.

If the dust and soil input parameters in the IEUBK model were adjusted using the absolute bioavailability data, there was no predicted exceedance ($\geq 10 \ \mu g/dL^8$) of the NHMRC blood lead investigation level that would result from living in the

⁸ 5 μg/dL is the current NH&MRC (2016) blood lead level for investigation.

Location	Mount Isa	Mount Isa	Mount Isa	Mount Isa
Data source	Queensland Health (2008)	Queensland Health (2011)	IEUBK model prediction (BAc approach) in this study	IEUBK model prediction (ABA approach) in this study
Test time	2006-2007	2010	2008 and 2010	2008 and 2010
Age group	1-4 years	1-4 years	1-4 years	1-4 years
Test number	400	167	67	67
Maximum (µg/dL))	31.5	22.4	11.2	3.19
Minimum (µg/dL))	1.3	1.9	1.6	1.18
Number 10 µg/dL or over	45	8	1	0
Percentage 10 µg/dL or over	11.30%	4.80%	1.50%	0
Geometric mean (µg/dL)	4.97	4.27	3.8	1.63
95% confidence interval	(4.69, 5.24)	(3.96, 4.61)	(3.35, 4.25)	(1.53, 1.72)
Number 5 µg/dL or over	203	73	17	0
Percentage 5 µg/dL or over	50.8	43.7	25.37%	0

houses sampled. The model predicted that the soil contributed 19 per cent (median value) of the blood lead and the various sources of dust, 51 per cent. Given the dominant role of ingestion as the transfer pathway of lead to children, it is likely that hand-to-mouth behaviour by young children in an environment where lead in soil and dust is present is a significant contributing influence on blood lead concentrations.

The predicted blood lead results produced by the IEUBK model are in the form of probability distributions rather than a single value for each house. The model predicts different values for children grouped according to age within the range of either 0.5–7 or 1-4 years. Thus, the output results are summarised in terms of geometric means for each house and the associated probability of exceedance of the recommended level.

When the more-conservative bioaccessibility numbers were used for the dust and soil samples, the IEUBK model predicted a mean value of the geometric means of the blood lead level for children living in each of the 67 houses of 3.8 μ g/dL, and a median of 3.4 μ g/dL, with 1 per cent of the children exceeding the recommended level of 10 μ g/dL or a median of 3.8 μ g/dL, with 1 per cent of the children exceeding the children exceeding the recommended level of 5 μ g/dL (see Table 128). The highest predicted levels were associated with the houses with the highest levels of lead in the dust and garden soils, and these were located in areas underlain by the Urquhart Shale.

The blood lead concentrations predicted by the IEUBK model were compared with blood lead screening programs undertaken by Queensland Health in Mount Isa in 2006–2007 and 2010 for children aged 1–4 years (only this age group was tested) (see the data from Table 139 'Comparison of blood lead concentrations between the IEUBK model's prediction and blood lead testing programs for children in Mount Isa' following this text).

The geometric mean of blood lead concentrations of the children tested by Queensland Health was 4.97 μ g/dL in 2006–2007 and 4.27 μ g/dL in 2010. Note also that the use of 'average' bioaccessibility data produced a closer match to the Queensland Health measurements of children's' blood lead levels in Mount Isa.

There are several possible explanations for the difference between the measured blood lead levels and the IEUBK model predictions using the preferred bioavailability of lead, including:

- the houses sampled for this study might not have been the same as those in which the children sampled in the Queensland Health study were living, and it is thus possible that there exist houses where children have higher exposures to lead than in those sampled in this study
- children with higher blood lead levels in the Queensland Health study might have been ingesting more dust or soil than the default amount of 100 mg/day set by the model (e.g. through eating dirt)

- the dietary intake of lead by children in Mount Isa might be higher than the assumed Food Safety Authority of Australian and New Zealand ('FSANZ') national diet data,⁹ which were used as input data for the model
- the children might have been exposed to additional sources of lead from lead-based paint, leaded petrol residues, and lead acid batteries that were not included in the IEUBK model input assumptions.

Sources of the Lead in the Mount Isa Environment

The results in this study indicate that the PM_{10} air particulates exiting from the Mount Isa smelter stacks were not the major sources of lead exposure via inhalation in the Mount Isa city area at the times the samples were taken. The major source of lead exposure is via ingestion in the community and is from air particulates (<250 µm diameter) that are on the ground from deposition as fallout.

This conclusion is based on measurements of lead isotope ratios that show a clear fingerprint of lead originating from the Urquhart Shale on the mine site and in Urquhart Shale outcrops in the city area. The copper smelter stack samples, on the other hand, have their own distinct fingerprint, and this was not visible in the samples obtained from the city during this study.

The XANES analysis of PM_{10} air particulates exiting from the Mount Isa lead smelter stack contained negligible lead sulfide, whereas near surface samples of dust and fallout from the lead smelter/ sinter plant area collected at the surface or at 2-3m above ground usually contained lead sulfide. Roof gutter dust did not contain lead sulfide.

Lead isotope ratios can show origin of lead regardless of chemical or mineral form while XANES analysis gives the chemical form. XANES analysis may show differences even when lead isotope ratios are shown to be the same.

Further, PM_{10} particles obtained in the lead smelter and from the lead slag stockpile showed smoother features than those from the city samples or the mining samples. This again indicates that the lead blast furnace and it slag product are not major contributors to the PM_{10} samples collected in the city.

This finding contrasts with that reported for Port Pirie, where the source of lead in the community has been attributed to both the lead smelter there and reentrainment of dusts. A sub-set of seven behavioural factors was most predictive of an elevated blood lead level for the 1982 Port Pirie blood lead survey (Wilson et al., 1986) and were incorporated in the program to reduce the risk of elevated blood lead levels in Port Pirie children. These were:

i. household members who worked with lead in their occupations

⁹ A national average based on foods regularly consumed by the Australian population such as from supermarkets that might be underestimate the dietary intake of a population who live in a mineral rich or smelling area and consume locally grown food items

- ii. living in a house with flaking paint on the outside walls
- iii. biting finger nails
- iv. eating lunch at home on school days
- v. when at school, appearing to have relatively dirty clothing
- vi. when at school, appearing to have relatively dirty hands
- vii. living on a household block with a large area of exposed dirt.

Some of these factors may also play a role in Mount Isa, particularly in cases where children are found to have higher blood lead levels. A key difference between locations is that Mount Isa has both mining and smelting of lead whereas Port Pirie has smelting, only.

The lead isotope ratio work indicated the existence of a second source of lead in the Mount Isa environment, tentatively identified as the Cromwell sequence located to the east and upstream of the Mount Isa city area. Lead from this source was found to have mixed, probably over geological time, with lead from the Urquhart Shale. This mixing was most apparent in garden soils, nature strip soils (referred to as 'footpath' samples), the soil PM_{10} fraction, PM_{10} in outdoor air, carpet dust and, to a lesser extent, window trough dust.

It was not possible from the lead isotope work to distinguish between lead originating from the Urquhart Shale in the residential area and that being mined on the mine site.

XANES analysis of samples showed that samples from Black Star open cut and the processing areas contained significant lead sulfide (PbS), but it was absent from the haul road, tailings dam surface material and the surface outcrops of the Urquhart Shale. In the latter three materials, the lead was predominantly present as lead–goethite.

The presence of lead sulfide in fallout, PM_{10} , carpet dust samples in the city indicates that some of the material collected originated from mining and/or processing activities. However, the presence of large proportions of lead–goethite in these samples makes it impossible to rule out dusts from other sources, such as garden soils and other exposures of bare earth in the city, haul roads and tailings dams.

Risk Reduction Measures

Use of the IEUBK model indicated that the key contributions to blood lead levels in Mount Isa children were from lead in soil, surface dust and food. The contributions from airborne dust and water were insignificant in comparison. The houses with the highest concentrations of lead in dust and soil were those with the highest predicted blood lead levels in children.

Queensland Health has found associations in Mount Isa between children's blood lead and factors, such as owning pets, chewing non-food items, and bare soil in the backyard (Queensland Health, 2008, Queensland Health, 2011).

Lead in carpet dust makes a significant contribution to blood lead levels as confirmed by the high correlation ($r^2 = 0.79$) between the IEUBK model's predicted blood lead concentrations for young children (1–4 years) and the bioaccessibility-adjusted data for lead in carpet dust. The IEUBK model also predicted that blood lead concentrations for young children are significantly correlated with bioavailability-adjusted lead in carpet dust ($r^2 = 0.79$); in comparison, the correlation with garden soil was somewhat lower ($r^2 = 0.35$). This finding confirms the significant contribution to blood lead level risk from lead in carpet dust as a health risk as well as a source of lead, and indeed a greater risk than that from garden soil.

The following measures could be taken to further reduce the exposure of Mount Isa children to lead and their consequent risk of having an elevated blood lead level:

- Industry operations: Continue to focus on effective measures to reduce mine dust transfers from key lead sources at the mine site operations, such as haul road dust, mining activities, surface tailings, crushed ore transfer, concentrate handling and the surface dust lying in the lead smelter area (as distinct from stack emissions which are deposited far beyond the Mount Isa city area). Ensure that clean-in, clean-out policies continue to be enforced in all lead work areas.
- Maintaining the home environment: Bare patches in gardens should be covered with grasses. Carpets should be replaced with timber or other hard floor coverings, and cleaned with phosphate-based cleaning agents. Phosphate is known to immobilise lead and reduce it's bioavailability upon ingestion. Houses should be cleaned frequently, by vacuuming and wiping away any accumulated dust (preferably with a damp cloth). Pet ownership should be reviewed in areas with elevated lead concentrations in the soils.
- *Personal hygiene:* Ensure children clean their hands frequently, particularly before meals. Try to reduce children's habits such as sucking non-food items. Keep children away from all potential sources of lead from both geogenic and anthropogenic origins.
- Attention to diet: Wash home grown fruit and vegetables thoroughly before eating/cooking; peeling root crops will also reduce lead exposure. Better still: avoid eating home grown vegetables and fruits whose skin cannot be peeled before consuming. Good nutritional food contains certain food components that can also reduce lead adsorption resulting in lower blood lead.

Areas that would benefit from further work

Areas that would benefit from further work include:

 A closer examination of the reasons for the differences between the blood lead levels predicted by the IEUBK model and those measured in the Queensland Health survey. As mentioned on page 18, these might include differences in the populations sampled in the two studies or additional sources of lead exposure that were not accounted for in the IEUBK modelling (such as a higher dietary intake than in the national food basket, higher than normal ingestion of such lead-containing materials as dirt, or exposure to a lead source not considered in the model).

- 2. More work to pinpoint the sources of lead at the mine site to enable further reductions in transfers from the mining and processing activities to the residential areas. Testing soils for houses overlying the Urquhart Shale area should be undertaken to determine whether they are an issue.
- 3. Investigation of homes of children with elevated blood lead levels to determine whether there are other sources of lead, such as lead paint on toys or lead incorporated into plastic toys, lead solder used in making stained glass, lead in batteries being recycled at residences, and lead in ceramic dishware or leaded crystal beverage containers.
- 4. More work to increase the number of measurements of bioavailability to improve the statistical relationship between bioaccessibility and bioavailability.
- 5. Consider the issues raised that would benefit from further work and determine whether this work is necessary.

RECOMMENDATIONS

- 1. Ensure that all Mount Isa residents, in particular young children, have their blood lead levels monitored. This is to ensure that health management actions are taken, any circumstances leading to elevated blood lead levels in children are identified early, and exposures to lead are minimised..
- 2. Maintain the existing mechanisms in place to minimise transfer of lead to the residential areas, such as the vehicle washing, clean-in, clean-out clothes policies, the AQC system, road sweeping and watering.
- 3. Continue to look for ways to minimise the transfer of dusts, particularly those containing lead and other heavy metals and the metalloid, from the active mining and processing areas to the city.
- 4. Emphasise the importance of a clean home environment in Mount Isa.
- 5. Consider replacing carpets with timber or other hard floor coverings, and cleaning these floor coverings with phosphate-based cleaning agents.
- Promote personal hygiene, such as cleaning children's hands frequently and before meals and minimising specific habits of very young children such as sucking non-food items and keep away from uses of lead including historical paint and petrol residues.

- 7. Wash all home grown fruit and vegetables thoroughly before eating/cooking; peeling root crops will also reduce lead exposure.
- 8. Highlight the improvement in children's blood lead levels that has occurred in Mount Isa as a result of actions taken by MIM and members of the Mount Isa community. These results show that measures being taken are helping to minimise children's blood lead levels and demonstrate that a diligent approach to reducing lead exposures does work.

GLOSSARY

	GEOGGART
Ad libitum	Latin, for 'in accordance with one's wishes'
Aqua regia	A highly corrosive mixture of concentrated nitric and hydrochloric acids, so named because it can dissolve gold
Air particulate	is a general name given to a tiny solid or liquid particle or piece of matter. It usually refers to particles in the air (airborne particulates)
Air quality objective	For an area or place, means - (a) for an air quality objective for an indicator that is the amount of the visibility in the air environment - the minimum amount of visibility that should be in the air environment of the area or place despite the presence of the indicator; or (b) otherwise - the maximum level that an indicator should be in the air environment of the area or place.
Air shed	A part of the atmosphere that behaves in a coherent way with respect to the dispersion of emissions
Alveolar	Relates to the alveoli (small air sacs) of the lungs
Anglesite	Lead sulfate mineral, PbSO ₄ . It occurs as an oxidation product of primary lead sulfide ore, galena
Arithmetic mean	The arithmetic mean of a group of values is commonly referred to as the 'average'. It is the sum of the values in the group, divided by the number of individual values. For example, the arithmetic mean of the numbers 1, 2, 3, and 4 is calculated as follows: $(1+2+3+4)/4 = 2.5$.
Background Concentration	Naturally-occurring, ambient concentrations in the local area of a site
Bioaccessibility (BAc <i>in vitro</i>)	The soluble fraction under laboratory-simulated physiological conditions, i.e. an indicator of bioavailability to the receptor (e.g. humans)
Bioaccessibility- adjusted concentration	The concentration of an element adjusted to reflect its bioaccessibility
Bioavailability (BA <i>in vivo</i>)	The fraction of dose that reaches the systemic circulation of a receptor (e.g. humans). It is expressed as the ratio of the systemic dose to the applied dose, i.e. what is able to have an effect on the body compared to the total concentration to which it is exposed

Blank	In an analytical technique, a 'blank' sample without the chemical species being measured (the 'analyte') that is analysed to determine the background level and the limit of detection
Carbonate	CO ₃ ²⁻
Certified Reference Materials	Are 'controls' or standards used to check the quality and traceability of products
Cerussite	Lead carbonate or white lead ore) is a mineral consisting of lead carbonate (PbCO $_3$)
Clearance standards	Standards used to determine whether it is safe for residents to return to a house after lead-removal activities have been completed. This is a US EPA standard and is used internationally in the absence of local equivalent standards.
Cuprite	A copper oxide mineral, Cu ₂ O
Diagenesis	The reconstructive process by which changes occur in sedimentary rocks during or immediately after their deposition while it is still at low temperature and pressure. It is caused by such forces as the weight of overlying strata or hot waters.
Dust	Fine powdery material such as dry earth or pollen that can be blown about in the air
enHealth	The Environmental Health Committee. It is a subcommittee of the Australian Health Protective Committee, which is responsible to the Australian Commonwealth Government's Department of Health and Ageing.
Environmental values	Particular values or uses of the environment that are important for a healthy ecosystem or for public benefit, welfare, safety or health and that require protection from the effects of contaminants, waste discharges and deposits.
Exposure	Contact of a chemical, physical, or biological agent with the outer boundary of an organism (inhalation, ingestion or dermal contact)
Exposure assessment	Exposure Assessment is the process of estimating or measuring the magnitude, frequency and duration of exposure to an agent, along with the number and characteristics of the population exposed. Ideally, it describes the sources, pathways, routes, and the uncertainties in the assessment.
Fallout	Solid particulates in the atmosphere onto the earth

Footpaths	The nature strips between houses and streets in Mount Isa are referred to in this study as footpaths. There might or might not be a paved footpath crossing these nature strips.
Galena	The natural mineral form of lead (II) sulfide. It is the most important lead ore mineral
Gavage	Introducing material into the stomach by means of a stomach tube
Geogenic	Of geological origin, including rocks and soil
Geometric mean	The geometric mean, in contrast to the arithmetic mean, is calculated by multiplying the values of a group of numbers together and then taking the n th root of the result (where n = the number of values in the group). For example, the geometric mean of 1, 2, 3 and 4 is calculated as follows: $\sqrt[4]{(1 \times 2 \times 3 \times 4)} = \sqrt[4]{24} = 2.213$.
	The geometric mean is more appropriate than the arithmetic mean (2.5 in the example shown) for describing increasing or decreasing trends. The result is normally lower than the arithmetic mean. Blood lead data are often reported as geometric means.
Ghost wipe	Are used to ease sample preparation and analysis of surface lead or surface dust. Ghost Wipes meet all ASTM E1792 specifications for sampling materials for lead in surface dust.

Guideline values Air particulates

The National Environment Protection (Ambient Air Quality) Measure ('Air NEPM') standards for ambient air quality provide guidelines relevant to airborne particles as particulate matter 10 μ m (PM₁₀) for a 1-day averaging period (50 μ g/m³ max) and lead for a 1-year averaging period (0.5 μ g/m³ max). Advisory reporting standards apply for 2.5 μ m (PM_{2.5}) fine particles (1 day 25 μ g/m³ max); 1 year 8 μ g/m³ max).

Queensland Environmental Protection Agency's Environmental Protection Policy (EPP) — Air includes lead for a 1-year averaging period (0.5 μ g/m³ max) and other metals (arsenic, cadmium, manganese, nickel and vanadium) and total suspended particles (TSP) for a 1-year averaging period (90 μ g/m³ max). The air-PM₁₀ is a subset of the TSP level.

Fall-out dust

There is no health risk guideline for fall-out.

House clearance standards The United States' Environmental Protection Agency ('US EPA') has developed 'lead clearance standards' for house floors, window sills and window troughs, but not carpet dust. The US clearance lead standards for houses are: 430 μ g/m² for dust on the floor; 2691 μ g/m² for dust on interior window sills; 4306 μ g/m² for dust in window troughs.

Soil

Soil and dust concentrations are compared against the NEPM 1999 criteria: HIL Level A Standard residential with garden/accessible soil (300 mg/kg for lead); and HIL Level E Parks, recreation, open space and playing fields including secondary schools (600 mg/kg for lead).

Blood lead

The National Health and Medical Research Council advises that all Australians should have a blood lead level below 10 μ g/dL.

- Hand to mouth Human behaviour, particularly for kids, who may ingest fine particles via this action
- Hazard assessment Is comprised of 'Hazard Identification' and 'Dose– Response Assessment'
- Humic substances Heterogeneous yellow-black organic materials that include most of the naturally dissolved organic matter in water. They are classified as humin (not soluble at any pH), humic acid (not soluble at pH < 2) and folic acid (soluble at all pH values)

Health Risk Assessment	The process of estimating the potential impact of a chemical, biological, physical or social agent on a specific human population system under a specific set of conditions and timeframe
Indicator	Measurement parameter or combination of parameters that can be used to assess the quality of water
<i>In vitro</i> test	Tube test
<i>In vivo</i> test	Whole organism (animal) test
Issue identification	Identifies issues for which risk assessment is useful and establishes a context for the risk assessment by a process of identifying the concerns that the risk assessment needs to address
Lanarkite	A form of lead mineral with formula Pb ₂ (SO ₄)O
Leadhillite	A form of lead mineral with formula Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂
Lead-goethite	Lead adsorption onto goethite
Lead oxide sulfate	A form of lead mineral with formula Pb ₂ O(SO ₄)
Litharge	PbO (red)
Magnetoplumbite	A magnetic oxide of iron, manganese and lead, with some titanium, with the chemical formula (Pb,Mn)(Fe,Mn,Ti) ₆ O ₁₀
Massicot	PbO (yellow)
Matrix	The material in which the arsenic and heavy metals in samples were found, e.g. soil or carpet dust
Median	The median is the numerical value separating the higher half of data in a sample from the lower half when the sample is arranged from highest to lowest value. For example, the median value of the set of numbers 3, 5, 5, 6, 8, 8, 9 is 6, as half the numbers in the series fall either side of it.
Mega-annum	Millions of years before the present date.
Mendipite	Pb ₃ O ₂ Cl ₂
Milli-Q [®]	A trademark of the Millipore Corporation for its ultra-pure water filtration system
Morphology	The structural features of particles (e.g. are they smooth or rugged, long or short, flat or rugged)
Molybdophyllite	A mineral Pb ₂ Mg ₂ Si ₂ O ₇ (OH) _{2.} 2H ₂ O consisting of a hydrous lead magnesium silicate

Mount Isa Inlier	The main geological province consisting of early and middle Proterozoic sediments (545 million years ago) and igneous rocks, which are intensely folded and covering 50 000 km ² in northern Queensland. The area is semi-arid and has a tropical monsoonal climate with a hot wet season from October to March. The main population centres are Mount Isa city and Cloncurry.
Natural mineralisation	Naturally occurring minerals in a geological setting
Necropsy	Post-mortem examination immediately after the animal was euthanased
NEPM Level A	Standard residential with garden soil/accessible soil
NEPM Level D	Residential with minimal soil access
NEPM Level E	Parks, recreational open space and playing fields including secondary schools
NEPM Level F	Commercial/Industrial
Osarizawaite	A form of lead mineral with formula $PbCuAl_2(SO_4)_2(OH)_6$
Parameter	A measurable or quantifiable characteristic or feature
Percentile	Interval in a graphical distribution that represents a given percentage of the data points
Pica	Behaviour of young children deliberately eating non-food substances, such as soil.
Plumbogummite	A secondary lead phosphate mineral, with the formula $PbAl_3(PO_4)_2(OH)_5.H_2O$
Plumbojarosite	A mineral composed of basic lead iron sulfate; it is isostructural with jarosite, $PbFe_6(SO_4)_4(OH)_{12}$
Pyromorphite	A form of lead mineral with formula Pb ₅ (PO ₄) ₃ Cl
Respirable	Suitable or fit for breathing
Quality assurance (QA)	The implementation of checks on the success of quality control (e.g. replicate samples, analysis of samples of known concentration
Quality control (QC)	The implementation of procedures to maximise the integrity of monitoring data (e.g. cleaning procedures, contamination avoidance, sample preservation methods).
Relative bioavailability	The comparative bioavailability of different forms of a chemical or for different exposure media containing the chemical and is expressed as a fractional relative absorption factor

Risk	A statistical concept defined as the expected frequency or probability of undesirable effects resulting from a specified exposure to known or potential environmental concentrations of a material, organism or condition. A material is considered safe if the risks associated with its exposure are judged to be acceptable. Estimates of risk may be expressed in absolute or relative terms. Absolute risk is the excess risk due to exposure. Relative risk is the ratio of the risk in the exposed population to the risk in the unexposed population
Risk assessment	A step in a risk management procedure. It is the determination of quantitative or qualitative value of risk related to a concrete situation and a recognised threat (also called hazard).
Risk characterisation	A step in a risk management procedure. It provides a qualitative and/or quantitative estimate, including attendant uncertainties, of the nature, severity and potential incidence of effects in a given population based on the hazard identification, dose–response and exposure assessments.
Sediment	The clay, silt or gravel carried by a flowing river or stream and deposited where the flow slows and results in alluvial deposition below the low water mark or up to the high water mark. Sediment comprises bed load material (> 63 μ m) that moves just above the bed and suspended material (< 63 μ m) that moves in suspension under the influence of turbulence. The fine sediment (< 63 μ m) is most representative for sampling purposes
Smithsonite	A zinc carbonate mineral, ZnCO ₃
Soil	The part of the earth's surface consisting of humus and disintegrated rock that is located above the high water mark of an adjacent river or stream
Solution concentration	Concentration of contaminants in the liquid phase
Speciation	Measurement of different chemical forms or species of an element in a solution or solid
Species	Chemical species are differing compounds of an element
Standard	An objective that is recognised in environmental control laws enforceable by a level of government
Supernatant	A substance floating on top
Systemic circulation	The body's blood circulatory system

Thimble sample	Extraction filters used for collecting particulates from moving streams in the smelter off-gas systems, similar in shape to a sewing thimble but larger, made from filter paper material
Thoracic	Of or pertaining to the thorax
Toxicity	The inherent potential or capacity of a material to cause adverse effects in a living organism
Type I error	In statistics, a Type I error occurs when a statistical test indicates that there is no relationship between the variables being tested when in fact one exists
Type II error	In statistics, a Type II error occurs when a statistical test indicates that there is a relationship between the variables being tested when in fact none exists
Uptake	A process by which materials are absorbed and incorporated into a living organism

LIST OF ACRONYMS, SYMBOLS AND UNITS

Acronym	Definition
>	Greater than
≥	Greater than or equal to
<	Less than
≤	Less than or equal to
°C	Degrees Celsius
σ	Two times standard deviation for lead isotope measurement
μg	Microgram (10 ⁻⁶ grams)
μg/dL	Micrograms per decilitre (a measure of blood lead concentration)
μL	Microlitres (10 ⁻⁶ litres)
μm	Micrometre (10 ⁻⁶ metres)
Å	Ångstrom, a unit of length (10 ⁻¹⁰ metres)
ABA	Absolute bioavailability
ADWG	Australian Drinking Water Guidelines
AQC	Air quality control
AH	Air PM ₁₀ samples from sites within the City of Mount Isa
AI	Chemical symbol for aluminium
ALF	Artificial lysosomal fluid, for mimicking the fluid found in lungs that comes into contact with the macrophages (cells that eliminate foreign materials) within the lung
ANBF	Australian National Beamline Facility
ANOVA	Analysis of variance, a statistical test
ANZECC/ARMCANZ	Australian and New Zealand Environment and conservation Council and Agriculture and Resource Management Council of Australia and New Zealand
ANZFSC	Australian New Zealand Food Standards Code maximum levels of metals and metalloid contaminants in aquatic foods
As	Arsenic

ATSDR	Agency for Toxic Substances and Disease Registry
ASTM	American Society for Testing Materials
ATC	Thimble samples collected in the copper smelter area
ATP	Thimble samples collected in the lead smelter area
AUC	Area under the curve
BA	Bioavailability
BAc	Bioaccessibility
BGR	Background rocks
BOM	Bureau of Meteorology
BSD	Base supply deport
BSE	Backscattered electrons
bw	Bodyweight
CAS	Chemical abstracts service
CCD	Charge-couple device, a means of taking high- quality digital images
CD	Carpet dust
CDC	The United States' Centers for Disease Control and Prevention
Cd	Cadmium
СММ	Centre for Microscopy and Microanalysis, part of the University of Queensland
CMLR	Centre for Mined Land Rehabilitation, part of the University of Queensland
Со	Cobalt
Cr	Chromium
CRM	Certified reference material
CS	Community soil; composite sample of soil
Cu	Copper
DF	Dilution factor
DIN	Deutsches Institut für Normung, the German standards institute
dL	Decilitre (100 millilitres)
EDS	Energy dispersive spectrometry

EDTA	Ethylenediaminetetraacetic acid, an organic acid that is often used to sequester metal ions
EXAFSPAK	An independent computer program for analysis of X-ray absorption spectroscopic data.
eV	Electron volt
FAO	Food and Agricultural Organisation of the United Nations
Fe	Iron
FMM	Mine site fallout dust samples
FSANZ	Food Standards Code Australia New Zealand
g	Gram
GI	Gastrointestinal
GM	Geometric mean
GSD	Geometric standard deviation
HBr	Hydrobromic acid
HCI	Hydrochloric Acid
HF	Hydrofluoric acid
HIL	Health Investigation Level
HNO ₃	Nitric acid
HR	Haul road
HVA	High volume air
IC50	Median inhibitory concentration; the concentration of a specified chemical in an exposure water that causes 50% inhibition (i.e., decrease) of an attribute, where the attribute could be growth, reproduction, etc.
ICMM	International Council on Mining and Metals
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IEUBK	Integrated Exposure Uptake Biokinetic Model
IPCS	International Programme on Chemical Safety of the World Health Organisation ('WHO')
JECFA	Joint Food and Agricultural Organization of the United Nations — World Health Organisation Expert Committee on Food Additives
keV	Kilo electron volt

kg	Kilogram
КО	Kruttschnitt Oval
L	Litre
LCF	Least-squares linear combination fitting
LOD	Limit of detection, defined as three times the standard deviation at or near the blank level
LP	Lead pathway
LPS	Lead pathway study
М	Molar; moles
mA	Milliamps, a unit of electrical current
Ма	Mega annum, a unit of geologic time equal to one million (10 ⁶) years
MC-ICP-MS	Multi-collector–Inductively-coupled Plasma–Mass Spectrometry
MDL	Method detection limit
mg	Milligram (10 ⁻³ grams)
ML	Mining lease
mM	Millimolar (1 millimole per litre)
MIM	Mount Isa Mines Limited
MIWB	Mount Isa Water Board
mL	Millilitre
mm	Millimetre
Mn	Manganese
n	The number of samples considered in a statistical test
NATA	Australian National Association of Testing Authorities
NEPC	National Environmental Protection Council
NEPM	National Environmental Protection Measure
NEPM (Air)	NEPM for ambient air quality
NHANES	National Health and Nutrition Examination Survey
NHMRC	National Health and Medical Research Council
ng	Nanogram (10 ⁻⁹ grams)
NIST	United States' National Institute of Standards and Testing

NMU	Natural mineralisation unit
NPI	National Pollutant Inventory
Pb	Lead
PBET	Physiologically Based Extraction Test
PCA	Principal component analysis
pg	Picogram (10 ⁻¹² grams)
PM	Particulate matter
PM ₁₀	Particulate Matter 10 micrometres size or less
PM _{2.5}	Particulate Matter 2.5 micrometres size or less
PM ₂₅₀	Particulate Matter 250 micrometres size or less
ppb	Parts per billion
PPE	Personal protective equipment
ppm	Parts per million
PS	Particle size
PTWI	Provisional tolerable weekly intake
Q-Q plot	Quantile-Quantile plot
QA	Quality Assurance
QC	Quality Control
QWQG	Queensland Water Quality Guidelines
RBA	Relative bioavailability
RC	Racecourse
RIF	The Radiogenic Isotope Facility at the University of Queensland
RG	Roof gutter dust
RIVM	Rijksinstituut voor Volkgezondheid en Milieu, the Dutch institute for population health and environment
RSD	Relative standard deviation
RSL	The Returned and Services League of Australia
S	Sulfur
SBET	Simplified bioextraction test, a type of bioaccessibility test
SD	Standard deviation; smelter dust; Sprague Dawley [®] (the name of a strain of rats bred for medical research purposes)
SE	Standard error
SEM	Scanning electron microscope
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SEM-EDS	Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy
SHIME	Simulator of human intestinal microbial ecosystem of infants, a bioaccessibility test
SRM	Standard Reference Material [®] , produced by the United States National Institute of Standards and Testing
SS	Source sample
TD	Tailings dust
TIMS	Thermal ionisation mass spectrometry
ті	Thallium
TSP	Total suspended particles, typically less than 50 μm diameter
US EPA	United States' Environmental Protection Agency
USGS	United States' Geological Survey
USP	United States' Pharmacopeia and The National Formulary, a book of public pharmacopeial standards published by the United States' Pharmacopeial Convention
VD	Vacuum dust same as carpet dust (CD)
WHO	World Health Organisation
XANES	X-ray Absorption Near Edge Spectroscopy
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction
Zn	Zinc

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1 INTRODUCTION

1.1 Purpose

Lead, which is widely present in mineralised areas and associated sites, is identified as a potential contaminant of the environment (IPCS, 1995). Lead mining, processing, smelting and concentrate handling facilities are identified as the largest sources of lead pollution in Australia (DEWHA, 2006). Apart from a minor contribution from metal ore mining and electricity generation (1 per cent), the total lead emissions to air, land and water from basic non-ferrous metal manufacturing during 2009–2010 was 160,000 kg at Mount Isa (NPI, 2012). Lead and other heavy metal emissions from various sources are potential hazards to the health of the Mount Isa community. The collective sources of lead in Mount Isa City may contribute to some, or all, of the levels of lead in the blood of people who live near, or work at, the lead facilities in Mount Isa City.

Lead is present in air, water and food in Mount Isa City. However, the contributions of various sources of lead to human health are not well understood because the exact molecular forms of the lead being absorbed are not always known. Lead compounds can cause a range of impacts from low impacts such as absorption by the receptor (e.g. lead sulfide) to high impacts (e.g. lead acetate), depending on their solubility (IPCS, 1995). Therefore, it is important to identify the various forms of lead from different sources and to assess the quantities being ingested from the various sources.

The aims of this *Lead Pathways Study* — *Air* are to:

- i. investigate the potential air–dust pathways of lead and other heavy metals and metalloids in the Mount Isa air shed
- ii. estimate the potential risks to human health of air-dust pathways on the Mount Isa residential area.

The specific purpose of this report¹⁰ is to provide findings of investigations designed to:

i. determine the contributions of lead-containing particles and fumes from sources in the Mount Isa mining and mineral processing operations to blood lead levels in the community, particularly of children less than five years old, via the air–particulate¹¹ pathway

¹⁰ The Lead Pathways Air Report dates from December 2012 and refers to guidelines that may have changed. These are identified where appropriate.

¹¹ Although air–dust is referred to in the EPP Air (2008) act, air–particulate is used throughout the report to describe airborne dispersion of particles

- ii. to estimate the risk of air particulates as a potentially significant lead exposure source for inhalation and ingestion by members of the community and, particularly, children.
- iii. to determine appropriate actions and follow up works to manage the risks.

In the first instance, data were compared with existing guidelines. The data were also used in dose–response assessments for risk assessment.

The study assessed heavy metals and metalloids concentrations in source materials, air particulates, garden soil and dust accumulation around Mount Isa City, and in the mine leases and background sites with minimal lead mineralisation. All potential sources of heavy metal and metalloid contaminants that may be linked to dispersion and exposure pathways of heavy metals and metalloids to the Mount Isa City were also estimated. The study also assessed if the effects of current levels of dispersed materials, historical mining sediments, urban activities and natural mineralisation were of significance to the air-dust pathway in Mount Isa.

The Ambient Air Quality National Environmental Protection Measure (NEPM) (National Environmental Protection Council (NEPC, 2002) sets uniform standards for ambient air quality. The Queensland Environmental Protection (Air) Policy (EPP, 2008) identifies primary management aims for the protection of air by:

- a. identifying environmental values to be enhanced or protected
- b. outlining indicators and air quality objectives for enhancing or protecting the environmental values
- c. providing a framework for making consistent, equitable and informed decisions about the air environment.

The project's purpose was achieved by using the following site assessment processes (enHealth, 2012, NEPC, 1999a):

- identifying environmental values to be protected
- selecting sampling sites, pathways and a sampling timeline
- conducting the sampling and analysis to understand the distribution and exposure pathways of heavy metal and metalloid contamination within the study areas
- measuring concentrations of heavy metals and metalloids
- measuring supporting information on morphology and speciation of particles
- determining the predicted bioavailability factor of total concentrations in sources and environmental receptors using bioaccessibility-adjusted concentrations for human health risk
- conducting human health risk assessments using bioaccessibility as an indicator of bioavailability to understand the site-specific potential toxicity of lead and other metals and metalloids to human health.

1.2 Components of the Study and Specific Objectives

Sustainable development of lead mining requires an understanding of the potential environmental and health risks so that production is undertaken and maintained safely (ICMM, 2003). Risk assessment helps to control adverse effects of environmental health hazards (Ricci, 2006, enHealth, 2012). The ultimate aim of an environmental risk assessment process is to: 'provide the best possible scientific, social and practical information about the risks, so that these can be discussed more broadly and the best decisions made as to what to do about them' (enHealth, 2012). Risk assessment considers relevant factors such as current or proposed human activities, physico-chemical and bioavailability characteristics of chemical hazards, and the potential for exposure to chemical or biological hazards (enHealth, 2012).

The accepted Australian framework for human health risk assessment is described in enHealth (enHealth, 2012) as shown in Figure 1. Issue identification determines the potential environmental hazards. In this case, the issue is that lead and other heavy metals and metalloids may have health impacts on people living and working in the study area. The potential sources of the lead, other heavy metals and metalloids are natural mineralisation, mining and mineral processing activities (concentrator, sinter, stockpiles, and tailings dam), and the local environment.



Source: modified from enHealth, 2012



Hazard assessment identifies the cause of the problem (enHealth, 2012). It is a qualitative description based on the type and quality of the data, complementary information and the weight of evidence from data describing various sources. A key step in hazard assessment for this project is to recognise the significant sources of hazards to human health, particularly for young children. Hazard assessment requires sound data on sources and environmental samples. Hazard assessment is optimised by using various sampling techniques for collecting

environmental samples that can be analysed to give molecular-scale information by using X-ray absorbance spectroscopy ('XAS') and by characterising the morphology of particles. Heavy metals and metalloid-containing particulates with different chemical compounds have various levels of bioavailability, which may induce varying levels of health risks. Potential health risks associated with exposure to various heavy metals and metalloids compounds need to be evaluated by measuring the bioavailability of samples. This study used both *in vivo* and *in vitro* experiments to estimate the potential exposure in the hazard assessment (enHealth, 2012).

Exposure assessment determines the frequency, magnitude, extent, duration and character of exposures to a hazard (enHealth, 2012). Exposure assessment assesses the extent human health risk given residents' exposure to hazard-containing particulates. This part of assessment was conducted by Queensland Health¹² and the data were used for this study (Queensland Health, 2008, Queensland Health, 2011).

Based on the outcomes of the issue identification, hazard assessment and exposure assessment steps, risk characterisation was undertaken as the final step of the risk assessment process. Risk characterisation 'integrates the information from hazard assessment and exposure assessment; provides an evaluation of the overall quality of the assessment and the degree of confidence the risk assessors have in the estimates of risk and conclusions drawn; describes the risks to individuals and populations in terms of nature, extent and severity of potential adverse health effects; communicates results of the risk assessment to the risk manager; and provides key information for risk communication' (enHealth, 2012). The characterisation of the risk from lead and associated heavy metals and metalloids to the population of Mount Isa City was described to further enable risk management to minimise future exposure pathways of potential hazardous materials.

Despite extensive investigations undertaken as part of the risk assessment, questions remained about the ongoing risks posed by potentially hazardous metals and metalloids in the air, soil, and dust of Mount Isa. Therefore, an air–dust quality study was undertaken with the objectives to:

- (1) investigate the potential pathways of lead and other heavy metals and metalloids by characterising physical and chemical properties of particles from mining, mineral processing activities, natural mineralisation, and community samples
- (2) identify the potential lead dispersion from mining and mineral processing activities to the community via air–dust exposure pathways

¹² The Queensland Health blood lead surveys at Mount Isa surveyed children 1-4 years of age.

- (3) determine the contribution of lead and other heavy metals and metalloids to major air–dust exposure pathways
- (4) evaluate the impacts of the local environmental controls on improving the health condition of residents
- (5) estimate the bioavailability and bioaccessibility of materials containing lead and other heavy metals and metalloids
- (6) use the enHealth risk assessment framework to assess potential risks of lead-containing particles in Mount Isa for their impact on human health.

1.3 Background to the Study Location

1.3.1 Mount Isa City

Mount Isa City is located in north-west Queensland, Australia (Figure 2). It covers an area of over 43,310 km² (MICC, 2008). The Mount Isa area has been explored as an important site with copper, lead, silver and zinc mineralisation since the early 20th century and the city was established because of the vast mineral deposits found on what became the Mount Isa Mines mining lease (ML 8058). Mount Isa City, as the administrative, commercial and industrial centre for Queensland's vast north-western region, had a population of about 22,000 as at June 2010 (ABS, 2010).

Most of the Mount Isa City lies on the eastern side of the Leichhardt River, but substantial portions of it are on the western side, including the suburbs of Soldiers' Hill, Parkside, Happy Valley and Miles End. Some of these suburbs are located on the Mount Isa Mines mining lease. The railway line to Townsville separates the community from the major copper–lead–zinc mining and mineral processing facilities, which lie on the western side of the river (MICC, 2008). The artificial Lake Moondarra and the Clear Water Lagoon barrier system, which is the primary water supply for the town and local industry after potable water treatment, is located about 20 kilometres downstream of the city, on the Leichhardt River (MICC, 2008).

1.3.2 Climate and meteorology

Mount Isa City is a semi-arid area, with a mean annual rainfall of 430 mm and average daily evaporation of 8.4 mm (BOM, 2012). It lies within the northern Australian tropical climatic zone. The differences between dry and wet seasons are clearly evident from the rainfall, temperature, evaporation and relative humidity data recorded in Mount Isa City (Figure 3 and Figure 4). There is a significant dry season from April to November, followed by the wet season from December through to March. Most rain falls within short period of the year, normally January and February. The annual mean temperature at 3 pm is 30.7 °C (Figure 3) and relative humidity is 27 per cent (Figure 4). During the dry season, Mount Isa City experiences prevailing winds from easterly, south-easterly and southerly directions for the recorded data to 2012 (Figure 5).

1.3.3 Geology

Regionally the Mount Isa Inlier is enriched with a variety of ore deposits, including the Mount Isa Mine lead–silver–zinc and copper deposits, Century Mine lead–silver–zinc deposit, Cannington Mine lead–silver–zinc deposit, and the Osborne and Ernest Henry Mines iron oxide–copper–gold deposits (Betts et al., 2006, Spikings et al., 2001, Oliver, 1995). The Mount Isa Mines Group includes Magazine Shale, Kennedy Siltstone, Spear Siltstone, Urquhart Shale, Native Bee Siltstone, Breakaway Shale, Moondarra Siltstone (Geoscience Australia, 2012), as shown in Figure 6. Within the Mount Isa Mines Group, all economic lead–silver–zinc mineralisation in the Mount Isa deposits is stratiform, confined to the upper 650 m of the Lower Proterozoic Urquhart Shale, in a zone measuring 1.6 km along the strike and 1.2 km down dip (Blake et al., 1990). Urquhart Shale is a unit of dolomitic and variably carbonaceous siltstone and rich in fine-grained pyrite (Painter et al., 1999).

Preserved in the Mount Isa Inlier is evidence from at least four episodes of extensive hydrothermal alteration over a protracted period from approximately 1740–1350 mega-annum (Ma¹³) (Betts et al., 2006). The intervals were 1750–1730 Ma, 1670–1610 Ma, 1600–1490 Ma and post-1490 Ma. During the second and third hydrothermal events, i.e. between approximately 1670–1490 Ma, economically significant base metal and precious metal mineralisation was produced. Lead–silver–zinc mineralisation formed within the Mount Isa Inlier was primarily associated with sedimentation and basin extension (approximately 1670–1610 Ma) (Chapman, 2004, Betts et al., 2006). During the deposition and subsequent diagenesis of successions of the Isa Super Basins, aged between 1670–1610 Ma, alteration products formed, characterised by low to moderate temperature (< 300 °C) fluid flow and metasomatism with circulation of basinal and surface-derived brines along large growth faults (Betts et al., 2006, Chapman, 2004, Betts et al., 2003, Cooke et al., 2000). A number of genetic models proposed in previous studies show the dominant characteristics as:

- participation of a metal-bearing hydrothermal fluid
- a network of intersecting faults and permeable strata to act as aquifers during basinal fluid flow and during precipitation of metal and sulfides the involvement of anoxic sediments as a chemical control on ore deposition (Betts and Lister, 2002, Cooke et al., 2000, Perkins and Bell, 1998, Large et al., 2005).

¹³ Ma is million years ago.





Source: Mount Isa Mines, 2008

Figure 2 Mount Isa City location (a), city geographical distribution (b), showing mine lease boundary (ML 8058)



Source: BOM, 2012





Figure 4 Mount Isa City mean daily evaporation (mm) and relative humidity (%) record



Figure 5 Rose of wind direction versus wind speed in km/h for data recorded to 2012



Source: Geosciences Australia 2012

Figure 6 Mount Isa Mines geology and city

1.3.4 Mining history

Mining activities in Mount Isa City started when the mineral deposits in the area were discovered. Prospector John Campbell Miles discovered silver–lead–silver ore in Mount Isa in 1923 (MICC, 2008). In January 1924, Mount Isa Mines Ltd was formed. In May 1931, milling and smelter operations started in Mount Isa and

the company made its first operating profit in 1937. Mount Isa Mines focused on lead–silver–zinc production, with a brief period of copper production during World War II to meet government needs. Copper production restarted in 1953, with the commissioning of a copper milling and flotation circuit in the Number 1 concentrator and of the copper smelter (Blainey, 1960). By the 1960s, Mount Isa was the hub of a lead–zinc–silver–copper supply network that included smelting, refining and recycling facilities. The Swiss-based company Xstrata purchased Mount Isa Mines in mid-2003. Xstrata merged with Glencore in mid-2013.

Currently, there are two major separate mining and processing streams in Mount Isa: copper (part of the Glencore Copper division) and lead–silver–zinc (part of the Glencore Zinc division). To process the George Fisher ores, Mount Isa Mines increased the plant's capacity in mid-2000, adding six additional IsaMills[™] for ultra-fine regrinding in the zinc circuit, and improving the cleaner flotation and thickener operations to increase the recoveries, concentrate grades and throughput. Xstrata Zinc's operations on the Mount Isa Mines lease include the Black Star and Handle Bar Hill open pit lead–zinc mines and the George Fisher underground lead mine (MIM, 2012b). A blast furnace treats sintered lead–silver concentrate to produce crude lead–silver bullion. Some drossing operations are undertaken to remove copper and arsenic from the bullion, which is then shipped to England to be further refined at the Britannia Refined Metals Northfleet Refinery (MIM, 2012b). Around 90 per cent of zinc concentrates from Mount Isa are exported to Asian and European smelters, with the balance being sold domestically (MIM, 2013).

1.4 Lead in the Environment

Lead is the 36th most abundant element in the earth's crust (mean concentration of 13 mg/kg) (Greenwood and Earnshaw, 1997). Lead is generally present as the 2^+ oxidation state in inorganic compounds and only rarely occurs as elemental lead in nature (Greenwood and Earnshaw, 1997). Lead is not sensitive to oxidation or reduction over the normal range of physico-chemical condition near the earth's surface (Greenwood and Earnshaw, 1997).

Lead mining and mineral processing activities create conditions for simultaneous release of arsenic, cadmium, copper, silver and zinc, and a large number of minor elements into the environment, particularly when polymetallic ores are being processed. The emissions from these elements have the potential to expose both the mining workforce and the wider population. The interaction of heavy metals and metalloids may also promote mixed-toxic action of the chemicals in samples (ATSDR, 2004), which would require a detailed assessment of their contributions to observed environmental loading.

Lead occurs as a major element in a wide variety of minerals (e.g. anglesite $[PbSO_4]$, cerussite $[PbCO_3]$, galena [PbS], pyromorphite $[Pb_5(PO_4)_3(CI,OH,F)]$), and as a trace element, by substitution for Ca²⁺ and K⁺ (e.g. lead-bearing apatites and jarosites) (Brown et al., 1999). Some parent minerals, such as bulk galena (PbS) and other metal sulfides, have limited bioavailability (Chaney et al., 2008, Dieter et al., 1993, Steele et al., 1990). Exposure to oxygen and moisture

promotes oxidation of sulfide minerals and leads to mineral dissolution, metal mobilisation, and precipitation of secondary minerals (Parker and Robertson, 1999). A portion of solubilised metals can migrate offsite in runoff from the source, while the remaining mobilised metals can reprecipitate as secondary minerals such as anglesite (PbSO₄), cerrusite (PbCO₃), and plumbojarosite (PbFe₆(SO₄)₄(OH)₁₂), forming layers on particle surfaces, or absorbing to the surfaces of iron or manganese–hydroxides and resulting in higher bioavailability (Stanton, 2000, U.S. EPA, 2007b). Over time, these primary minerals in mine wastes undergo geochemical transformations that convert lead from relatively refractory phases into phases with greater mobility and bioavailability (Schaider et al., 2007).

Selected samples from Mount Isa open pits and sinter plants were analysed by X-ray diffraction ('XRD') (Table 1) (McKnight, 2003b, McKnight, 2003a, McKnight, 2004, McKnight, 2006a, McKnight, 2006b), to enable identification of primary and secondary lead minerals in mineralisation and mineral processing.

Common forms of lead in the natural environment also include lead absorbed into goethite or to humic substances in soil (Ostergren et al., 1999). Plumbogummite, plumbojarosite, goethite-absorbed lead (lead–goethite), and humic acid that have absorbed lead are common in environmental samples (Morin et al., 2001, Ostergren et al., 1999, Pingitore et al., 2009).

Description	Source
Galena, PbS	Mining
Cerussite, PbCO ₃	Mining
Anglesite, PbSO₄	Mining and processing
Leadhillite Pb4(SO ₄)(CO ₃) ₂ (OH) ₂)	Mining
Plumbojarosite PbFe ₆ (SO ₄) ₄ (OH) ₁₂	Mining
Lead Oxide Sulfate (Pb ₂ O(SO ₄))	Mining and processing
Pyromorphite Pb ₅ (PO ₄) ₃ Cl	Mining
Plumbogummite PbAl ₃ (PO4) ₂ (OH) ₅ .H ₂ O	Mining
Osarizawaite	Mining
Massicot, PbO (yellow)	Processing
Litharge, PbO (red)	Processing
Plumboferrite, PbFe ₄ O ₇	Processing
Ca-Pb silicate, Ca ₂ Pb ₃ Si ₃ O ₁₁	Processing
Pb-Fe silicate, Pb ₂ Fe ₂ Si ₂ O ₁₉	Processing
Glass, Ca-Pb-Fe silicate	Processing
Lanarkite, Pb ₂ OSO ₄	Processing

Table 1 Lead minerals from Mount Isa mining and processing identified by XRD

1.5 Significance of Lead to Human Health

Globally, lead is arguably one of the most widespread heavy metal contaminants and has had a significant effect on human health (Nriagu, 1978, Nriagu, 1998). Diverse physiological and biochemical effects in animals and humans have been induced by lead (Markowitz, 2000, Maynard et al., 2005, ATSDR, 2004, IPCS, 1995, Lanphear et al., 2005).

Accurate and extensive chemical and physical characterisations of natural mineralisation, mining sources, mineral processing sources, and community environmental samples are critical for predicting environmental transport and the fate of heavy metals and metalloids in Mount Isa City. These characterisations are key components of the *Lead Pathways Study* for understanding and minimising important human and ecological exposure pathways (Figure 7).



Figure 7 Hypothetical pathways for lead transfer from mining and processing to the community

The body absorbs lead through ingestion and inhalation (Figure 8). Absorption through the skin is considered to be insignificant (IPCS, 1995). Lead circulates through a number of biological systems in the body after it is absorbed (IPCS, 1995). The adverse health effects caused by lead include toxicity of nervous, hematopoietic, renal, endocrine, and skeletal systems, with the central nervous system as the major target organ (IPCS, 1995). Lead does not have any role in bodily functions and, in excessive levels, can result in adverse effects such as mitochondrial dysfunction, deregulation of protein turnover. abnormal neurotrophic factor expression, mental retardation, learning disorders, and attention-deficit and hyperactivity disorder (Nigg et al., 2008, Bellinger, 2008). Lead displaces calcium by cation exchange processes and becomes the key mineral component of bone formation due to similarity of its atomic properties in charges and ionic radii (Pounds et al., 1991). The bone becomes a long-term source of lead deposition and, therefore, likely to be a continuous internal source of lead to human blood stream (IPCS, 1995). Lead is poorly excreted from the body (Manton et al., 2000). A lead uptake study indicated that 20 per cent of dosed lead was bound to the skeleton after three weeks (Heard and Chamberlain, 1984). The half-life of lead in human body is approximately 30 days in blood stream and 10–30 years in bone (JECFA, 2011). Two important routes of lead excretion from the body are urine and faeces (IPCS, 1995). The greatest concern of lead toxic response for infants and young children is impairment of cognitive and behavioural development, because children have high ingestion efficiency and rapid neural development during their brain and nervous system growth (Peraza et al., 1998, IPCS, 1995, Lanphear et al., 2005).



Source: U.S. EPA (U.S. EPA, 1994a)

Figure 8 Lead pathway via environmental exposure sources, absorption compartments, critical body tissue compartments, and elimination

Heavy metals can negatively affect people's health if they exceed toxic threshold concentrations. Most of time they have no beneficial function to the human body. Some of these elements are also micro-nutrients required for human health and development (e.g. cobalt, zinc, copper, chromium and nickel), whilst others are carcinogenic or toxic, affecting, among others, the central nervous system (arsenic, lead and mercury), the kidneys or liver (cadmium, copper, lead and
mercury) skin, bones or teeth (cadmium, copper, chromium and nickel) (JECFA, 2011).

The blood lead level recommended by Australian National Health and Medical Research Council ('NHMRC') is for all Australians to be below 10 µg/dL¹⁴ ('< 10 µg/dL') (NHMRC, 2009). The last Australian survey of blood lead levels for children aged 1–4 years children was conducted in 1995 by the Australian Institute of Health and Welfare ('AIHW') (Donovan, 1996). Results for 1575 children sampled across Australia indicated that of those children living close of mine sites and lead processing facilities, 92.7 per cent had blood lead levels < 10 µg/dL. Close to mine sites and lead processing facilities 7.3 per cent had blood lead levels \geq 10 µg/dL, and 0.25 per cent had blood lead levels \geq 25 µg/dL, with the maximum blood lead level 32.7 µg/dL. The arithmetic and geometric mean blood lead levels were 5.72 µg/dL and 5.05 µg/dL, respectively. Of 270 children sampled in Queensland, 95.2 per cent of the samples had blood lead levels < 10 µg/dL with an arithmetic mean of 5.59 µg/dL (Donovan, 1996). None of the children surveyed were from Mount Isa and would still have included exposure from lead in petrol.

1.5.1 Ingestion pathway

Human health risk assessments have found that ingesting soil and dust can be a major route of exposure to immobile soil contaminants (Paustenbach, 2000, Calder et al., 1994). Direct correlations were found between blood lead and children's log-transformed rates of hand-in-mouth (r = 0.564, n = 22, p = 0.006) and object-in-mouth (r = 0.482, n = 22, p = 0.023) behaviours, respectively, by using 2 h video recording of childrens' behaviours during outdoor play in urban residential yards (Ko et al., 2006). These data confirm the direct relationship between hand-to-mouth activities and blood lead levels. Dust has been recognised as the major contributor to children's blood lead levels near the primary lead–zinc smelter at Boolaroo in New South Wales, Australia (Gulson et al., 2004).

Associations between soil lead and blood lead levels have been estimated in a number of studies, and methods of different experimental designs have been summarised by (Laidlaw and Filippelli, 2008). Specifically, particulate resuspension of lead-enriched soils was identified as a continued source of bioavailable lead both outside and inside homes that could be modelled and shown to be related to blood lead (Laidlaw and Filippelli, 2008). A general review of cross-sectional studies indicated a positive association between soil lead and blood lead (Jin et al., 1997). A large number of studies point to an effective decrease in blood lead levels after soil abatement (Lanphear et al., 2003, von Lindern et al., 2003a, Aschengrau et al., 1994, de Freitas et al., 2007),

¹⁴ The NH&MRC blood lead level for investigation is currently 5 μg/dL NHMRC (2016) 'Managing individual exposure to lead in Australia – a guide for health practitioners'. National Health and Medical Research Council, Commonwealth of Australia. Canberra. April 2016.

particularly for sites adjacent to the contamination source (de Freitas et al., 2007). This finding indicates an association between the high contributions of soil or soil-borne materials and high blood lead in children.

Food in the stomach and intestine is a very important factor in lead absorption. Previous studies evaluated lead isotope absorption by volunteers who were fed lead with meals or specific foods, or on fasting. For the volunteers who were fasting, as much as 71 per cent of soluble lead was absorbed (Heard et al., 1983). However, when the lead was ingested with a meal, absorption fell to a range of 3–7 per cent of the dose (Heard et al., 1983, James et al., 1985, Maddaloni et al., 1998). Calcium and phosphorus were mainly responsible for reducing the gastrointestinal absorption of lead in human subjects. The effect of calcium was greater than phosphorus on gastrointestinal absorption (Blake and Mann, 1983). Calcium competes with lead absorption by a calcium-transport protein in the small intestine, but also to form co-precipitates with phosphate and lead (Heard et al., 1983).

Age is a significant variable for lead absorption and metabolism. The portion of ingested lead taken up by the body is typically less than 5 per cent for adults, but as high as 50 per cent for children (Zeigler et al., 1978). Infants and toddlers are at greater risk due to increased exposure (mouthing behaviour), increased ability to absorb lead, the susceptibility of their rapidly developing central nervous systems, and their less-developed gastrointestinal tract (Maynard et al., 2005).

1.5.2 Inhalation pathway

The inhalation pathway is restricted to fine airborne particulate matter ('PM') that can get into the airways and into the lungs.

Particulate matter is categorised according to various diameters or sizes based on the physical property of airborne material (NEPC, 2002). PM_{10} and $PM_{2.5}$ are mixtures of solid particles and liquid droplets found in the air, with particle size less than 10 µm and 2.5 µm, respectively (NEPC, 2002). They pose the greatest problems for human health, because they can penetrate deep into the lung and get into the bloodstream (IPCS, 1995) (Figure 9).



Source: Modified from SKC (2009) (used with permission from SKC)

Figure 9 Demonstration of human respiration system and relative particle size

Fine particles capable of penetration deep into the lung are believed to be completely absorbed into the blood stream (U.S. EPA, 2007a).

Particles larger than about 7 μ m tend to deposit on the walls of the airways (the thoracic region) and become part of the mucus that is moved up to the mouth and then swallowed (IPCS, 1995). PM_{2.5} gives an approximation for fine mode particles, and therefore alveolar deposition, while PM₁₀ indicates the thoracic aerosol component (Raunemaa, 2002).

1.5.3 Human health exposure studies

1.5.3.1 *Introduction*

Elevated blood lead levels in children were initially considered to be due to ingestion of lead-based paints (Chisolm and Harrison, 1956). It was not until the mid-1970s that environmental lead and its possible effect on human health, particularly the health of young children, was investigated extensively. Lead-contaminated dust and soils have been increasingly recognised as potential sources of high blood lead levels. Lepow et al. (1975) investigated sources of lead in the environment of urban children and found that the ingestions of lead-contaminated dirt and dust by children with pica not only elevated blood lead levels in the children, but they also maintained blood lead levels at 40 to $60 \mu g/dL$.

1.5.3.2 Australian and international studies

The relationship of levels of lead in the blood of people with exposure to various lead sources has been studied at lead smelting sites all over the world (ATSDR, 2004). Previous studies reviewed by ATSDR provided evidence of the high risks

for children living in the vicinity of a lead smelter from the ingestion or inhalation of lead from airborne emissions, lead-bearing soils, dust (including household dusts, entrained dusts by wind or human-oriented events); water supplies, and food. Studies on high concentrations of lead in the environment resulting from stack emissions, fugitive emissions (Ohmsen, 2001), and the use of slag (Morrison, 2003) showed that a range of artificial lead compounds may be present in environment close to mine sites and lead processing facilities.

Several case studies, from both Australia and overseas, have been critically reviewed and compared (Table 2).

Table 2 Summary	of selected	environmental	studies
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Site	Operational period	Sampling period	Materials	Environmental situation	Notes
Mount Isa, Queensland,	1931–present	1997	soil	3.4–456.0 mg/kg	Parry (2000)
Australia		1997–1998	air PM ₁₀	4–27 ng/m ³	Parry (2000)
Port Pirie, South Australia,			air lead	Air–lead decrease from 3.18 μg/m ³ (1974) to 0.6 μg/m ³ (1982)	Landrigan(1983)
Australia	1889–present	1981	dust fall	6.61 mg/m²/d (1.4 km) and 1.4 mg/m²/d (3.0 km)	Landrigan (1983)
			soil	4–2100 mg/kg	Landrigan (1983)
	1885–present Close to mine	1994–1996	entry floor wipes	Pre-remediation 3775 μ g/m ² .Close to mine sites and lead processing facilities from 10 districts–7535 μ g/m ² and 10 months after remediation 155–304 μ g/m ²	Boreland and Lyle (2006)
Wales, Australia	sites and lead processing		internal window sills	Pre-remediation 301–677 μg/m ² and 10 months after remediation 1387–2494 μg/m ²	Boreland and Lyle (2006)
	facilities	Not specified	vacuum dust	40–12,100 mg/kg	Gulson et al. (1995b)
		Not specified	soil	No differences in lead isotope ratios for bulk soil and soil fine fractions (38–53 μm)	Gulson et al. (1995b)
Boolaroo, New South		1991	soil	Mean 1430 mg/kg (20–21,460 mg/kg)	Dalton and Bates (2005)
Wales, Australia	1897–2003	1991	carpet dust	Range 631–2328 mg/kg	Dalton and Bates (2005)
		1991	air	0.1 μg/m ³	Dalton and Bates (2005)
			air	92 μg/m³ (1971) to 0.13 μg/m³ (1994)	Landrigan and Baker (1981)
El Paso, Texas, US	1887–1985	1994	soil	537 mg/kg (maximum level)	Díaz-Barriga et al. (Díaz-Barriga et al., 1997)
Trail, British Columbia, Canada	late 19th century		air	1.1 μg/m³ (1996) to 0.28 μg/m³ (1998)	Hilts (2003)
Midvale, Utah, USA	1910–1971	1993	soil	Mean soil concentration > 500 mg/kg	Lanphear et al. (2003)
Bunker Hill, Idaho, USA	late 19th century	early 1980s	soil	Mean soil concentration > 2500 mg/kg	Sheldrake and Stifelman (2003)

Granite City, Illinois, USA				Ranges in soil 1500 - 48,000 mg/kg for	
(closed lead smelter and				industrial sites and 106–9493 mg/kg for	
battery recycling)	1950s - 1983	1988	soil	backyard sites	Kimbrough et al. (1995)

For example, the primary lead–zinc smelter in Port Pirie, South Australia, currently operated by Nyrstar NV, is the major source of lead contamination in that city (Maynard et al., 2005). The smelter has been operated since 1889 and has the capacity to smelt 300,000 tonnes of ore concentrates annually and to produce approximately 230,000 tonnes of refined lead. Lead levels in airborne materials, dust falls, surface soils, and rainwater tanks were assessed (Wilson et al., 1986, Body, 1986a, Body, 1986c, Body, 1986b, Alphen, 1999). The important factors identified were age, pica habits, ingestion of paint and soil or dust through inhalation pathways, and the success of decontamination programs in some areas in Port Pirie. The dominant wind direction in Port Pirie differs from Mount Isa with respect to location of the city. A key difference between locations is that Mount Isa has mining and smelting of lead whereas Port Pirie has smelting, only.

Lead exposure and absorption by children in Port Pirie have been reviewed, showing that children, in particular, from the population in Port Pirie have been exposed to lead from several sources and via multiple environmental pathways (Maynard et al., 2005). The highest concentrations of lead in surface soil and air at Port Pirie were found within 2 km of the smelter; the level found decreased with distance from the smelter (Landrigan, 1983). Lead emitted from the smelter reached children at Port Pirie by a variety of pathways. Two major routes were identified: inhalation of airborne lead and ingestion of lead deposited from air in dust and soil (Landrigan, 1983). The relative importance of these two routes varied with the age of children. Ingestion was not particular important for older children, whereas younger children, because of their normal hand-to-mouth behaviour, were at risk of exposure by both routes (Landrigan, 1983).

The geographic clustering of children with elevated blood lead levels in Port Pirie were closest to the lead smelting facility (Landrigan, 1983). This fact, accompanied by elevated lead concentrations in soil (range 4–2100 mg/kg), house dust (mean 4740 mg/kg) and rain water tanks (geometric mean 50 µg/L), strongly indicated that the lead–zinc smelter was the major source of lead contamination at Port Pirie (Landrigan, 1983). Two high volume air sampler monitoring locations monitored airborne particulate lead levels at Port Pirie and showed a decrease from 3.18 µg/m³ to 0.6 µg/m³ from 1974 to 1982 at Solomontown 1.8 km from the main smelter stack and lower annual mean concentrations of 0.71–1.43 µg/m³ at Orana, 2.6 km from the stack. Lead concentrations in dustfall in Pirie did not decrease appreciably over the previous decade ranging from 6.61 mg/m²/day 1.4 km from the main smelter stack to 1.4 mg/m²/day 3.0 km from the stack. Thus fallout dust had remained a key issue at Port Pirie while airborne lead TSP levels were not excessive.

Airborne deposition of lead-contaminated dust appears to be the important pathway of contamination for children in Port Pirie (Maynard et al., 2005, Alphen, 1999). Blood lead levels and spatial air lead distribution between two high-risk sites near the smelter were compared (Calder et al., 1994). Although the results showed a progressive decline in the proportion of children above the recommended blood lead level, an analysis of the blood lead data by risk area in Port Pirie suggested that the reduction in blood lead levels appeared to be

greater in the low risk area, farthest from the probable source of continuing contamination, compared with high risk areas in the northern part of Pirie West, relatively close to the smelter (Calder et al., 1994). In addition, the two high risk areas showed different patterns of reduction from each other. Air monitoring data clearly showed that the air lead levels declined rapidly with distance from the smelter and associated works in Port Pirie (Calder et al., 1994). These results indicated the significance and importance of air pathway to the children's blood lead levels in a community near a lead smelter facility. Dust at Port Pirie was transported mainly through wind, primarily re-entrainment, from the lead smelter and new fugitive emissions. Human, vehicle and material handling activities also assisted dust to rise (Maynard et al., 2005).

The prevalence of elevated blood lead levels in children in the 3–5 year age group (16.1% with > 30 μ g/dL; mean 22.0 μ g/dL) from a total of 1239 children at Port Pirie in 1982 was more than three times higher than for the older 6–14 year age group (5.0% with > 30 μ g/dL; mean 17.9 μ g/dL) (Landrigan, 1983). From a total of 230 children in the 3–5 year age exceeding a blood lead level of 30 μ g/dL, the number of children from the high risk area was 32 out of 78 examined (41.0%) compared with 5 out of 152 examined (3.3%) from the other (low risk) areas. Thus there was a clear connection with blood lead > 30 μ g/dL from the high risk area.

Table 3 shows five of 16 behavioural factors were distinctively associated elevated blood lead levels (Landrigan, 1983). The relative importance of environmental and behavioural factors as determinants of children's blood lead levels was listed as relative risk by Landrigan (1983) in order to show the role played by behaviour compared with environment. They also found that lead from the smelter operation was of greater significance than lead in paint and in petrol as the source of lead. A sub-set of seven behavioural factors was most predictive of an elevated blood lead level for the 1982 Port Pirie blood lead survey (Wilson et al., 1986) and was incorporated in the program to reduce the risk of elevated blood lead levels in Port Pirie children. The factors were:

- i. household members who worked with lead in their occupations
- ii. living in a house with flaking paint on the outside walls
- iii. biting finger nails
- iv. eating lunch at home on school days
- v. when at school, appearing to have relatively dirty clothing
- vi. when at school, appearing to have relatively dirty hands
- vii. living on a household block with a large area of exposed dirt.

Factor	Relative Risk
Residence in polluted area near smelter	12.4
Placing objects in mouth	4.0
Nail biting	2.3
Dirty clothing	2.7
Dirty hands	3.0
Eating lunch at home	2.2

Table 3 Relative risk of children's behaviour in Port Pirie

Source: Landrigan 1983

Positive associations of blood lead levels of two-year-old children with surface soil lead concentrations also suggested a strong influence from soil-borne dust on blood lead concentrations in early childhood at Port Pirie (McMichael et al., 1985).

The distribution of elevated soil lead concentrations around the smelter at Port Pirie was roughly concentric. The mean dust lead concentrations in the homes of 23 children with elevated blood lead levels examined in the control case study was 4470 mg/kg (Landrigan, 1983). Rainwater tanks had two contributory sources of lead: lead dust and lead paint from roofs and gutters. As many as 47.5 per cent of the rainwater samples collected contained more than World Health Organization's ('WHO') guidelines for lead concentrations in drinking water (0.05 mg/L) (Landrigan, 1983).

Lead decontamination programs have been conducted in Port Pirie since 1984. Abatement programs involved identifying children with elevated blood lead levels, decontaminating houses, treating soils, general city greening, family education, and support and community education (Calder et al., 1994). The general strategy developed for the decontamination program was based on the premise that the major source of lead in Port Pirie was a substantial lead sink in the city, from which lead-contaminated dust readily re-entrained, although substantial contributions also came from lead-based paint and contaminated rainwater. The blood lead monitoring program showed the most significant decrease in children's mean blood lead levels were in areas that were remote from the smelter (Calder et al., 1994).

1.5.3.3 Mount Isa–specific studies

Lead mining, processing, smelting and concentrate handling facilities are identified as the key sources of lead pollution in Australia (NPI, 2012). These sources may contribute some or all of the blood leads of people who live or work near lead facilities such as at Mount Isa. Lead, widely present in mineralised areas and associated sites, is identified as a potential contaminant and therefore attracts the public attention to blood lead level, particularly for the vulnerable

young age group. Therefore, several Mount Isa–specific studies have been undertaken to address these issues.

A geochemical survey of metals and metalloids (arsenic, cadmium, copper, lead, sulfur and zinc) in soils, PM₁₀ aerosol and surface water in the vicinity of Mount Isa was conducted by Parry (2000). Concentrations of metals and of lead isotopes were analysed. Lead isotopes have been used to fingerprint the source of lead, as the ratios of lead isotopes, such as ²⁰⁸Pb/²⁰⁶Pb or ²⁰⁶Pb/²⁰⁴Pb, are unique to each lead deposit. Soil samples from 42 sites around Mount Isa, out to a distance of more than 100 km, were collected, but the sites were mostly west of the smelters. The topsoil (0-2 cm and 0-10 cm) heavy metal and arsenic concentrations were highest adjacent to the mine and smelters; the concentrations decreased exponentially with distance from the smelters in a north-westerly direction, downwind of the smelters. XRD analysis of clay separations indicated that all near-surface soils, except for cracking clay soils (smectite-dominant) were kaolinite-, illite- and goethite-dominant, sometimes with small amounts of smectite. There were slight differences showing the ratio of ²⁰⁸Pb/²⁰⁶Pb decrease from 2.2 to the mean level of 2.05 with increasing distance from the copper smelter. Samples from four PM₁₀ aerosol samples sites were collected and analysed from October 1997 to September 1998. Metal concentrations and lead isotope ratio data were compared for PM₁₀ aerosol samples from three sites, all north-west of the Mount Isa Mines mineral processing facilities. The mean PM₁₀ concentrations of lead from these three sites decreased with distance from the mineral processing facility: from 27 ng/m^3 (20 km from the copper smelter) to about 4 ng/m³ (100 km from the copper smelter). Significant seasonal differences were monitored in lead concentrations (they were higher in dry season) in lead isotopic ratios (²⁰⁸Pb/²⁰⁶Pb were 2.1370 and 2.0351 for PM₁₀ samples 20 km north-west of the copper smelter during the dry and wet seasons, respectively, compared with 2.2150 for Mount Isa orederived lead; these values also compare closely with those for lead derived from the copper ore bodies at Mount Isa $[^{208}Pb/^{206}Pb = 2.2184]$ indicated in Section 3.2, page 202). The NPI lists lead emissions from MIM as 540 t in 1999-2000 compared to the 160 t quoted for recent emissions in this report and the 120 t quoted in the 2011–2012 NPI report (NPI, 2012).

Surface-water samples were also collected as close as practically possible to soil sampling sites (28 sites) in December 1997 (early in the wet season) and March 1998 (late in the wet season). Mean filtered (particles < 0.45 μ m passed through the filter) lead concentrations showed a slight decrease from 2.1 μ g/L in December 1997 to 0.8 μ g/L in March 1998, which was considered reasonable during the wet season in Mount Isa (Parry, 2000).

Unleaded petrol was introduced to Australia in 1986. A post-1986 study of lead isotopic compositions on a ceiling dust sample and four high volume air filter samples collected from Mount Isa was conducted using thermal ionisation mass spectrometry (Gulson et al., 1997a). A two-component mixing model was used in this study to try to determine the sources of the lead in the samples. The researchers used the ²⁰⁶Pb/²⁰⁴Pb ratios to identify the lead from petrol (the ²⁰⁶Pb/²⁰⁴Pb ratio ranged from 16.77 to 16.85 for air particulates collected from

highly trafficked area in Brisbane during August 1996 and December 1996) (Gulson et al., 1997a). They estimated that Mount Isa mine lead contributed 14–41% of the total for high volume air filters and 86% ceiling dust based on the results of lead isotope ratios (Gulson et al., 1997a).

Whilst lead isotope ratio measurements at Mount Isa did not show a difference from lead in petrol, measurements from near the Cockle Creek smelter in New South Wales demonstrated that the contribution of lead from petrol is small compared with 55 to 100% of lead derived from the smelter emissions for a community near a primary zinc-lead smelter at North Lake Macquarie, New South Wales, Australia (Gulson et al., 2004) and was probably due to the phase out of lead in petrol completely by 2002 (Australian Government, 2009). In comparison, lead isotopic measurements in petrol and high-volume air filters showed that more than 90% of the lead in Sydney air was derived from petrol and that high-volume air filters provided valid information on the petrol source (Chiaradia et al., 1997b).

Sadler et al. (1990) conducted a study of heavy metal and metalloid contamination at the original location of St Paul's Lutheran Church, which was located on the west bank of the Leichhardt River, adjacent to the copper smelter. Surface and depth soil samples, roof gutter dust samples, and vegetable samples were analysed for heavy metals and the metalloid arsenic. Copper, lead, and zinc recorded levels that exceeded acceptable levels (ANZEC, 1990) for all the sites, but with no obvious correlation between the presence of one trace metal and another. Unlike later results (Parry, 2000), Sadler et al. (1990) found the 20—30 cm depth soil samples contained higher levels of heavy metals than the surface layer samples taken from St Paul's Lutheran Church. Evidence of significant movement of lead and cadmium, copper and zinc in the airborne particulates was also found in the roof gutter dust (Pb 9990 mg/kg, Cd 70 mg/kg, Cd 160 mg/kg, Cu 4900 mg/kg and Zn 4.2 %), and on indoor furniture (Pb 890 mg/kg, Cd 13 mg/kg, Cu 640 mg/kg and Zn 6700 mg/kg).

The solubility of lead and lead minerals is controlled by the pH of water (Chester et al., 2000). Generally, lead becomes much less soluble with increasing pH (> 6) and alkalinity of the water (Chester et al., 2000). The neutral and slightly alkaline pH of the water in the Leichhardt River therefore prevents dissolution of trace metals into the water, particularly of lead (Noller et al., 2012).

Runoff from the Leichhardt River is captured downstream in Lake Moondarra, which is approximately 20 km downstream of Mount Isa City. The water in the lake is naturally filtered via an artificial lagoon and reed bed system and is used for potable purposes by the residents of Mount Isa City. In addition to the mineral processing activities on the western edge of the city, the Mount Isa City Council disperses and reuses its treated sewage on local paddocks, parks and playing fields on the eastern edge of the city, with some of the effluent discharged into channels that drain into the Leichhardt River, upstream of Lake Moondarra. These sources do not affect drinking water quality at Mount Isa (Noller et al., 2012).

The potential environmental risk and impact of trace metals affecting Leichhardt River water and sediment in Mount Isa were examined (Noller et al., 2012). The tissues of seven fish from Lake Moondarra were analysed for their cadmium, copper, lead and zinc concentrations. Total concentrations of metals and metalloids in the water and sediment samples from the Leichhardt River indicated certain elements exceeded the levels established by various guidelines (ADWG, 2011, ANZECC/ARMCANZ, 2000, QWQG, 2009). Aquatic toxicity assessments in water and sediment showed a range of toxicity effects, from moderate to acute, to aquatic test species at different locations along the Leichhardt River below 23rd Avenue crossing. There were no toxic effects to aquatic test species for background sediments upstream of Mount Isa city even though extensive natural mineralisation is demonstrated in upstream sediments (Noller et al., 2012).

Due to increasing interest from the general community, in 2006 Queensland Health launched a blood lead screening program in Mount Isa City for children aged 1-4 years. The main purpose of the survey was to identify children with elevated blood lead levels, to work with their families to improve their blood lead level, and to provide key data to promote further community action (Queensland Health, 2008). The four hundred children recruited for the study were representative of the general population of 1-4 year olds in Mount Isa City by age, sex and indigenous status. Results of the survey indicated that the mean blood lead level for the children tested was 5.0 µg/dL (geometric mean value), with the minimum level of 1.3 µg/dL and the maximum of 31.5 µg/dL (Table 4) (Queensland Health, 2008). About 11.3 per cent of the study group (45 children) had blood lead levels greater than or equal to 10 µg/dL¹⁵. Of these children, two (0.5 per cent of the study group) had blood lead levels greater than 20 µg/dL. Indigenous children were reported to be about four times more likely to have a blood lead level over 10 µg/dL than were non-indigenous children. The results also showed that for all children tested, those aged less than three years were more likely to record an elevated blood lead level than children aged three years or over. This demonstrated that age is an important factor in blood lead levels and is likely to relate to general play activities (e.g. playing in soil and sand, and with pets) and hand-to-mouth behaviour. The results did not show significant links between elevated blood lead levels and gender, or length of time living in Mount Isa City. It was concluded that hygiene improves when casual factors of soil and dust are reduced (Queensland Health, 2008).

As a follow-up study, *Queensland Health released the Mount Isa Community Lead Screening Program 2010 Report* (Queensland Health, 2011), in which 167 children of the same age group were sampled for lead analysis. The follow-up study showed a significant improvement in the lead levels of children in Mount Isa City, compared with 2006–2007 screening program (Queensland Health, 2011). The 2010 study indicated a decline in both mean blood lead levels (from 4.97 μ g/dL to 4.27 μ g/dL) and the percentage of children's blood lead levels at, or

 $^{^{15}}$ The percentage of children from the study group having blood lead greater than or equal to 5 $\mu g/dL$ will be more.

above, 10 μ g/dL. Eight children (or 4.8 per cent of the sample) had blood lead levels greater than 10 μ g/dL. One child had a blood lead level higher than 20 μ g/dL. The 2010 study also indicated an improvement in children's blood lead after successful environmental intervention with people who lived near the mining and mineral processing activities in Mount Isa City.

No distinct spatial patterns of elevated blood lead levels within Mount Isa City emerged from either study, although participants were evenly distributed across the community. Household tests carried out for children with elevated blood lead levels (greater than $10 \mu g/dL$) for both surveys showed that chewing, sucking or eating non-food items, living in a property with bare soil, and pet ownership were common among the group with elevated blood lead levels (Queensland Health, 2008, Queensland Health, 2011). Although care should be taken in interpreting declines in data, this improvement in the lead levels of children indicated the importance of community education and wiping down surfaces in houses for living safely with lead. Improving household hygiene and hand–mouth behaviours are significant approaches to improving blood lead levels as reported in studies of young children undertaken in other locations (Maynard et al., 2005, Lanphear et al., 2003, Sheldrake and Stifelman, 2003).

Location	Australian national	Mount Isa	Mount Isa	Port Pirie	Port Pirie	Broken Hill	Broken Hill	Broken Hill	Boolaroo	Boolaroo	Midvale	Midvale	Trail	Trail
Screen time	1995	2006–2007	2010	1982	2004	1991	2003	2011	1991	2005	1989	1998	1975	1996
Data source	Donovan et al (1996)	Queenslan d Health (2011)	Queenslan d Health (2011)	(Wilson et al., 1986)	(Maynard et al., 2005)	(Lyle et al., 2006)	(Lyle et al., 2006)	(Lesjak, 2011)	(Galvin et al., 1993)	(Dalton and Bates, 2005)	(Lanphear et al., 2003)	(Lanphear et al., 2003)	(Schmitt et al., 1979)	Hilts et al. (1998)
Age group	1–4 years	1–4 years	1–4 years	5–14 years	1–4 years	1–4 years	1–4 years	1-4 years	1–4 years	1–5 years	0.5–6 years	0.5–6 years	1–3 years	0.5–10 years
Test number	1575	400	167	1239	618	781	496	554	62	69	73	167	92	46
Maximum (µg/dL)	32.7	31.5	22.4	-	-	-	-		38	38	-	-	-	-
Minimum (µg/dL)	< DL*	1.3	1.9	-	-	-	-		6	1	-	-	-	-
Number over 10 µg/dL	115	45	8	-	-	-	-		53	-	8	2	-	-
Percentage over 10 µg/dL	7.3%	11.3%	4.8%	-	60%	-	-		85.5%	17%	11%	1%	-	-
Geometric mean (µg/dL)	5.05	4.97	4.27	17	10.6	16.3	7.1	4.9	15	8	5.6	3	22.5	11
95% confidence interval	-	(4.69, 5.24)	(3.96, 4.61)	-	-	-	-		-	-	(4.9, 6.3)	(2.8, 3.2)	-	-
95% confidence interval	-	(4.69, 5.24)	(3.96, 4.61)	-	-	-	-		-	-	(4.9, 6.3)	(2.8, 3.2)	-	-

Table 4 Summary of lead screening programs in Mount Isa and other industrial sites

Note: * < DL (less than detection limit) means the blood lead concentration tested less than 0.04 µmol/L (0.8 µg/dL).

1.6 Exposure Pathways

1.6.1 PM₁₀ and PM_{2.5}

There are approximately 200 lead and zinc smelters and refineries across 37 countries in the world (Batonneau et al., 2004). The release of fumes and dust through the stacks of smelters using pyrometallurgical processes is recognised as a source of fine particulate matter containing various metallic compounds (Sobanska et al., 1999). Other sources of airborne lead, zinc, and associated metals, such as resuspension of aerosol size particles of surrounding ores stocks, polluted top-soils, and smelter waste slag, have been considered for their effect on health (Batonneau et al., 2004). Fine ores, soil, and waste particles, particularly PM_{10} particles, can be suspended in the troposphere by wind or by mechanical disturbances, therefore, potentially resulting in exposure of for the community. Dust and airborne PM_{10} have been suggested as being primary lead pathways in lead–zinc mining and mineral processing areas, as described in several studies (Landrigan, 1983, McMichael et al., 1985, Laidlaw and Filippelli, 2008, Young et al., 2002).

The air quality control ('AQC') system was established in 1973 in Mount Isa City to maintain the air quality in the City of Mount Isa (Wrigley, 1992). The AQC system controllers shut down the smelters and cease certain dusty operations when necessary to maintain the air quality. The AQC controllers monitor emissions and observe emerging weather patterns using real-time air quality data. The current AQC system includes 10 real-time sulfur dioxide (SO₂) monitoring stations that display their readings to the controllers, 5 passive monitoring stations, 9 high-volume dust samplers, and 10 dust depositional gauges (MIM, 2012a). The AQC controllers also work proactively to reduce or stop smelting operations based on weather forecasts of wind speed, direction, and atmospheric and ground temperatures. The control of fumes is only ancilliary to SO₂ control (MIM, 2012a).

MIM has monitored air quality using high-volume air sampling for TSP for over 20 years. Since 2001, MIM has reported high-volume air PM_{10} samples at for heavy metals and arsenic at five sites in Mount Isa City at Kruttschnitt Oval, Miles St, the Mount Isa Racecourse, the RSL Club, and the BSD (Base Supply Depot, now the acid plant car parking area) (Queensland EPA, 2009). However, no comprehensive risk assessment studies have been undertaken on the significance of inhalation as an independent pathway of lead exposure for the community of Mount Isa.

1.6.2 Resuspension of soil

Due to the high potential of soil contribution to PM_{10} and PM_{250} through resuspension and its significance to children's blood lead levels via inhalation and ingestion, it is important to study the exposure risk resulting from soil origin PM_{10} and PM_{250} in Mount Isa City.

Soils act as the repository for human exposure to a number of environmental contaminants, including lead (Laidlaw and Filippelli, 2008). Lead-contaminated dust and soil can be carried into the home or other buildings attached to shoes (Hunt et al., 2006) or on the feet of family pets. Thus, lead-contaminated soils and dusts from outside may contribute to high lead exposure rates for children inside buildings (Laidlaw and Filippelli, 2008).

A strong seasonal relationship was found in Jersey City, New Jersey, between atmospheric particulate loadings and blood lead levels in preschool children (Yiin et al., 2000). Laidlaw et al. (2005) found that weather and soil moisture data invariably predicted seasonal changes in children's blood lead levels in a number of US cities. They also concluded that weather and soil moisture variables were proxies for seasonal soil resuspension and exposure of children to lead contaminated urban soils, with the potential to use site-specific weather and soil moisture determinations to better assess clinical blood lead data. Under high temperature and maximised evapotranspiration, soil dust was resuspended and deposited, and could cause lead-enriched PM₁₀ and elevated lead dust to be dispersed to the urban environment. This relationship could be explained by the fact that when temperatures are high, relative humidity is low and soil moisture decreases, increasing soil dust resuspension (Laidlaw and Filippelli, 2008).

Soil resuspension can entrain significant quantities of lead into the air. Chow et al. (1992) illustrated the contribution of lead in soil to PM₁₀ materials in a study of six sites in California. They found that primary geological material (rocks and soil generated therefrom) accounted for 30–62 per cent of the annual PM₁₀. Harris and Davidson (2005) calculated that resuspension of soil was responsible for generating 54,000 kg of airborne lead each year in the South Coast Air Basin ('SOCAB') of California. A lead isotopic study conducted in Yerevan, Armenia, suggested that 75 per cent of atmospheric lead was derived from resuspended soil bearing lead from past petrol emissions (Kurkjian and Flegal, 2003).

The contribution of contaminated soil to concentrations of lead and other trace elements in the air, however, has not been documented in detail. One study on resuspension of soil as a source of airborne lead near industrial facilities and highways showed that 1 g of dry soils generated mean levels of 0.169 to 0.869 mg of PM_{10} , depending on the particle size of the bulk soil (Young et al., 2002). More importantly, total production of PM_{10} -bound lead from the soil samples varied between 0.012 and 1.2 mg of lead/kg of bulk soil. The PM_{10} fraction isolated from bulk samples of uncontaminated California soils was 5.36–88.7 times higher compared with the original bulk sample (Young et al., 2002). Contributions of soil from contaminated sites to lead balances are important in particular situations and should, therefore, be considered when undertaking risk assessment or attempting to control airborne lead levels (Adgate et al., 1998, Young et al., 2002).

1.6.3 Dust in homes

Understanding the entry of lead into homes from outside was based on identifying particulate pathways, which have point sources (e.g. particulates on

clothes, shoes, pets, etc.) and diffuse sources. The levels of penetration are related to the 'leakiness' of a home or apartment (Laidlaw and Filippelli, 2008). In a study of an occupied home, Wallace et al. (2002) observed that the strongest influence on air change rates was opening windows, which could increase the rate of dust transfer. Doors and windows were the primary entry points of lead-bearing dust entering homes.

Attic dust accumulations in arid and semi-arid areas have also been found to be substantial and were composed primarily of soil particles, which was a strong indicator of soil resuspension (Davis and Gulson, 2005). However, in urban areas, lead-containing dust was generally derived from lead paint or the (former) use of leaded petrol (Billick et al., 1980, Gulson et al., 1996). In communities with lead-based activities, the most obvious sources of lead-containing dust were mining or smelting processes (Gulson et al., 1996, Hilts, 2003, von Lindern et al., 2003a, von Lindern et al., 2003b).

1.6.4 Other sources of lead

Unleaded petrol was introduced to Australia in 1985 and leaded petrol was completely phased out in 2002 (Australian Government, 2009). A comparison of lead isotopic measurements in petrol and high-volume air filters (Chiaradia et al., 1997b) showed that more than 90 per cent of the lead in Sydney's air was derived from petrol. The report showed that high-volume air filters, together with vacuum cleaner dust, wipes, fallout and soil provided valid information on identifying the petrol source. The isotopic measurements in a study after the phase out demonstrated that the contribution of lead from leaded petrol was by then small (Gulson et al., 2004).

Lead in paint was reduced to 1 per cent in Australia in 1973, then further reduced to a maximum lead content of < 0.1 per cent in 1997 (DSEWPC, 2009). Generally if a property was built before1970 in Queensland, it was likely that it had been painted with lead-based paint.

Gulson et al. studied the sources of lead in houses near the smelter at Boolaroo, New South Wales, and found that many houses, especially those closest to the smelter, were more than 50 years old and contained leaded paint (Gulson et al., 2004). In the past, the presumed dominant source of soil lead contamination in older houses was lead-based house paint (Adgate et al., 1998, Gulson et al., 1995a) but, while elevated levels of lead were found in dusts near painted externals surface, a relationship between lead-based paint and blood lead levels could not be demonstrated in Port Pirie against the large contributions from other sources (Body, 1986c).

In the Broken Hill mining community, in western New South Wales, high-precision lead isotope ratios demonstrated that paint and petrol were contributors to blood lead in families, but the dominant source was lead derived from the local ore bodies (Gulson et al., 1996).

For many years, diet has been recognised as a contributor to blood lead levels (IPCS, 1995) because the lead contaminant is either dissolved or finely divided

and suspended. Transfer of the lead source into the blood is expected to be more efficient when there is either complete dissolution of a solid source in the stomach or sufficient transfer of inhaled lead-bearing particles in the lungs. Lead concentrations in food and drinking water are regulated according to the recommendations of various authorities such as the Australian New Zealand Food Standards Code (FSANZ, (2004) and the Australian Drinking Water Guidelines (2011). Diet is generally a minor contributor to blood lead in Australia (Gulson et al., 1999, Gulson et al., 1997b) and universal distribution of lead from food in a community is expected; therefore, food is not usually considered as a distinct source of lead in investigations, except for the contamination of foods within the home during food preparation as reported in a Port Pirie study (Body et al., 1991).

1.6.5 Implications for the current study

Previous studies have indicated that the primary lead pathways from various sources to the receptors were inhalation and ingestion of materials containing lead. The effects of exposure media were also important (Davies et al., 1990, Maynard et al., 1993). Therefore, this study, *Lead Pathways Study — Air*, focuses on inhalation and ingestion pathways to demonstrate their potential risks to the Mount Isa community. The risk assessment approach (enHealth, 2012) will be used to better understand the key lead pathways and further guide risk management in Mount Isa City.

1.7 Guidelines for Environmental Management

1.7.1 Introduction

Limiting the effects of processing activities on nearby communities is vital for sustainable development in mining and mineral processing. Australia is a mineral-rich country, and mine sites are potential sources of metals and metalloids. If not properly managed, mine activities may cause adverse environment and human health impacts (ICMM, 2007). To avoid health risks to communities from mining activities, good prediction and planning is required, together with well-designed monitoring that will enable detection of any adverse trends.

The Brundtland Commission's definition of sustainable development is that development must meet the needs of the present without compromising the ability of future generations to meet their own needs (Brundtland, 1987). In the mining and minerals sector, this definition is taken to mean that investments in minerals projects should be financially profitable, technically appropriate, environmentally sound and socially responsible (MCA, 2005). The Berlin Guidelines (UNEP, 2000) highlight the relevance of sustainability to the mining industry, specifically the management of potential environmental impacts (UNEP, 2000). The International Council on Mining and Minerals (ICMM, 2003) developed ten principles and supporting elements for sustainable development in the mining and minerals industry. These ten principles have been adopted in Australia in the form given in *Enduring Value: The Australian Minerals Industry*

Framework for Sustainable Development (MCA, 2005). This framework is designed to assist the industry implement an industry commitment in a practical and operational way, targeted at the site level (MCA, 2005). In particular, Principle 4 of the ICMM's ten principles is about, 'implementing risk management strategies based on valid data and sound science' (MCA, 2005).

Following enHealth's risk assessment approach (enHealth, 2012), a variety of guidelines, standards and procedures were employed for this study. The following sections outline the relevant guidelines that were consulted for the framework for environmental management required at in Mount Isa. The scope of this study covered lead and other metals and metalloids as environmental and health risks.

1.7.2 Air particulates

1.7.2.1 *Air–particulate sampling*

The Australian Standard *Methods for sampling and analysis of ambient air* specifies a gravimetric method for determining suspended particulate matter in ambient air as total suspended particulate matter (< 50 µm) or PM_{10} (< 10 µm) (see Section 1.5, page 71). Sampling is normally undertaken for a 24-hour duration to average out daily variations in particle levels and to allow a sufficient mass of particulate matter to be collected. Ambient air quality measurement of particulate levels for air NEPM standards are measured using AS 3580 (Standards Australia, 2003).

1.7.2.2 National Environment Protection Measure

National Environment Protection (Ambient Air Quality) Measure ('Air NEPM') standards (NEPC, 2002) are uniform standards for ambient air quality in Australia (Table 5) and provide guidelines relevant to airborne particles as particulate matter 10 μ m (PM₁₀) for a 1-day averaging period and lead for a 1-year averaging period. Since 2003, the additional parameter of advisory reporting standards for 2.5 μ m fine particles have been added. The Air NEPM does not include indoor air criteria. These NEPM criteria are useful in the absence of site-specific criteria.

1.7.2.3 Queensland Environmental Protection Policy (Air)

The full complement of air quality indicators relevant to Mount Isa are given in the Queensland Environmental Protection Agency's Environmental Protection Policy (EPP) — Air (EPP, 2008). The EPP includes lead and other metals (arsenic, cadmium, manganese, nickel and vanadium), $PM_{2.5}$, PM_{10} , and total suspended particles (TSP) and outlines goals and maximum allowable exceedances (Table 5). The air-PM¹⁰ is a subset of the TSP level.

Pollutant	Averaging period	Maximum ambient concentration	Goal/maximum allowable exceedance	References
Particles as PM ₁₀	1 day	50 μg/m³	5 days a year	(NEPC, 2002)
	1 day	25 µg/m ³	Goal is to gather sufficient data nationally	(NEPC, 2002)
Particles as PM _{2.5}	1 year	8 μg/m ³	to facilitate a review of the Advisory Reporting Standards as part of the review of this Measure scheduled to commence in 2005.	(NEPC, 2002)
Total suspended particles	1 year	90 µg/m³		(NEPC, 2002, EPP, 2008)
Lead in total suspended particles ('TSP')	1 year	0.5 µg/m ³	None	(NEPC, 2002, EPP, 2008)

Table 5 PM ₁₀ and PM ₂₅ air quality standard	Table 5	5 PM ₁₀ and	1 PM ₂₅ air	quality	standards
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1.7.3 Fall-out dust

'Dust' is a generic term for describing fine particles that are suspended in the atmosphere. Any dust that falls out of suspension, and is collected using a dust deposition gauge, is referred as 'deposited matter'. Fallout may be material that can be ingested (< 250 µm (larger particles do not adhere as readily to the hands (Ng et al., 2010)); Figure 9) once deposited to the ground. The most simple and cost-effective method for undertaking dust monitoring is to monitor deposition rates using a dust deposition gauge. The dust sampling method in this study followed the description in *Australian Standard 3580 Methods for sampling and analysis of ambient air (Standards Australia, 2003).*

1.7.4 House and clearance standards

1.7.4.1 Australian Standard for contaminated soil and deposited dust

The Australian Standard 4874 Guide to the investigation of potentially contaminated soil and deposited dust as a source of lead available to humans (Standards Australia, 2000) sets out procedures for collecting deposited dust and soil samples to determine whether the lead present is able to cause toxicity in humans. Special emphasis is placed on infants and the collection of samples from areas this population group would come into contact with. There is a detailed description of dust sampling approaches for soil and dust in houses.

The Australian Standard 4874 guide does not give guidelines for contaminated houses, but it does identify appropriate international criteria, such as those from the United States Environmental Protection Agency (U.S. EPA, 2001).

1.7.4.2 US EPA house clearance standards

The United States' Environmental Protection Agency ('US EPA') has developed 'lead clearance standards' for house floors, window sills and window troughs, but not carpet dust. These standards determine whether it is considered safe to live in the house after lead-removal activities have been completed. Comparison of results for surface wipes is made against the standards given in the US EPA regulation, *Lead* — *Identification of Dangerous Levels of Lead, Final Rule, Federal Register Friday January 5 2001, Part III Environmental Protection Agency "Clearance Standards for Dust"* (US EPA, 2001). The US clearance lead standards for houses are:

- 430 µg/m² for dust on the floor
- $2691 \,\mu g/m^2$ for dust on interior windowsills
- 4306 μ g/m² for dust in window troughs.

1.7.5 Soil

The NEPM¹⁶ (Assessment of Site Contamination) provides the soil guidelines used in Australia to assess health and ecological effects on a site-specific basis (NEPC, 1999b). A site may be assessed based on investigation levels, or a site-specific assessment can be undertaken. The NEPC provides a framework for investigation levels (NEPC, 1999b), which are principally described as 'Investigation Levels' or 'Response Levels'.

Investigation Levels are generally either Health Investigation Levels ('HILs') or Ecological Investigation Levels ('EILs'). To accommodate the range of human and ecological exposure settings, a number of generic Investigation Levels have been set (NEPC, 1999). HILs and EILs are only used for assessing existing contamination and are intended to prompt an appropriate site-specific assessment where levels indicate there is the potential for adverse effects on human health or ecological values for that site. The site should be sufficiently characterised and appropriate Investigation Levels selected to ensure the comparison is meaningful and appropriate.

In cases of minor exceedances of investigation levels or exceedances related to contaminants that have low human toxicity and limited mobility, a qualitative risk assessment may be sufficient. The risk assessment process (enHealth, 2012) may lead to the development of site-specific response levels generated by the

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NEPC(2013) National Environment Protection (Assessment of site contamination) Measure guideline on investigation levels for soil and groundwater. Amendment of the NEPM 1999. National Environmental Protection Council. Canberra, Australia. The revised soil contamination Health Investigation Levels (HIL) are as follows: Residential A (Low-density with garden) Lead 300 mg/kg; Residential B (High-density minor garden) Lead 1200 mg/kg; Residential B (Highdensity minor garden) Lead 1200 mg/kg; Residential C (Open-space recreational) Lead 600 mg/kg; Residential D (Commercial/industrial) Lead 1500 mg/kg.

risk assessment and agreement between the professionals assessing the site and regulatory authorities. The Tier II risk assessment process described by NEPC (1999) allows for toxicity assessments when HILs for the designated category or land use are exceeded.

Soil and dust concentrations are compared against the NEPM criteria (NEPC, 1999d): HIL Level A Standard residential with garden/accessible soil (300 mg/kg for lead); and HIL Level E Parks, recreation, open space and playing fields including secondary schools (600 mg/kg for lead).

The Australian Standard 4482.1 *Guide to the investigation and sampling of sites with potentially contaminated soil. Part 1: non-volatile and semi-volatile compounds* (Standards Australia, 2005) provides guidance for collecting sufficient and reliable information for the assessment of a site potentially contaminated by lead and other metals and metalloids, apart from other non-volatile and semi-volatile compounds. This standard does not establish regulatory limits but supports those of the NEPC document (NEPC, 1999b).

1.7.6 Exposure assessment

1.7.6.1 Blood lead recommendation

The National Health and Medical Research Council advises that all Australians should have a blood lead level below 10 μ g/dL¹⁷ (NHMRC, 2009). The recommended level was used to compare the predicted blood lead level from modelling in this study.

The United States' Centers for Disease Control and Prevention ('CDC') formerly used a threshold 'level of concern' if a child's blood lead level was $\geq 10 \ \mu g/dL$. However, it abandoned the use of the term 'level of concern' in 2012 and now uses a blood lead 'reference level' of 5 $\mu g/dL$. This reference level is based on the blood lead level exceeded by only 2.5% of the US population of children aged 1–5 years (U.S. CDC, 2012). The CDC has not changed its recommendation for level (45 $\mu g/dL$) at which to use medical treatment to reduce children's blood lead levels (U.S. CDC, 2012).

The recommended maximum blood lead level for Australians is being reviewed and a decision may not be released until 2014 (NHMRC, 2009).

1.7.6.2 Blood lead prediction

In the absence of guidelines, methods based on health risk assessment can be applied (enHealth, 2012). These approaches depend on comparison with an established safe dose rate for lead or other metals or metalloids. An alternative

¹⁷The NH&MRC blood lead level for investigation is currently 5 μg/dL NHMRC (2016) 'Managing individual exposure to lead in Australia – a guide for health practitioners'. National Health and Medical Research Council, Commonwealth of Australia. Canberra. April 2016.

method developed by the US EPA (U.S. EPA, 1994a) is the Integrated Exposure Uptake Biokinetic Model for lead in children (IUEBK model¹⁸). The IUEBK model is used to estimate child blood lead concentrations from the ingestion of the mass of soil and household dust. The prediction can be compared with an acceptable upper level for blood lead.

Dose-response analyses has been previously used in conjunction the risk assessment process (enHealth, 2012) to determine if the magnitude of effect associated with identified levels of dietary and other ingested lead exposure is of significance. However, in 2011 the Committee of the Joint FAO–WHO Expert Committee on Food Additives (JECFA, 2011) withdrew the provisional tolerable weekly intake ('PTWI') for lead levels, concluding they could no longer be considered health protective. This action was taken because the dose-response analyses did not provide any indication of a threshold for the key effects of lead. To assess the health risk associated with lead ingestion from soil and dust, the only technique available was the IEUBK Model (U.S. EPA, 1994a). This model was used to undertake the health-risk assessment step for lead (Section 2.5).

¹⁸ The Queensland Health blood lead surveys at Mount Isa surveyed children 1-4 years of age. The USEPA (2010) Integrated Exposure Uptake Biokinetic (IEUBK) model for blood lead prediction uses an age range of 0.5-7 years as default.

2 METHODS

2.1 Justification of the method and study approach

Many factors influence the potential for lead-bearing emissions to contribute to blood lead levels. These factors include particle size, shape, composition, and matrix incorporating the lead-bearing phase (Ohmsen, 2001). Particle size determines the pathway of the lead into the body. PM_{10} and $PM_{2.5}$ particles are the relevant size that can penetrate the lung via the inhalation route, whereas larger particles are relevant for the ingestion pathway. Particles < 250 µm, which can also include particles below 10 µm that have accumulated in mucus brought up from the respiratory tract to be swallowed, will be ingested (U.S. EPA, 2007a).

The types and sources of emissions from various forms of lead processing can affect both the workforce and the wider population in different ways (Calder et al., 1994, Landrigan, 1983, Landrigan et al., 1975). Thus, understanding the potential exposure of children living adjacent to lead mining and smelting facilities requires more detailed examination of the operations within the lead processing facilities, so that individual contributions to the observed environmental loading can be evaluated. Knowledge of the metallurgical operations and phase relations associated with primary lead smelting is the key to understanding the relationship of mineralogy of fugitive emissions.

Metallurgical processing at Mount Isa takes two forms. The first, usually referred to as 'mineral processing' in the mining industry, involves crushing and grinding the ore to a sufficiently fine size to break apart the individual mineral grains (referred to as 'liberation' of the mineral grains), followed by froth flotation, in which chemicals are added to the ground ore to allow the mineral grains to be separated through selective attachment to air bubbles (Munro, 1993). This produces lead concentrate. The second processing stage is smelting, which involves sintering the lead concentrate to remove sulfur to form lead oxide that binds, together with added fluxes, to form lumps known as 'sinter'. These sinter lumps are partially crushed and then placed in the blast furnace to remove oxygen and iron to form crude lead bullion and slag. The bullion is refined at Mount Isa to remove copper and some arsenic, before being shipped to the United Kingdom for final refining (Ramus and Clift, 1993).

The mineral processing steps change the physical size of the minerals, but not alter their chemistry. The sintering and smelting steps chemically transform the minerals into a simple chemical structure. The size reduction in the mineral processing steps makes the lead minerals more prone to reaction with oxygen in the environment and so the minerals mined, such as galena, can subsequently be transformed into oxidation products, such as lead sulfate.

Both composition and particle size simultaneously influence the degree of bioavailability of dusts and, therefore, a detailed examination of the characterisation of emissions from various lead processing procedures is

necessary to understand the different chemical forms of lead that exist and the particle size distributions of the emissions.

The risk assessment process is undertaken to determine the potential exposure of the community to lead in the Mount Isa environment, which may have natural or man-made origins.

The hypothetical pathways model developed for this project to examine lead transfer from sources to environmental receptors is shown in Figure 7 (page 71). The model connects each sequence of 'source–pathway–receptor' that can be identified. The pathways model can be refined and used to better understand human and ecological uptake of lead by undertaking measurements such as bioaccessibility ('BAc') and particle size distribution to more accurately explain observed bioavailability ('BA') (Bruce et al., 2007).

This chapter will now develop the basis for selecting a range of analytical techniques and analytical approaches to create an integrated approach to enable the lead pathways to be understood and to elaborate on the objectives of the pathways study. No other studies have used such a comprehensive approach to a study of lead pathways in Australia.

Section 2.2 outlines an integrated approach to range of analytical techniques and bioavailability and bioaccessibility tests and justifies their selection for the inclusion in the risk assessment framework. Section 2.3 will describe the sampling strategy needed to provide an appropriate set of samples to apply the integrated approach to the risk assessment framework. Section 2.4 describes the actual analytical techniques that were used. Section 2.5 describes IEUBK model and its application to the data generated by these analytical techniques, and some of the default values and assumptions that were also used in the model. Section 2.6 describes the statistical techniques applied to the analytical data.

2.2 Selection of analytical approaches

The analytical approaches used in this study for the human health risk assessment included:

- total concentrations
- isotope distribution
- molecular properties
- physical properties
- bioavailability and bioaccessibility.

2.2.1 Total concentrations

Environmental samples containing metals and metalloids generally are digested in aqua regia based on the US EPA (200.2) method. To achieve accurate and precise concentration data from sample digest solutions, inductively coupled plasma–mass spectrometry ('ICP-MS') and inductively coupled plasma–optical emission spectrometry ('ICP-OES') are the preferred techniques for determining trace and major elements. ICP-MS and ICP-OES are widely used in environmental studies (Eggins et al., 1997, Robache et al., 2000). ICP-OES has higher detection limits and is suitable for samples with elevated concentrations. ICP-MS combines the advantages of multi-element spectroscopic analysis with the great sensitivity of mass spectrometry and its ability to measure isotope ratios, which has reinforced its wide application in environmental studies. The main disadvantage of these two techniques is that solid samples must be digested before they can be analysed. The dissolution procedure was used extensively in this project because of the ease in preparing samples for ICP-OES and ICP-MS analysis.

2.2.2 Isotope distribution

Lead has four stable isotopes: ²⁰⁴Pb (1%), ²⁰⁶Pb (24%), ²⁰⁷Pb (23%), and ²⁰⁸Pb (52%). ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb are the radiogenic end-products of the uranium ²³⁸U, ²³⁵U and thorium ²³²Th decay series, respectively (Dickin, 2005). Lead isotope abundances are usually not affected by physical or chemical processes in natural environments, but they are a reflection of the initial concentrations of the parent uranium and thorium isotopes when the ore body was created in the source rocks (Dickin, 2005). Anthropogenic lead, supplied from petrol, lead mineral processing procedures, and other activities, has a distinct range of lead isotopic signatures ²⁰⁶Pb/²⁰⁷Pb (Gulson et al., 1994, McGill et al., 2003, Segal and Halicz, 2005, Gulson, 2008). Although ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios can be measured with a higher precision than the ²⁰⁶Pb/²⁰⁴Pb ratio, the ²⁰⁶Pb- based ratios have less discriminatory power, with values approximating 2 for the ²⁰⁸Pb/²⁰⁴Pb ratio and 1 for the ²⁰⁷Pb/²⁰⁴Pb ratio, compared with values of 16 to 19 in the ²⁰⁶Pb/²⁰⁴Pb ratios (Gulson et al., 2015). With the high precision measurements obtained by multi-collector inductively coupled plasma mass spectrometry ('MC-ICP-MS') used in this study it is possible to clearly distinguish ²⁰⁶Pb/²⁰⁴Pb ratios of 16.0 from 16.1.

Availability information about the total concentrations and mineral compositions of lead is not sufficient for an accurate evaluation of source of contamination. Due to their distinctive characteristics, lead isotopic compositions provide an efficient and direct approach for environmental studies to fingerprint contamination sources and contamination destinations at local and regional scales (Ishizaka et al., 2009, Lawrence and Neff, 2009, Gwiazda and Smith, 2000). The first successful use of lead isotopes to trace the sources and distribution of anthropogenic lead was in 1965 (Chow and Johnstone, 1965). In this study, Chow and Johnstone (1965) found that the lead isotope features of Lassen snow in Sierra Nevada, California, was close to the lead isotope features of aerosol from Pasadena, Los Angeles County in California, and fell within the range of lead isotope compositions of local leaded petrol. A later study indicated distinct differences in the lead isotope compositions of atmospheric particulate matter in the eastern United States compared to those in eastern Canada (Allègre, 2008). Preliminary data by Maring et al. (1987) suggested that stable lead isotopes were effective in identifying aerosol sources from a variety of industrial lead emission sources in complex atmospheric systems. The isotopic composition of lead depends on the source of the different inputs of lead, distances from industrial areas, prevailing wind directions, and rainfall density (Bird et al., 2010).

The predominant influence of mining and mineral processing activities on adjacent contaminations of the atmosphere, soils, and sediments is supported by various lead isotope studies (Ettler et al., 2006, MacKenzie and Pulford, 2002, Monna et al., 2000, Ettler et al., 2004). By comparing lead concentrations and isotopic compositions of soil profiles from two sites close to a historical lead smelting and battery processing company, Ettler et al. (2004) applied a two-endmember model to evaluate the percentage contribution from each potential lead source. The coupled concentration and lead isotope approach confirmed the predominant role of lead smelting on the measured levels of lead in spoil in the study area (Ettler et al., 2006). In another study, the results of lead and zinc concentrations and stable lead isotope ratios for mining waste, river sediments, bedrock, and ²¹⁰Pb-dated peat bogs from the area of a lead-zinc mine in central Scotland indicated a significant source of contaminant heavy metals from the mining operation for several hundred years (MacKenzie and Pulford, 2002). Also, in the Czech Republic, lead isotopic tracing of possible contaminant sources suggested a distinct role of mining activities and primary lead metallurgy, rather than recent secondary lead smelting (car battery processing) and bedrocks (Ettler et al., 2006).

The technique of MC-ICP-MS has recently attracted attention because it enables the precise measurement of isotope compositions for a wider range of elements, compared with some traditional techniques, such as quadrupole ICP-MS and thermal ionisation mass spectrometry ('TIMS'). Mulitiple-collector ICP-MS is preferred for high ionisation efficiency, high precision and accuracy of the analytical data, high sample throughput, and the simplicity of the analyses over the TIMS technique (Halliday et al., 1998, Dickin, 2005, Rehkämper et al., 2001). Based on the use of ²⁰⁵TI for the correction of mass discrimination by external normalisation, a higher precision of lead isotope ratio measurements is achieved by MC-ICP-MS. With this approach, lead isotope ratios from MC-ICP-MS are more precise than conventional TIMS results and the precision achieved by double and triple-spiking TIMS methods by a factor of 3–4 (Rehkämper et al., 2001). Continued development of the MC-ICP-MS technique has seen its sensitivity increase by two to three orders of magnitude compared to TIMS (Collerson and Palacz, 1999).

Lead isotope ratios have been used to estimate the contribution or mixing of lead from different sources (Gulson et al., 2004). The data interpretation of an isotope systematic of a two-component mixture was discussed by Faure (1986) when two components are isotopically different. The mixing hyperbola of lead isotope ratios can be transformed into a straight line by plotting lead isotope ratio versus 1/Pb (ppm⁻¹). This process enables a straight line fit to data points in coordinates of lead isotope ratios (e.g.²⁰⁸Pb/²⁰⁴Pb) and 1/Pb. The mass balance and relative contribution of the two sources can be determined using the two-component mixing model that quantifies the fraction (F) of each source with the following Equation 1 (Faure, 1986):

$$F_{B}(\%) = \frac{(^{208}Pb/^{204}Pb)_{sample} - (^{208}Pb/^{204}Pb)_{A}}{(^{208}Pb/^{204}Pb)_{B} - (^{208}Pb/^{204}Pb)_{A}}$$
 Equation 1

Where:

A is component A B is component B F_B is a fraction of component B (%).

2.2.3 Molecular properties

2.2.3.1 X-ray absorption spectroscopy

The bioavailability of lead changes widely among different lead species in various environmental matrices. Appropriate understanding of the relationship between speciation and bioavailability for human health and environmental risk assessment requires comprehensive identification of lead species in specific environmental media, such as air particulates, dust and mine waste (Brown et al., 1999). Information on the binding environment of heavy metals and metalloids helps to optimise remediation strategies and to assess their potential hazard to humans and other organisms (Brown et al., 1999).

Synchrotron radiation-induced X-ray absorption spectroscopy ('XAS') techniques have been applied extensively to determine the lead speciation at the molecular scale of solid phase samples at contaminated sites (Brown et al., 1999, Manceau et al., 2002, Morin et al., 1999, Ostergren et al., 1999). X-ray absorption spectroscopy is an element-specific, bulk-sensitive and non-destructive method that is able to identify discrete compounds of a particular element, down to trace levels (such as lead < 50 mg/kg) (Brown et al., 1999, Funasaka et al., 2008, Gräfe et al., 2007, Kawai et al., 2003, Manceau et al., 1996, Manceau et al., 2002, Matanitobua et al., 2007, Ostergren et al., 1999). X-ray absorption spectroscopy techniques enable poorly crystalline and fine-grained amorphous species to be identified. These are likely to control lead bioavailability to biota and mobility in natural systems, but are difficult to characterise using traditional techniques, such as XRD (Brown et al., 1999).

The XAS spectrum has two kinds of measurement covering different energy ranges: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) (Brown and Parks, 1989). XANES is generally defined as the energy range that includes the pre-edge, edge, and near edge (up to 50 eV past the absorption peak), is characterized by multiple scattering, and is generally qualitative; the edge is sensitive to formal oxidation states and coordination chemistry (e.g. octahedral, tetrahedral coordination) of the absorbing atom. EXAFS begins at about 50 eV past the absorption edge, is characterized by single scattering, and is quantitative enabling the determination of accurate inter-atomic distances and coordination number of the absorbing atom (Newville, 2004). The equations used to describe the EXAFS region break down at low photoelectron kinetic energy (near the edge), which is why XANES is less quantitative (Brown and Parks, 1989)

Data reduction is a crucial step in analysis of both XANES and EXAFS data. This involves the subtraction of background from the raw spectrum, which includes contributions from both sample- and detector-based phenomena (Weng et al.,

2005). These contributions can vary significantly between samples that contain similar analytes in diverse matrices and between spectra recorded under marginally different experimental arrangements. For this reason, XANES is very rarely used as a quantitative analytical technique for determining elemental concentrations. The data reduction process also includes a normalisation step in which the spectrum is converted such that the scale of the ordinate is expressed in terms of a molar absorptivity (entirely analogous to what is done with UV-Visible spectroscopy). Successful data reduction allows the direct comparison of XANES spectra recorded from samples with diverse analyte concentrations and matrices, or recorded using different detector arrangements, or even at different beamlines (when their energy resolution is comparable). It also minimises the uncertainty in the determination of effective average coordination number from EXAFS. The data reduction process employed here is essentially identical to that described by Weng et al. Weng et al., 2005) but is achieved using different software (EXAFSPAK; (George and Pickering, 2000)). This reference provides an in depth discussion of the process and the errors that arise when it is poorly executed.

2.2.3.1.1 X-ray absorption near-edge spectroscopy

The absorption edge energy in XANES is sensitive to the oxidation state of elements, and the position of the edge increases with an increase in oxidation state. The absorption energy required to liberate core shell electrons increases as the oxidation state increases, because ions with a higher oxidation state have fewer valence electrons (a more negative charge) and thus the core electrons are bound more tightly to the nucleus (Brown and Parks, 1989) XANES is applicable to solution or solid-phase samples, is element and oxidation state-specific, and is sensitive to parts per million concentrations. XANES gives empirical chemical composition by comparing sample spectra to known compounds (standard compounds) (Matanitobua et al., 2007, Funasaka et al., 2008). XANES is practical because it gives a direct measurement of the composition of environmental materials in relation to the oxidation states and binding environments of elements that may be present in original samples and selected fractions. By using XANES, it is possible to compare the spectra of known lead compounds with samples and to fit the XANES spectra by spectral deconvolution and least-squares linear combination fitting ('LCF') (George and Pickering, 2000). This technique gives the proportion of known compounds in a sample and may be applied to XANES spectra of lead compounds to examine lead molecular forms in solid-phase samples dispersed from lead mining and smelter facilities (Funasaka et al., 2008). Therefore, the XANES spectral technique provided a key step in developing the detailed lead pathways for particular mining operations and confirms the findings of other studies that molecular-scale characterisation of lead compounds and mineral forms is needed to understand the behaviour of, and health risks posed by, lead in the natural environment (Brown et al., 1999). Matanitobua et al. (2007) showed that chemical forms can be accurately measured in solid-phase mine wastes by statistical analyses of XANES spectra using appropriate model compounds. It is also possible to examine XANES spectra of biological tissues directly at cryogenic temperatures (Diacomanolis et al., 2010). Identifying lead speciation in environmental samples will enable a better understanding of the role speciation has in lead toxicology and this has been undertaken in this study using XANES spectra. No related study of this kind using XANES spectra has been reported in Australia.

Another important approach for interpreting XANES spectra is the use of principal component analysis ('PCA') coupled with target transformation (Beauchemin et al., 2002). Principal component analysis provides a statistical basis for choosing the number of standard species to include in the fitting model. Target transformation identifies which standards are statistically more likely to reconstitute the spectra of the samples. The PCA approach is recommended as a useful complement to other spectral fitting techniques because it provides statistical criteria that allow a more objective approach to fitting than in previous studies (Beauchemin et al., 2002, Ressler et al., 2000). PCA can also demonstrate similarities and differences between samples by plotting PCA scores for different sample groups so that samples with different, or similar, lead species are likely to be identified.

2.2.3.1.2 Extended X-ray absorption fine structure

Direct determination of the speciation and short-range molecular structure information of trace metals in environmental samples is a challenge for instrumental analytical techniques. EXAFS has been applied successfully in numerous environmental studies. Lead species in three tailings materials could not be properly characterised by traditional techniques such as electron probe micro-analysers, but were able to be characterised by using EXAFS in combination with conventional analytical techniques (Ostergren et al., 1999, Scheckel and Ryan, 2004). Contaminated soils generated from different types of industrial activities (lead-zinc smelting and recycling of lead acid batteries) were examined and the comparison of reference EXAFS spectra for lead compounds and environmental materials showed the technique could be used to fingerprint the structural environment of lead in multi-element and multiphasic matrices (Manceau et al., 1996). The dominant lead species most likely to affect lead bioavailability in the environment can be identified with the molecular-scale information provided by EXAFS analysis (Brown et al., 1999). These studies highlighted EXAFS as a significant tool for molecular-scale characterisation as a basis for understanding the behaviour of, and health risks posed by, lead in environment samples.

2.2.3.2 X-ray diffraction

The degree of bioavailability of materials is strongly influenced by chemical composition and mineralogy. XRD is a versatile, non-destructive technique that reveals detailed information about the chemical components and bulk crystallographic structures of natural and manufactured materials that are the matrix of environmental samples. However, XRD is relatively insensitive and can only detect greater than 0.1 per cent of a mineral phase. It generally does not detect amorphous material, which are frequently found in environmental samples (Ohmsen, 2001). In this context, the XAS and XANES techniques predominantly used are far more sensitive than XRD, while XRD is used to confirm a mineral's

presence in an environmental sample (Beauchemin et al., 2011, Rasmussen et al., 2011).

In crystals, atoms are arranged to form a series of parallel planes separated from one another by a distance, d, which varies according to the nature of the material. When a monochromatic x-ray beam is projected onto a crystalline material at an angle, *theta* (' θ '), diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number, n, of wavelengths. By varying the angle, Bragg's Law (Equation 2) is satisfied by specific d-spacing in the target polycrystalline materials. By plotting the angular positions and intensities of the resulting diffracted peaks of radiation, the feature of the sample is recorded. Based on the principle of XRD, a wealth of structural, physical, and chemical information about the target material can be obtained from Equation 2 (Cullity and Stock, 2001).

$$n\lambda = 2d\sin\theta$$
 Equation 2

Where:

- n is an integer
- λ is the wavelength of the incident X-ray beam
- *d* is the lattice spacing
- θ is the angle between the incident ray and the scattering planes.

X-ray diffraction has been successfully applied for environmental and geological samples. Trace amounts of two zinc minerals, sphalerite (ZnS) and hemimorphite, were detected in two particle samples (< 37 µm) analysed by XRD (Schaider et al., 2007). XRD identified a mixture of PbS, ZnO, and ZnS associated with one or more of the chlorine-bearing phases Pb(OH)Cl, PbCl₂, Pb₄O₃Cl₂, Na₃Pb₂(SO₄)₃Cl, Pb₁₀(SO₄)Cl₂O₈, Pb₄SCl₆, and Pb₇S₂Cl₁₀ in fugitive emissions and dust samples generated during sintering, smelting, copper drossing, refining, and slag fuming at a primary lead–zinc smelter (Ohmsen, 2001). XRD was used to characterise particulate pollutant fallout from smelting operations in Missouri. An identification technique has been developed that only needs 1–15 mg of collected material from a high-volume air filter (Foster and Lott, 1980). Compound identification reveals changes in toxic lead compounds, after which corrective action is taken in the manufacturing process if required (Foster and Lott, 1980).

2.2.4 Physical properties

2.2.4.1 Particle size

Particles of different sizes may have variable health influences. Smaller particles have greater reactive surface area per unit of mass, and are therefore more important for inhalation exposure and for rates of ingestion via hand-to-mouth contact with contaminated soils (Duggan et al., 1985) and metal absorption from ingested particles (Figure 9, page 75) because they will dissolve faster and thus release lead faster. Therefore, size-dependent variability in metal concentration

has important implications for assessing human and ecological exposure and risk.

The particle size of lead-containing soil and dust is important because it governs the penetration efficiency in the human respiration system (Figure 9) and can influence the bioavailability of lead (Laidlaw and Filippelli, 2008). Transport of metal-rich particles from stockpiles and subsequent human exposure are dependent on particle size. Paode et al. (1998) observed that the size distribution of atmospheric lead peaked in the 0.5 μ m size fraction. The concentrations of copper, lead, and zinc were higher in the finer particles of fallout depositing on southern Lake Michigan in than in the coarser fallout particles. Abt et al. (2000) observed that outdoor particles (0.02–0.5 μ m and 0.7–10 μ m) were found to contribute significantly to indoor particle levels and that higher efficiencies occurred for smaller particles entering the indoor air space of homes.

Particles of different size have different exposure pathways (Figure 9). PM_{10} and $PM_{2.5}$ are critical particle sizes for the inhalation pathway. Particles < 250 µm have a higher chance of being ingested via hand-to-mouth activity because they are more likely to adhere to hands (Ruby et al., 1996). Particles < 250 µm are therefore more significant for the ingestion pathway, although PM_{10} is also likely to be ingested (U.S. EPA, 2000).

Particle size can be influenced by natural weathering and anthropogenic activities. Significant differences were found in particle size distributions across various processing areas in a North American primary lead smelter, with aerosols in the blast furnace area found to be finer than those in the sinter plant (Spear et al., 1998). Generally, blast furnace fumes are condensed vapours, whereas the sinter plant aerosols contain more dust. Samples from an abandoned lead and zinc mining site showed significant particle size–dependent characterisation (Schaider et al., 2007). Concentrations of metals and metalloids in particles < 37 μ m were 3–9 times higher than concentrations in the original bulk samples, and the smallest respirable particles (< 10 μ m) contained 15–22 times higher concentrations of cadmium, lead, and zinc than bulk mine waste samples (Schaider et al., 2007).

Particle size also influences the distances that particles will travel, with finer particles being carried farther than coarse particles because they stay suspended longer in the atmosphere. Stokes' Law (Equation 3) was previously used to calculate the distance fine particles can be transported to and from a stack at a particular wind speed (Mattielli et al., 2009, Finlayson-Pitts and Pitts Jr, 2000). This present study used Stokes' Law to estimate the distance that lead-containing particles could travel under different atmospheric conditions. For a single event, the relationship between mass, volume, and density (ρ) of the particle can be applied, as demonstrated by Equation 3 (Finlayson-Pitts and Pitts Jr, 2000):

$$v = \frac{g(\rho_p - \rho_{air})D^2}{18\mu}$$
 (for D > 1.5 µm) Equation 3

Where:

v is the particle velocity (m/s) g is the gravitational acceleration (9.8 m/s² at sea level) ρ_p is the mass density of the particles (kg/m³) ρ_{air} is the air density (1.2 × 10⁻³ g/cm₃ at 20 °C and 1 atm pressure) D is the particle diameter (m) μ is the gas viscosity (Pa·s).

Figure 12 (page 121) shows the application of this equation and shows the distance travelled by various particle sizes. Stokes Law is only applicable to particles for D > 1.5 μ m.

Several techniques have been developed to measure the particle size distributions of samples. For example sieves, sedimentation, electrozone sensing, and microscope and laser diffraction have all been used. Traditional methods such as sieves and sedimentation either give poor reproducibility or have other limitations in the experimental process (such as the density, moisture and morphology of the samples) and they are time consuming (Rawle, 2008). The mechanical action of sieving can also alter the size distribution of soft particles. Electrozone sensing is an excellent technique for blood cells rather than environmental samples. Microscopy helps collect the morphology information with the benefit of directly looking at the particles, but it is not suitable for analysing batches of complex environmental samples. Therefore, the laser diffraction technique is preferred (ISO, 2009) and was the method employed in this study for particle size analysis of solid phase environmental samples.

2.2.4.2 Scanning electron microscopy

Morphology and composition are key parameters for the bioavailability of materials. Scanning electron microscopy ('SEM') is a versatile and widely used tool for identifying morphology and composition. SEM allows both morphology and chemical composition of biological and physical materials to be studied. The image of samples can be shown directly on a computer display by connecting a charge-coupled device ('CCD') camera to the microscope.

An electron beam is scanned across the surface of a sample. When the electrons strike the sample, a variety of signals are generated, and the detection of specific signals produces an image that corresponds to the sample's surface features or morphology. The image also gives the sample's elemental composition by detecting X-rays that are produced from the collision of electrons with various atoms in the sample.

The three signals that provide the greatest amount of information in SEM are: secondary electrons, backscattered electrons, and X-rays (Gabriel, 1985).

Secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface. The contrast in the image is determined by the sample morphology. A high-resolution image can be obtained because of the small diameter of the primary electron beam.

Backscattered electrons ('BSE') are primary-beam electrons that are 'reflected' from atoms in the solid sample. The contrast in the image is determined by the atomic number of the elements in the sample. The image will therefore show the distribution of different chemical phases in the sample. Because these electrons are reflected from sample atoms occupying a finite depth in the sample, the resolution of the image is not as good as with secondary electrons.

Interaction of the primary beam with atoms in the sample causes shell transitions, which result in the emission of X-rays. The emitted X-rays have an energy characteristic of the parent element. Detection and measurement of the energy (Energy Dispersive Spectroscopy ('EDS')) permit elemental analysis. EDS can provide rapid qualitative or, with adequate standards, quantitative analysis of elemental composition with a spot size of between 1–2 microns in width and depth (Gabriel, 1985). X-rays can be mapped or used to produce line profiles, showing the elemental distribution on a sample surface.

Thus, by scanning an electron probe across a specimen, high-resolution images of the morphology or topography of a specimen can be obtained. Detailed maps of elemental distribution can be produced from multi-phase materials, and characterisation of source and receptor materials (see Figure 7, page 71) in terms of mineral size, shape, and spatial distribution can be determined, as well as statistical analyses of these parameters.

For example, two dry-deposition plate samples from Metaleurop Nord SA's major lead-zinc smelter and refinery in France were selected and examined by Scanning Electron Microscopy Energy Dispersive X-ray Spectroscopy ('SEM-EDS') (Mattielli et al., 2009). Dry deposition between 190 and 1250 m from the main stack of the refinery showed a high level of large (> 10 µm) zinc, sulfur, iron and oxygen containing aggregates that were associated with resuspension of slag heaps and local emissions from operational units. In contrast, from 1720 to 4560 m from the stack, dry deposition consisted of small (PM₁₀) particles including spherical zinc-containing aggregates. Similar elemental associations were typical in dust emitted by the refinery, as reported in a previous study (Sobanska et al., 1999). Microscopic observations of a sample taken 190 m from the main stack were mainly composed of aggregates with diameters of around 5-12 µm. Two major groups of zinc chemical compositions were observed. In the first, zinc was commonly associated with lead and was trapped in particles containing sulfur, oxygen and iron. In the second, zinc and lead were associated with oxygen, silica or, to a lesser extent, aluminium, which was contained within the ore matrix (Sobanska et al., 1999). Many minor compounds were found in small heterogeneous particles (< 5 µm) while homogeneous particles of furnace dust, amorphous carbon with a mixture of lead and cadmium compounds were often detected by SEM-EDS.

SEM-EDS was used in this present study to examine morphology and elemental composition in air particulates.

2.2.5 Bioavailability and bioaccessibility

Using total contaminant concentrations in samples provides a conservative approach to assessing human health effects because it assumes that all of the metal in the environmental matrices can enter the bloodstream. However, this approach does not clearly demonstrate cause–effect relationships and is not necessarily a reliable measure of potential health effect because the varying characteristics of the lead materials mean that some of them are not readily absorbed into the body (Ng et al., 2010). In risk assessment studies, a more practical approach is to use accurate and reliable bioavailability and bioaccessibility data. Bioavailability is the 'gold standard' for measuring uptake of lead by the body, but practical considerations (such as cost and the need to use living animals) mean that bioaccessibility data are usually more available. This allows for greater testing to compensate for restrictions placed on generating bioavailability data.

Within this study, measurement of bioavailability of a small, but representative, set of samples was measured to enable the relationship with bioaccessibility data to be calculated so that the bioavailability can be predicted for each bioaccessibility measurement. The animal uptake (rat) studies were undertaken according to the Animal Ethics Committee (Queensland Health Forensic and Scientific Services) Approval Number AEC: 07P05 'Arsenic, cadmium, lead interactions with other essential metals and the effect on bioavailability' (Appendix 6).

Details giving background to the measurements of bioavailability and bioaccessibility for health risk assessment purposes are given in the following two sub-sections (Section 2.2.5.1 and Section 2.2.5.2).

2.2.5.1 Bioavailability

Bioavailability is one of the essential tools in pharmacokinetics because bioavailability must be considered when calculating dosages for non-intravenous routes of administration. Bioavailability is 'the amount of a contaminant that is absorbed into the body following skin contact, ingestion, or inhalation' (Ng et al., 2010). This definition, under the clinical setting, has since been widely adopted by various environmental jurisdictions. There are many definitions of bioavailability (NRC, 2003). Because of this variation in definitions, bioavailability is often best expressed as a process as illustrated in Figure 10.



Figure 10 Bioavailability processes in soil or sediment¹⁹

Taking into consideration the multiple exposure pathways, bioavailability is defined by this project as the amount of a contaminant that is absorbed into the systemic circulation of the body following skin contact, ingestion, or inhalation.

More specific definitions for bioavailability (NRC, 2003) include:

- i. **Absolute bioavailability** is the fraction or percentage of a compound that is ingested, inhaled, or applied to the skin that actually is absorbed and reaches systemic circulation.
- ii. **Relative bioavailability** is referred to the comparative bioavailability of different forms of a chemical or for different exposure media containing the chemical and is expressed as a fractional relative absorption factor. In the context of environmental risk assessment, relative bioavailability is the ratio of the absorbed fraction from the exposure medium in the risk assessment (e.g. soil) to the absorbed fraction from the dosing medium used in the critical toxicity study.

Bioavailability is determined using living organisms. Because of the ethical issues of using people, most of the tests to determine bioavailability of samples of leadcontaining materials (such as dirt and dusts) are carried out using animal test subjects.

¹⁹ The figure includes release of a solid-bound contaminant and subsequent transport, direct contact of a bound contaminant, uptake by passage through a membrane, and incorporation into a living system as illustrated by A, B, C and D. E denotes the process on which a substance reaches a target site to exert its biological effect.
Determining the bioavailability of metals and metalloids from a number of environmental samples was successfully undertaken over a period of years on several animal species, such as juvenile swine (Casteel et al., 1997); rats (Ellickson et al., 2001, Freeman et al., 1992), rabbits (Freeman et al., 1993), and monkeys (Freeman et al., 1995). Human tests of soil lead bioavailability were also conducted using lead-stable isotopes (206 Pb/ 207 Pb ratios) (Maddaloni et al., 1998). Six adults fasted overnight before being dosed with 250 µg lead/70 kg of bodyweight ('bw') (i.e. 85.5 mg soil/70 kg) in a gelatine capsule. Six additional subjects were subsequently studied, but they ingested soil immediately after a standardised breakfast. The average bioavailability measurements were 26.2 per cent ± 8.1 for the fast group and 2.52 per cent ± 1.7 for the fed group.

For this LP study, the absolute bioavailability ('ABA') of lead specifically for the ingestion exposure route was assessed in a set of samples representing various categories of Mount Isa mine waste and city materials and soils. The bioavailability data were used in the subsequent risk assessment for calibrating measured bioaccessibility values for a larger set of samples to collectively enable the potential exposure via ingestion of lead-containing materials by human receptors in Mount Isa.

2.2.5.2 Bioaccessibility

Bioaccessibility refers to 'the fraction of a compound that is soluble in the gastrointestinal tract and is therefore available for absorption – which is specifically referred to when *in vitro* assessment models are used' (Ng et al., 2010). Bioaccessibility data are specifically determined in a test-tube environment (*in vitro*) and represent the fraction of contaminant available for absorption by the gastrointestinal tract or lung prior to the blood stream (U.S. EPA, 1994a). Reliable analysis of the potential hazard to children of ingesting lead from environmental media depends on accurate information on a number of key parameters, including the rate and extent of lead absorption from each (U.S. EPA, 2007b). When reliable data on the bioavailability of lead and other heavy metals and metalloids in soil, dust, air particulates or other waste materials at a site are available, this information can be used to improve the accuracy of exposure and risk assessment at specific geographic locations (Ruby et al., 1999).

The concept of bioaccessibility was developed as a predictive tool for estimation of bioavailability. The in-vitro BAc assay reduces the need to use living animals once the former has been validated against an animal model. In-vitro BAc methods (arsenic and lead) have been adopted by NEPC as a tier-two site contamination assessment in Australia (NEPC 2013) The bioaccessibility of lead is determined using a simulated digestive system, mimicking the chemical environment in the stomach and intestines, or a simulated lung system, mimicking the fluids found in lungs. One such test is the 'physiologically-based extraction test' ('PBET') (Ruby et al., 1999). Results from these bioaccessibility tests tend to be higher than from absolute bioavailability (ABA) tests (Bruce et al., 2007, Diacomanolis et al., 2007)²⁰. The simulation of the digestive system is undertaken in laboratory equipment that is typically some form of glassware, such as test tubes or flasks, and hence it is referred to as '*in vitro*' (from the Latin *vitro* for glass), in contrast to tests carried out with animals, which are referred to as '*in vivo*' (Latin for 'that which is alive').

Although *in vivo* models reflect physiological conditions to a large extent, faster and cost-effective *in vitro* extraction tests based on human physiological conditions have been developed from previous nutrition studies to estimate the bioaccessibility of elements from various media (Oomen et al., 2003). The analogue digestive tract methods use extractions that mimic a combination of one or more of the sections of the digestive tract (or 'compartments') illustrated in Table 6 (page 115). Table 6 summarises the order and conditions in each compartment. The analogue methods discussed here only consider the biochemical environment and disregard the effect of active transport mechanisms and the role of micro-organisms in the gastrointestinal tract (Wragg and Cave, 2002). Bioaccessibility of soil contaminants depends on soil type and contaminant type (U.S. EPA, 2007b, Ruby et al., 1999, Steele et al., 1990). For example, lead is more easily absorbed from certain types of lead minerals (e.g. cerussite, manganese lead oxide), while other forms are poorly absorbed (e.g. galena, anglesite) (U.S. EPA, 2007b, Dieter et al., 1993, Ruby et al., 1999).

Decisions on the method used to estimate bioaccessibility should consider the validation status of a method, the ease of use, and the degree to which the method mimics the human gastrointestinal environment (Wragg and Cave, 2002). The PBET was designed around the gastrointestinal tract of a child of 2–3 years old, the age group that is supposed to be at the greatest risk from accidental soil ingestion (Ruby et al., 1993). Compared with other *in vitro* methods, the PBET test can give a more realistic assessment of lead bioaccessibility under fasting and fed conditions when considering the high dissolution of lead at low pH²¹. The PBET test is a more complete, detailed, *in vitro* model for lead (Wragg and Cave, 2002, Bruce et al., 2007).

Estimates of metal bioaccessibility using the PBET also display close correlation with *in vivo* bioavailability after ingestion for some metals, as measured in laboratory animal studies. The PBET model showed linear correlation with the Sprague Dawley[®] rat²² model ($r^2 = 0.93$ between *in vitro* and *in vivo* ABA results,

²⁰ This study also indirectly confirms that relative bioavailability (RBA) and BAc (gastric phase) could over estimate potential risk as already suggested in published studies.

²¹ An important detail to recognise is that gastric-only bioaccessibility measurement will overpredict bioavailability of lead; this can be demonstrated by using the USEPA IEUBK model to predict blood lead increase from ingestion of only soil by children. Food in the stomach and intestine is a very important factor in lead absorption. Following solubilisation in the stomach lead is transferred with nutrients from food to the intestine whether absorption of lead occurs. Lead absorption occurs via the intestinal phase and not from the gastric/stomach phase where solubilisation occurs.

²²The Sprague Dawley[®] rat is a strain of rat developed for medical research.

n = 7) (Ruby et al., 1996). Extensive effort has gone into validating a PBET for predicting lead bioavailability (U.S. EPA, 2007b). This research indicates that invitro data can be used to predict RBA using the equation: RBA = $0.878 \cdot IVBA - 0.028$. This equation supports the notion that in-vitro data are higher than in-vivo estimates of RBA.

The stomach phase of the test was used for determining lead in house dust (Smith et al., 1997) and the data were correlated with blood lead levels in children living in the houses where the dust was sampled (Smith et al., 1997). Data collected in previous studies indicated that the PBET is a good indicator of oral lead bioavailability (Bruce et al., 2007, Ruby et al., 1993, Ruby et al., 1996).

2.2.5.2.1 Categories of methods for determining bioaccessibility via ingestion

Bioaccessibility tests are generally divided into two categories (Wragg and Cave, 2002):

- i. chemical extraction tests in which the easily extractable metals, usually under low pH conditions, are likely to be bioaccessible
- ii. gastrointestinal analogue tests that attempt to mimic the biochemical conditions in human or animal gastrointestinal tracts.

Chemical extraction tests generally fall into three categories (Wragg and Cave, 2002):

- i. Single extraction tests that mimic the leaching of potential contaminants from soil or waste by rainwater or landfill leachate. This test was developed to measure potential mobilisation of contaminants from soil or waste piles by rainwater or landfill leachate.
- ii. Single extraction tests that are designed to determine the phytoavailability of chemicals within the soil.
- iii. Multiple extraction tests designed to either extract specific physicochemical soil phases to determine the distribution of metals within the soil, often referred to as sequential extraction tests.

Some chemical extraction tests are based on the method first proposed by Tessier et al. (1979). The distribution of the metals is operationally defined by five categories: exchangeable, carbonates, reducible, oxidisable, and residual. Modifications of this test have appeared in the literature over the years. One typical example is the Commission of the European Communities method, which defines the extraction of exchangeable, reducible, and oxidisable fractions (Ure et al., 1993). The results of these tests give a broad idea of how mobilised the target contaminants are; however, the extraction conditions and the extraction reagents are not representative of human gastrointestinal tracts. Therefore selective extraction tests were designed to simulation the changing conditions in the human gastrointestinal tract. These tests are now described.

2.2.5.2.2 A selection of *in vitro* methods

i. Simplified bioaccessibility extraction test

The simplified bioaccessibility extraction test ('SBET') is a simplified form of the PBET, developed specifically for lead bioaccessibility measurements and validated for lead animal models (Medlin, 1997, Drexler and Brattin, 2007) (Table 6, page 115). A correlation coefficient of 0.85 was obtained for 15 soils. The coefficient indicated that the extent of lead dissolution in an acidic stomach environment was predictive of relative bioavailability in two animal models (weanling rats and young swine). Bioaccessibility from the other methods produced slightly higher values for lead (Oomen et al., 2002). These results may indicate that the simplified procedure of using a stomach compartment extraction (pH = 1.5) instead of a combination with a lower intestine compartment extraction may be appropriate (Medlin, 1997, Oomen et al., 2002).

ii. US Pharmacopeia method

The US Pharmacopeia ('USP') (US P, 1990) method uses a synthetic gastric solution of sodium chloride, hydrochloric acid, and pepsin at 37 °C for two hours to extract heavy metals in soils (US P, 1990). It was developed by US Pharmacopeia to simulate drug dissolution and its application was extended by other researchers (Hamel et al., 1998). The results indicated the bioaccessibilities for soils were both sample- and element-based, but the bioaccessibility was affected slightly by changing the liquid and soil ratios (Hamel et al., 1998).

iii. Mass balance and soil recapture method

An *in vitro* method was developed by Hamel et al. (1999). It is based on the USP method to simulate three body compartments and extract the soluble metal and metalloid fractions from soil samples at 37 °C water bath (Table 6, page 115). Good agreement was detected between the extracted metal fractions and the decrease in metal concentration in the original soil (Hamel et al., 1999).

iv. German Deutsches Institut für Normung 19738 method

The Deutsches Institut für Normung ('DIN') test is for mobilising pollutants in contaminated materials using synthetic digestive juices containing both electrolytes and organic chemical components (Wragg and Cave, 2002). The sample is treated with gastric juice (pH 2.0) for two hours, followed by a six-hour small intestine phase (pH 7.5). The use of nitrogen to create anaerobic conditions is optional for special purposes and the whole system is kept agitated at 37 °C.

v. Simulator of human intestinal microbial ecosystem of infants

The stomach conditions for simulator of human intestinal microbial ecosystems ('SHIME') of infants were adjusted to pH 4.0, which is a more realistic model of fed conditions. The results for all metals were consistently lower by a factor of five to ten, compared to the other methods, due to the relatively high pH of the stomach (Wragg and Cave, 2002). However, no validation data against *in vivo* studies are available for this test for metals in soils.

vi. Rijksinstituut voor Volksgezondheid en Milieu in vitro digestion model

The Rijksinstituut voor Volksgezondheid en Milieu ('RIVM') *in vitro* digestion model is a three-stage sequential extraction method using a five-minute saliva exposure at pH 6.5, followed by a two-hour stomach extraction at pH 1.07 and a two-hour small intestine extraction at pH 5.5 (Oomen et al., 2002). There are no validation data for this test against *in vivo* studies for metals in soils.

vii. Toegepast Natuurwetenschappelijk Onderzoek Gastrointestinal Model

The TIM method (TNO Gastro-intestinale modellen – Gastrointestinal Model) developed by TNO Nutrition, The Netherlands, is a dynamic and comprehensive model. It simulates three phases of human body: saliva, stomach, and intestine (Oomen et al., 2002). The pH levels are adjusted to relevant levels to human body system (Table 6, page 115). The comparison of bioaccessibility of different in vitro models for soil samples indicated relatively lower lead bioaccessibility given by TIM model (Oomen et al., 2002).

viii. Relative bioaccessibility leaching procedure

The relative bioaccessibility leaching procedure ('RBALP') was developed to evaluate the potential hazard to children of ingesting lead (U.S. EPA, 2007b). RBALP was verified with tests on swine (Drexler and Brattin, 2007, U.S. EPA, 2007b). A linear model was recommended, based on the correlation between the lead concentrations from the in vitro and in vivo experiments (U.S. EPA, 2007b). The details of the RBALP method, compared with others techniques, is displayed inTable 6 (page 115).

ix. European safety of toys method

The European safety of toys ('EST') method is based on the European Toy Safety Protocol and was applied in a Canadian study of the urban environment (Rasmussen et al., 2011). More details on the method are given in Table 6 (page 115).

x. Physiologically based extraction test

The PBET is essentially a two-stage extraction using various enzymes to simulate both gastric and the small intestine compartments with extraction carried out at 37 °C. Potentially contaminated samples are introduced into the simulated gastric solution to solubilise any bioaccessible metal. The conditions are then modified after a stomach sample has been collected to simulate the small intestine. The reaction vessels for the extraction are argon-purged to keep the system under anoxic condition. The metal concentrations of the extracts are determined by ICP-MS (Ruby et al., 1993).

2.2.5.2.3 Comparison of different digestive bioaccessibility tests

A review of five *in vitro* digestion methods for assessing bioaccessibility of soil contaminants was conducted (Oomen et al., 2002). The methods tested were: the SBET method; the DIN method; the *in vitro* digestion model; the SHIME

method, and the TIM method (Oomen et al., 2002). Bioaccessibility of lead varied between 4 per cent and 91 per cent, with SBET and SHIME methods as the most severe and mild methods. Oomen et al. (2002) discuss several factors that might have influenced lead bioaccessibility: (i) the residence time of soil in the gastrointestinal compartments; (ii) the ratio between the amount of liquid and soil in the gastrointestinal compartments; (iii) filtration procedures; (iv) different bile concentrations and bile salts; (v) addition of food; and (vi) effects of gastric pH.

PBET was chosen as the method for this LP study when commenced because it has been used for simulating the whole gastrointestinal tract conditions and has been applied to mining waste materials²³. This method was validated against more than one animal species (Ruby et al., 1996) and has been used in a number of other mine waste studies by the authors of this study for over ten years (Bruce et al., 2007, Diacomanolis et al., 2007).

²³ An average pH representing the fast, semi-fed and full-fed states of the stomach and the near neutral pH of the intestine is selected to provide an intermediate pH for testing in the PBET and represents a nutritional status intermediate between fasting and fed states. This also represents a more realistic exposure scenario of a daily life rather than the most conservative assumption that exposure only occurs during the fast-state (hunger).

Method	Туре	Compartments	рН	Т (°С)	Food	L/S ratio	Residence time	Analysis	Metals tested	Validation status	Ease of use
		Note ^a				Note ^b	Note ^c	Note ^d		Note ^e	Note ^f
PBET	Batch	2 3	1.3,2.5,4 7	37	N N	100/1	1 h 4 h	Solution	Arsenic, lead	Rat, V/swine, monkey (lead)	Original 3 Modified 7
SBET ^①	Batch	1.5	1.5	37	N	100/1	1 h	Solution	Arsenic, cadmium, lead	V/swine(lead)	9
US P ²	Batch	2	ca.1	37	N	1000/1	2 h	Solution	Arsenic, cadmium, chromium, lead, nickel	NV	9
MB & SR ³	Batch	1 2 3	ca.1	37	N N N N N	160/1 2160/1 4770/1	5 s 2 h 4 h	Solution+ solid	Arsenic, cadmium, chromium, lead,	C/human (lead)	3
DIN [®]	Batch	2 3	2 7.5	37	Y Y	50/1 100/1	2 h 6 h	Solution	Arsenic, cadmium, chromium, lead	V/swine (unpublished)	5
SHIME ^④	Batch	2 3	4 6.5	37	Y Y	2.5/1 4/1	3 h 5 h	Solution	Arsenic, cadmium, lead	С	5
RIVM ^④	Batch	1 2 3	6.5 1.1 5.5	37	N N N	15/1 37.5/1 97.5/1	5 m 2 h 2 h	Solution + solid	Arsenic, cadmium, lead	С	6
TIM⊕	Flow - through	2 3	5,3.5,2 6.5,6.8,7.2	37	N N	5/1 30/1 51/1	5 m 1.5 h 6 h	Solution	Arsenic, cadmium, lead	С	2
RBALP (5)	Batch	2	1.5	37	N	100/1	1h	Solution	Lead	V/swine	9
EST [©]	Batch	2	1.5	37	N	50:1	2h	Solution	Lead	С	9

Table 6 Summary of the main features of gastrointestinal analogue extraction tests

Table modified from Wragg and Cave (2002).

Note a — 1 refers to an oral cavity; 2 refers to the stomach; 3 refers to small intestine.

Note b — Liquid-to-solid ratio used in the extraction.

Note c — Time of reaction in each compartment; nr indicates that a time was not reported.

Note d — Indicates the nature of the sample taken for analysis from each compartment.

Note e — NV indicates no validation against other bioavailability or bioaccessibility methods. V indicates the method has been validated against a bioavailability model (human or animal). C indicates the method has not been validated but has been compared to other bioaccessibility tests or techniques.

Note f — Ease of use scale 1 to 10. Ten represents a relatively fast test with simple apparatus (suitable for large batches of samples) and 1 represents a relatively slow test with very complex apparatus (not suitable for large batches of samples).

(1) Medlin (1997); (2) Hamel et al., (1998); (3) Hamel et al., (1999); (4) Oomen et al., (2002); (5) US EPA (2007b); (6) (Rasmussen et al., 2011).

2.3 Sampling

2.3.1 Introduction

Sampling takes a set from a defined data population that represents the population as a whole in relation to a specific variable (Maher et al., 1994). Sampling is an error-generating process (Gy, 1986). Sampling processes, together with sub-sampling and analysis, contribute to the total error of the estimate of interest (Maher et al., 1994). Considering the heterogeneity of a target sampling site, it is also important to make sure representative samples are collected and that the size of sampling units is enough to answer the research questions. Selection of appropriate sampling sites must be based on accurate and reliable site-specific information. Professional experience and judgement can be helpful to ensure adequate coverage in planning the collection of samples from tailings dams, smelters, and other artificial structures. Highly reliable information about the Mount Isa sites ensured the application of the stratified history-based judgemental sampling method in this study, following NEPC methods (NEPC, 1999b)²⁴.

Selecting an appropriate sampling program should be based on accurate and reliable site-specific information. The recommended order for sampling patterns (NEPC, 1999b) is based on:

- Site history-based judgemental sampling: Judgemental sampling is usually used at locations where the contamination source of the studied site is identified. This sampling method requires knowledge of the history of the site and, 'a high level of confidence in the reliability of information about the site and the information (should) reflect the current state of the site' (NEPC, 1999b). All the site data and information, including local geology, hydrogeology, meteorology, historical environmental monitoring data, and mineral processing procedures were either available from government websites or provided by MIM.
- *Grid (systematic) sampling*: Systematic sampling permits the whole site to be covered. It sometimes involves applying a regular or offset grid pattern to suit the site and the topography. Grid sampling is often conducted where the site history is not sufficient or where the contamination of the sites is not sufficiently well known to use the judgemental sampling method.
- *Stratified sampling*: Stratified sampling is used for large, complex sites by dividing the site into different sub-areas.

²⁴ The revision of the National Environment Protection (Assessment of site contamination) Measure - guideline on investigation levels for soil and groundwater (NEPC, 2013) gives additional advice on sampling design.

• Composite sampling: Composite sampling is not suitable for health-risk assessments due to uncertainties. Composite samples must be mixed thoroughly and treated as one item to ensure that representative results can be obtained. Composite samples, give average chemical and physical information about such sites spatially or temporally (in this study mainly spatially). It is thus important to detect hot spots and estimate the mean concentrations of the sampling area without increasing sample number (U.S. EPA, 2012). That is the reason that composites sampling (soil, carpet dust and roof gutter dust) were applied in this study.

Both local geology and hydrogeology can play key roles in the distribution of potential contaminants at sites (NEPC, 1999b). Topography can show local geology through exposure of geological strata, but hydrological and hydrogeological conditions usually affect the distribution of contaminants. While some hydrological dispersion of contaminants may occur at Mount Isa during the wet summer months, it is not considered a dominating process during the rest of the year when conditions are essentially those of an arid environment (Figure 3, page 66, and Figure 4, page 66). Therefore, the distribution of contaminants across a specified area, such as Mount Isa, is influenced by the local geology and natural or man-made altered emission features in the area or at a particular site. The distribution of contaminants within the subsurface is affected by 'geological structures, variations in the permeability of soil and rocks, geochemical, biological and mineralogical variations and the presence of preferential pathways', such as loose fill around modified landform features (NEPC, 1999b).

Certain sites at Mount Isa are naturally enriched with lead mineralisation in the surface associated with exposure of the existing geological features, notably the Urquhart Shale sequence (Figure 6, page 68). It is therefore necessary to have some understanding of the background quality of geological sequences and other materials at Mount Isa to evaluate potential contamination risks for both human health and the environment. The LPS Water Report gives details of river sediment metals and metalloid concentrations at Mount Isa and shows extensive copper and lead mineralisation in the upper Leichhardt River catchment and with the Urquardt Shale sequence at and below Mount Isa city, apart from historical mining activities for over 100 years (Noller et al., 2012).

Significant source and environmental samples were collected using a judgemental approach so that the fate of lead-containing particles dispersed from the mine site via the air-dust pathway could be followed to the residential area. Sources at the mine site were identified from an inventory of the materials that were stored and could be dispersed (supplied by MIM). Significant sources that may contribute to exposure pathways were then selected based on the combination of kind of materials, total concentrations of metals and metalloids and location.

Crucial factors that were taken into consideration regarding sample collection were:

- samples to enable lead exposure assessment
- major wind direction pathway, geological background (lead-enriched Urquhart Shale and other outcrops in the residential area)
- spatial distribution of sampling sites
- specific houses (background sites, comparison of upwind with downwind following the major proportions of wind direction and particular health concerns),
- access to house properties for sampling
- existence of fixed monitoring sites.

For this LP project, significant source and environmental samples were identified and collected using a judgemental approach to determine if significant leadcontaining particles moved from mine site to the residential area via air–dust exposure pathways.

2.3.2 Conceptual sampling model and particle dispersion

A detailed conceptual lead pathway model (Figure 11) displaying lead dispersion from potential sources to the community via various exposure pathways, namely, mine site activities, natural mineralisation, dietary, drink and others including historical sources not originally from mining in Mount Isa (lead in petrol, lead in paint, lead–acid batteries and fishing sinkers). In particular, it demonstrates the mode of the focus of this study (air–dust pathway, blue arrows in Figure 11) in relation to other lead exposure dispersion pathways in the study area.

Based on the conceptual model for lead pathways (Figure 11), information needed to be collected on the key lead emission sources at the study area:

- potential lead sources from the mine site
- potential emission locations (crushed ores, waste rock stockpiles, tailings dam material, lead-zinc and copper concentrators, the sinter plant, blast furnace, copper and lead slag stockpiles, lead smelter stack and the copper smelter off-gas duct)
- geological backgrounds (lead-enriched strata, outcrops, historical data on minerals at Mount Isa)
- geographical information (locations of different mining and mineral processing infrastructure, active community locations, climate and meteorology information)
- environmental concerns
- human health exposure concerns.

Various chemical and physical parameters were designated to test and characterise different groups of samples such as potential lead sources from the mine site and natural mineralisation and the direct environmental exposure metrics.



Figure 11 Lead pathways model (blue arrows indicate potentially significant lead pathways in Mount Isa)

An addition to the conceptual model (Figure 11) was predicting particle dispersion to give an idea of the distances particles travelled, which is relevant to the human health risk assessment. A combination of calculations on the basis of Stokes' Law (Equation 3, page 104) and meteorological and air modelling data focused the research in this study. Stokes' Law calculations (Figure 12) were undertaken for particle emissions from sources of varying heights that were relevant at Mount Isa (270 m for the lead stack and 15 m for surface processing activities on mine site). The calculated results (temperature 25 C, atmospheric pressure 1 atm (= 1.01325×10^5 Pa) and low humidity (Appendix 2)) showed that for one dispersion event:

- particles < 10 μm (PM₁₀) can travel over 130 kilometres when dispersed from a point source at 270 m, and consequently they are only partly deposited locally
- lead minerals with particle size < 10 µm can be transported to 7.3 kilometres when the maximum wind speed is 40 km/h from a nearsurface point source at a height of 15 m (e.g. a stockpile)
- large particles (> 250 μm) may be deposited within 20 metres from the emission source.

These preliminary comparisons from Stokes' Law calculations indicated that finer lead-containing minerals may be taken from the mine site to the city's residential area by strong wind, but PM_{250} commonly associated with fallout may be not transported directly via this pathway; several episodes may be required to transfer larger particles to the city area following multiple resuspension steps. Note that the soil and lead sulfide particles referred to in Figure 12 are examples for illustrative purposes only. Lead sulfide and soil would not actually be emitted from the lead smelter stack. However historical mine waste was used to fill in gullies and various places in Mount Isa city where clean up occurred (Noller et al., 2009; Sadler et al. 1990).



Figure 12 Distance travelled (km) by Stokes's Law when wind speed is 40 km/h

Figure 12 gives the modelling prediction that PM_{10} from a 15-metre-high lead emission source may travel 7.3 kilometres when the wind speed is 40 km/h. This assumed wind scenario is at variance with the long term weather records by Bureau of Meteorology (BOM, 2012). The historical record showed that the frequency of wind at the speed of 40 km/h from west to the east at the study area were less than 5%, as shown in Section 1.3.2 (page 63). When the wind speed is less than 32 km/h, lead-containing PM_{10} will not reach 6 kilometres. On this basis, the prediction in Figure 12 does not invalidate the practical selection of the background site at a location of 6 km upwind of the mining activities, as shown in Section 2.3.5 (page 124).

2.3.3 Statistical sample prediction of houses

For a sound statistical analysis, a minimum number of houses needed to be selected for detailed house dust studies. This minimum number is required to allow the ability to detect differences between houses. The proposed starting point for determining the number of houses to use was the Queensland Health Lead Screening program 2006–2007, which studied the blood lead of 400 children, aged 1–4 years, from the Mount Isa community (Section 1.5.3, page 75) (Queensland Health, 2008). The Mount Isa children blood lead studies were organised by Queensland Health and were not part of the current study.

To determine the minimum sample size to obtain a designated confidence interval, a statement of the designated degree of confidence and the approximate length of the interval is required (Hahn, 1975). This approach specified the required precision for the selected sample size.

The results of the Queensland Health study (Queensland Health, 2008) showed that the geometric mean blood lead level for the children tested was 5.0 μ g/dL, with the lowest being 1.3 μ g/dL and the highest 31.5 μ g/dL (range = 30.2 μ g/dL). Forty-five children (11.3 per cent of the study group) had blood lead levels greater than or equal to 10 μ g/dL. Two children (0.5 per cent of the study group) had blood lead levels greater than 20 μ g/dL. Although the standard deviations ('sd') were not given in the report, they were provided by Queensland Health (Queensland Health, 2010):

- arithmetic mean = 5.8, sd = 3.692
- geometric mean = 5.0, sd = 1.764.

The differences in the arithmetic and geometric means and their respective sd's suggest that they are not similar enough to assume normality. As neither is a perfect match to the data, the lognormal appeared to be a better approximation. Blood lead measurement must be measured reliably to a minimum analytical difference of 1.2 μ g/dL (Ng, 2009).

The calculation of the minimum sample size (n) was based on Equation 4, as discussed by Kupper and Hafner (1989), assuming no confounding factors. The use of the sample size equation with this correction was checked and validated on 22 May 2010 by a statistician Associate Professor Hong-Dar Isaac Wu, Department of Applied Mathematics, Institute of Statistics National Chung-Hsing University, Tai-chung, Taiwan (Wu, 2010).

$$n = 2\{(\frac{\sigma}{\delta})(Z_{\alpha} + Z_{\beta})\}^2$$
 Equation 4

Where:

n is the minimum sample size

 σ is the standard deviation (square root of residual or error variance)

 δ is the minimum difference between treatment means that is deemed important to detect (1.2 $\mu g/dL)$

 Z_{α} is the critical value corresponding to pre-chosen Type I error, two-tailed For $\alpha = 0.05 Z_{\alpha} = 1.96$ from tables of cumulative normal frequency distribution Z_{β} is the critical value corresponding to pre-chosen Type II error, two-tailed For $\beta = 0.05 Z_{\beta} = 1.64$ from tables of cumulative normal frequency distribution. To account for the random nature of the sample variances and improve the reliability of the sample size prediction, Kupper and Hafner (1989) gave sample size formulae that included a value from a chi-square distribution of sample variance for the desired probability (p = 0.05) and presented tables of corrected sample size values based on Equation 4. The minimum sample size to reflect variations in the blood lead test for children using Equation 4 and the geometric sd (1.764) was initially 56 and following correction the number was 74 based on using the table of one sample tolerance probability comparison publish by Kupper and Hafner (1989) when $\alpha = 0.05$.

2.3.4 Selection of houses

A systematic residential house sampling program was conducted from 2007 to 2011 to select approximately 70 houses to be representative across different locations in the Mount Isa City residential area. The final number of houses sampled was 67.

Three key factors were considered in selecting houses for dust sampling:

- i. to ensure an even geographical spread across Mount Isa City
- ii. to select sites where sample collections were of sufficient size to enable all analyses to be undertake
- iii. to ensure samples were collected from a range of housing types and from a wide range of living standards.

Houses were selected based on information offered by MIM employees:

- i. Glencore-owned managers' houses
- ii. Glencore-rented transit accommodation and vacant houses and units rather than tenanted residences, some that had been cleaned and some that had not been cleaned
- iii. vacant houses owned by the Department of Housing and other residents of Mount Isa who volunteered access to their homes.

However, there was a practicality of getting access to the minimum number of houses for the study without having the flexibility to decide on selecting houses occupied by families with children that would reflect other potential sources of lead in Mount Isa.

Because study involved assessing risk to human health, it was important that a comprehensive scenario was incorporated into the sampling plan following recommended practice (eNHealth, 2012). Samples taken from houses included garden soil, roof gutter dust, carpet dust, carpet wipes, floor wipes, veranda wipes, window-sill wipes and window-trough wipes during the dry season, which is the time when there is increased resuspension of soil and dust into atmosphere due to the low relative humidity in the study area and to the absence of rainfall.

Thus the dry season represents the worst case situation for lead exposure of children because more dust is present compared with periods of rainfall that occur during the wet season and scavenge dust from the air column.

2.3.5 Selection of sample sites for characterising background and source materials

Sample sites on the MIM leases were located with the help of MIM staff and based on listing the location of all major types of activities onsite, as shown in Figure 13a and b. To estimate the baseline contribution from the non-mineralised natural geochemical background, background samples were collected from houses on Breakaway Drive from the most easterly part of the city (about 6 kilometres upwind of the mine site).

The background site was chosen based on three factors:

- i. the historical meteorology record showed less than 5 per cent occurrence of wind direction from east to west, that is, from the mine site to the residential area according to (Figure 4)
- ii. Stokes' Law calculation (Figure 12) predicts that PM_{10} from a 15 metre high lead emission source will not reach 6 km for a wind speed less than 32 km/h
- iii. the area to the east of the selected background sampling site was an uninhabited pastoral area and mostly covered by sparse vegetation.

Source samples were collected as grab samples (with particle sizes < 10 cm) from all identified potential key emission sites, including crushed ores, waste rock stockpiles, tailings dams, lead–zinc concentrator, sinter plant, blast furnace area, copper and lead smelting slag, lead smelter stack, copper smelter off-gas ducts and the copper smelter area (Appendix 1 and Figure 13).



Figure 13 Locations of sampled residential houses, the mine site, and geological sequence outcrops²⁵

²⁵ BGR are background rocks comprising bulk bedrock samples from different geological units not associated with Uquhart Shale lead mineralisation in and beyond Mount Isa City residential area.



Figure 14 Locations for sampled air particulates and fallout from residential houses and the mine site

2.3.6 Sample collection and preparation

2.3.6.1 Inhalation pathway

Different samples were collected to estimate lead pathways from natural and environmental sources to receptors via either inhalation (PM_{10}) or ingestion pathways (PM_{10} and dust). The details are given in Appendix 1.

2.3.6.1.1 Air PM₁₀

Air PM_{10} from city residential areas (31 indoor samples and 12 outdoor samples) and mine sites were collected during three different sampling episodes: 4–26 November 2009, 17 November–14 December 2010 and 4 May–10 June 2011. The wind directions and speeds were plotted for each individual air PM_{10} sampling period, respectively for the years 2009, 2010 and 2011(Figure 15). The wind speeds were typically lower than 30 km/h (8.3 m/s in Figure 15) for all the three sampling periods. The mean wind speed was 12.9 km/h, 13.6 km/h, and 13 km/h for the 2009, 2010, and 2011 sampling periods, respectively. The dominant wind directions were from the south, east, and north. The wind from the west was less frequent. The southerly and south-south-easterly directions accounted for 54 per cent of the 2011 sampling period, compared with only 20 per cent and 31 per cent for 2009 and 2010 sampling periods respectively.



Figure 15 Wind rose (m/s) of three air PM10 sampling episodes (2009, 2010 and 2011) at Mount Isa city

Air PM₁₀ collections of indoor and outdoor air used membrane filters in cyclones and pumps with constant flow rates of air (Figure 16). The membrane filters (25 mm size PALL PVC membrane filter, 5 µm pore size) were weighed with an electronic balance in the laboratory (Model C-38, ATI Cahn balance) following a conditioning period within the laboratory to allow equilibration with the local humidity before weighing. SKC Conductive Plastic Respirable Dust Cyclones (see Figure 16) were set up in a pump system and run at appropriate sampling sites in the community or close to potential lead emission sites for 1–2 weeks, with an air flow of \approx 2.2 L/min. Samples and blank filters were weighed and stored separately in new 5 mL screw-capped polypropylene tubes for future use. Two downwind comparative 'control' sites, downwind of mine site, were also visited during each sampling episode. One site is about 5 kilometres west of the mine site and the other one is 25 kilometres west of the mine site. The lead smelter was not operating and was under maintenance during the 2010 sampling period.



Figure 16 Air PM₁₀ sampling in the community: (a) SKC cyclone unit components and (b) sampling setting up in the Mount Isa City for outdoor PM₁₀ collection

For safety reasons, no lead smelter sampling sites were visited for air PM_{10} sampling (SKC Conductive Plastic Respirable Dust Cyclones method), but thimble samples were collected by Xstrata environmental staff.

High performance cellulose extraction thimbles (Whatman 2800-300) were used to collect 10 dust samples from the lead smelter and 10 from the copper smelter (Figure 17). These were all single sample collections per site and time. The site descriptions are given in Appendix 1. Cellulose extraction thimbles have excellent mechanical strength and 10 μ m nominal particle retention. These thimbles were used in Soxhlet extraction units and provided a safe, convenient, and efficient method of solvent extraction of particulates from the respective smelter facility.



Figure 17 Air PM₁₀ sampling — thimble sampling setting in smelter (a) and HVA sampler in the community (b)

High volume air ('HVA') samplers (Figure 17) were collected from five routine monitoring stations in Mount Isa City (Kruttschnitt Oval, the BSD, the RSL Club, Miles Street and the Mount Isa Racecourse) over a 24-hour period on a six-day cycle to collect air particulates. The HVA PM₁₀ filters collected from five sites in early 2008 were prepared for various analyses used in this study (Appendix 1).

2.3.6.1.2 Soil PM₁₀ fraction

One kilogram samples from the top 10 cm of soil from Mount Isa residential yards were collected with a clean stainless steel trowel, placed in new plastic bags and sealed. The soil samples were dried in the Centre for Mined Land Rehabilitation ('CMLR') laboratory at 40 °C overnight, sieved to < 2 mm and stored for future use. An SKC cyclone (Figure 16a) was set up in the laboratory to separate the < PM_{10} fraction in the dried soil, with one side connected to a 25 mL glass volumetric pipette using tubing, with the other end of the tubing connected to a vacuum pump with an air flow of 1.2 mL/min. Separated PM_{10} samples from the < 2 mm soil fractions were collected from the filter (25 mm size PALL PVC membrane filter) in the cyclones, and kept in new 5 mL screw-capped polypropylene containers for future analysis. The size fraction of the separated < PM_{10} fraction in the dried soil was subsequently confirmed by particle size analysis (Section 2.4.4.1, page 142).

2.3.6.2 *Ingestion pathway*

2.3.6.2.1 Garden soil samples

Representative samples of soil (0.5 kg) were taken from gardens of the selected Mount Isa City houses (Figure 13). The samples were a composite made up of bare surface soil (up to 10 cm deep) from different areas of the gardens to minimise the potential influence of organic matter in the soil. The samples were collected using either a stainless steel or plastic trowel and placed in a new sample bag. Soil samples were dried in the CMLR laboratory at 40 °C overnight,

sieved according to the NEPC (1999c) to the < 2 mm fraction and later to the < 250 μ m fraction for bioaccessibility determination²⁶. The samples were stored in 120 mL polypropylene natural-coloured, capped sample bottles (SARSTEDT Australia, South Australia) and retained for future analysis. Soils and sediments were also prepared as described in Noller et al. (2009). One composite sample of soil ('CS') was prepared by mixing equally-weighed proportions of 40 samples that were then mixed and ground with an agate mortar and pestle to give a homogeneous sample of approximately 20 g. This composite was used for several different measurements. Sub-samples were sieved to < 250 μ m for PBET analyses (Section 2.4.5, page 143).

2.3.6.2.2 City footpath samples

Fourteen samples were collected from the surface (< 10 cm) of frequently visited nature strips (referred to as 'footpaths' in this study) between houses and streets in Mount Isa City (Appendix 1). None of the sites was covered with grass. One location was close to a high school and another close to a primary school. Since the size of sample material was large, gravel-sized agglomerated soil the whole samples were dried and sieved to the < 250 μ m fraction. Some of the agglomerated soils broke up during the screening process. The samples were stored in 120 mL polypropylene, natural-coloured, capped sample bottles (SARSTEDT Australia, South Australia) and retained for analysis.

2.3.6.2.3 Roof gutter dust samples

Roof gutter dust was collected from houses using a clean spatula and plastic spoon, and transferred to a clean plastic container (Figure 13). Any leaf or other litter was removed from the sample by sieving. A composite sample of roof gutter dust ('RG') was prepared by mixing equally-weighed proportions of five samples that were then mixed and ground with an agate mortar and pestle to give a homogeneous sample of approximately 20 g. The samples were stored in 120 mL polypropylene, natural-coloured (to avoid potential of metal contamination from pigments in plastic), capped sample bottles (SARSTEDT Australia, South Australia) and retained for analysis.

2.3.6.2.4 Fallout dust samples

New twenty-litre plastic buckets for collecting fallout samples were set outside buildings in Mount Isa City's residential area and at the mine site during fine weather (Figure 13). Four buckets were set up at each sampling site, two at 1.2 m and the other two at 1.8 m to correspond with the height of children and adults respectively. The fallout in the buckets was collected by wiping the internal surface with a plastic spatula and Whatman filter paper (12.5 cm diameter) and putting the recovered material into a clean 120 mL propylene, natural-coloured,

²⁶ The use of < 250 µm fraction for bioaccessibility determination of arsenic and lead in soil was confirmed when the revision of the National Environment Protection (Assessment of site contamination) Measure - guideline on investigation levels for soil and groundwater (NEPC, 2013) was released.</p>

capped sample bottle (SARSTEDT Australia, South Australia). The fallout samples were weighed on the AG64 balance (Mettler Toledo Ltd, Australia) located in the air sampling analytical laboratory at Mount Isa Mines and the weights were recorded.

2.3.6.2.5 Carpet dust samples

An area of 10 m² of carpet was chosen in each house sampled (Figure 18) and cleaned with a Dyson Stowaway DC-23-MOTORHEAD vacuum cleaner. The sampled carpet area from each house covered the living area and bedroom or bedrooms, which were frequently visited by children. Dust samples were collected and stored in new 120 mL propylene, natural-coloured, capped sample bottle (SARSTEDT Australia, South Australia) and as much of the lint or fluff as possible was removed from the sample with clean tweezers. The vacuum cleaner was cleaned extensively with fresh wipes (initially in 2008 fragrance free baby Huggies wipes and from 2009 onwards Ghost Wipes meeting ASTM E 1792) between sample collections. The amount of dust collected at each house was weighed following collection.

A fresh wipe was placed over the screen of the Vacuum's exit filter. All carpeted areas were vacuumed to cover an area of 10 m² carpet, ensuring that the whole of the carpet sampling area was vacuumed. A composite sample of carpet dust ('CD') was prepared by mixing equally weighed proportions of 13 samples, which were then mixed and ground with an agate mortar and pestle to give a homogeneous sample of approximately 20 g. The sample was stored in 120 mL polypropylene, natural-coloured, capped sample bottle (SARSTEDT Australia, South Australia) and retained for analysis.

2.3.6.2.6 Carpet wipe samples

Carpet wipe samples were taken from up to two locations in each house. A fresh Ghost Wipe (refer to Section 2.3.6.2.7, page 132) was used to wipe over the surface of the carpet within a 30 cm x 30 cm aluminium frame placed on the floor. The sample was collected by wiping within the frame area first in one direction (i.e. from left to right across the whole sample area), and then re-wiping in a direction at right angles to the first direction (i.e. top to bottom across the whole sample area). The wipe was then placed in a clearly labelled new sample container for transport and storage until analysed.



Figure 18 Recommendations for dust lead sampling in the community (U.S. EPA, 2008)

2.3.6.2.7 Floor and veranda dust samples

Floor-wipe samples were taken by wiping the prescribed area from up to three locations (Figure 18) in each house using a 30 cm x 30 cm aluminium frame. Wiping within the prescribed sampling area in the frame space was undertaken with fresh Ghost Wipes, which are lead-free and meet all the American Society for Testing Materials Designation E1792 specifications for sampling materials for lead in surface dust (ASTM, 2011). Wipe samples were collected within hightraffic areas of the house, for example near the front and back doors, and in front of toilets and dining rooms. The sample was collected by wiping within the frame area first in one direction (i.e. from left to right across the whole sample area), and then re-wiping in a direction at right angles to the first direction (i.e. top to bottom across the whole sample area). The wipe was then placed in a new 120 mL polypropylene, natural-coloured, capped sample bottle (SARSTEDT Australia, South Australia) and retained for analysis. There is some variation in the location of the samples, which was determined by the shape and configuration of the house. Veranda wipes were collected in a similar fashion to floor wipes.

Larger-area floor wipes and veranda areas were collected at three houses to obtain sufficient sample to undertake measurements including XANES analysis for lead composition and lead isotope ratios that required more analyte than was present in a standard 30cm x 30cm floor wipe. These floors wipe were collected by wiping the entire floor area in a room using one Ghost Wipe (ASTM, 2011) and measuring the floor dimensions using a graduated measurement tape to give the exact room dimensions to calculate the areas sampled (range for three houses was 7.7-11.6 m²).

The wipe was then placed in a new 120 mL polypropylene, natural-coloured, capped sample bottle (SARSTEDT Australia, South Australia) and retained for analysis.

2.3.6.2.8 Window sill and window trough dust samples

Wipe samples were taken from one or two window sills and window troughs at each house. Fresh Ghost Wipes were used to wipe the accessible window sill or surface adjacent to the window. The sample was collected by wiping within the area first in one direction (i.e. from left to right across the whole sample area), and then re-wiping in a direction at right angles to the first direction (i.e. top to bottom across the whole sample area). Because many window sills are too narrow to wipe within a 10 cm wide frame, a measured 30 cm section of the window sill and the full width of the window sill was wiped. The width and length of the window sill was recorded so that the area could be calculated at a later stage. The wipe was then placed in a new 120 mL polypropylene, natural-coloured, capped sample bottle (SARSTEDT Australia, South Australia) and retained for analysis.

A similar approach was used to sample larger quantities of wipe material from window sill, window trough at the same three houses as described above for large area floor wipes (Section 2.3.6.2.7).

2.3.6.2.9 Mine site samples

Different types of mine site dust and bulk samples were collected based on the mining and mineral processing activities of the site. At an early stage of the project, a list of potential source emission sites from the mine site was discussed with Glencore staff at Mount Isa Mines. This batch of samples was called general source samples ('SS') in this project. They were collected by MIM Environment Department personnel from areas where there was likely accumulation of dust and the authors of this study were advised of the general locations from which the samples were collected. There remains some doubt in the authors' minds as to the exact location of all samples. In some instances, the location from which the sample was obtained will affect the type of lead present in the dust. For example, in the lead smelter, samples from near the concentrate filters and the sinter plant pelletiser would be expected to have significant galena present, whereas in some other parts of the lead smelter, galena would be expected to be absent. They included the dust from both lead (Figure 19) and copper mining and mineral processing activities from Mount Isa Mines, such as the lead ore open cuts, ore material storage site, lead and copper concentrators, and lead and

copper smelter dusts. Stack or off-gas duct dust samples from the lead and copper smelters were also collected to characterise the potential lead-containing particles released from the smelter stacks²⁷. Following the requirement for better understanding of key emission sources, a follow-up sampling plan was implemented. Samples from haul road ('HR') (associated with frequent physical disturbance from trucks on the mine site), surface tailings materials ('TD'), dust from copper and lead smelting facilities ('SD'), and fallout dust from the mine site ('FMM') (the same sampling setting for the residential area). Samples of MIM concentrate stockpiles from the Townsville port storage facility ('TV') were also collected. Samples were dried in CMLR's laboratory at 40 °C overnight, sieved to < 2 mm, and stored in clean vials for future analysis. Solid or aggregate materials, such as slags, were dried and ground using rock grinding equipment in the Earth Sciences preparation laboratory at University of Queensland. The grinders were cleaned carefully between samples.

2.3.6.2.10 Outcrop samples

Two categories of natural outcrop samples were collected from Mount Isa City and the surrounding area (Figure 13, Appendix 1):

- i. outcrops from the Urquhart Shale sequence (Figure 6, page 68) referred to as a natural mineralisation unit ('NMU')
- ii. non-Urquhart Shale geological sequences in and around Mount Isa City's residential area referred to as natural outcrops or background geological rocks ('BGR').

Urquhart Shale (Figure 6) hosts all the economic lead–silver–zinc mineralisation in the Mount Isa deposits (Blake et al., 1990). Representative outcrop samples were collected from various geological units. Specimens sized about 10 cm x 8 cm x 4 cm were collected. The surface rocks were removed and a fresh portion was kept in a new sampling bag to avoid any potential contamination. Each outcrop sample was oven dried, and ground in the Earth Sciences preparation laboratory at The University of Queensland to < 70 μ m to make the samples homogeneous for future analysis.

²⁷ The stack dust samples were collected from flowing gas streams within the respective smelter and reflect the air particulates that would be discharged via the smelter stack exit point at the top of each smelter. These particulate gas stream samples are also distinguished from dust/particulate samples collected at the surface or near surface air , e.g. as fall-out or air particulates from the external area surrounding the sinter and smelter plant facilities.



Figure 19 Lead ore smelting flow chart

2.4 Analytical techniques

2.4.1 Total concentrations

Various standard methods were used for the analysis of elemental concentrations in the soil and dust samples, as discussed in previous documents (NEPC, 1999c²⁸, U.S. EPA, 1994b, NOISH, 2003, Standards Australia, 1997). Samples for total elemental determinations were digested in aqua regia using US EPA (200.2) or an equivalent method. Prepared soils and dust samples from the houses in Mount Isa were sent to different laboratories for total concentration analysis. Details of laboratories used for different types of samples are shown in Table 7. Further details of methods for total concentration determinations are listed in Appendix 2. No interlaboratory comparisons were carried out. Different types of samples were analysed at different times in different laboratories, but all were NATA accredited.

Category	Sample types	Analysed laboratory	Note	Methods
A	Wipes (floor, window sill, window trough, veranda), carpet dust	Queensland Health Forensic & Scientific Services ²⁹	Samples from 23 houses collected in 2008	AS 4482.1 for carpet dust
В	Wipes (floor, carpet, window sill, window trough, veranda), roof gutter dust	Australian Government National Measurement Institute (NMI) ²⁹	Samples from 44 houses collected in 2010	US EPA 6010 for ICP-AES, and US EPA 6020 for ICP-MS (U.S. EPA, 1980)
С	Garden soil, carpet dust, soil PM10, thimbles, mine dust	ALS (Brisbane Environmental Laboratory) ²⁹	Samples from 44 houses collected in 2010 and all soils (< 250 µm)	US EPA SW 846 by ICP-AES (U.S. EPA, 1980)
D	Air particulates and fallout dust, natural outcrops	Earth science geochemistry laboratories and CMLR laboratories in The University of Queensland		Laboratory developed methods with aqua regia or HF+HNO ₃ on hot block

Table 7 Summary of analytical laboratories used for this study

i. Categories A, B, and C

The quality control for samples analysed in Categories A, B, and C (Table 7) are given in Appendix 3.

²⁸ Some methods are given in the revision of the National Environment Protection (Assessment of site contamination) Measure - guideline on investigation levels for soil and groundwater (NEPC, 2013.

²⁹ NATA accredited laboratories against ISO 17025.

ii. Category D

The following paragraphs describe the method used for the analyses of the Category D samples analysed at the University of Queensland.

Air–particulate filters split into four equal portions from the filter centre, fallout dust samples and outcrop samples were acid-digested in a closed-vessel hot block system at 140 °C overnight with acids (double distilled nitric acid + single distilled hydrofluoric acid). Samples were weighed (~0.1 g) and totally digested at 140 °C on hot block system overnight, following the procedure described in Appendix 2. One portion of each air–particulate filter was digested with aqua regia at 140°C on a hot block overnight, following the method described in Appendix 2. The concentrations of trace elements were determined using a Thermo X7 ICP-MS, cooling with a Peltier temperature-controlled spray chamber. Sample preparation and analytical procedures followed those outlined in Eggins et al. (1997) (Appendix 2).

Blanks and replicates were analysed for each batch as quality control. Precision (as a relative standard deviation ('RSD')) of the analysis was determined based on duplicate analyses of sampling for selected samples (Appendix 3). The overall precision for lead in blanks is better than other metals and metalloids. The RSDs for all replicates were < 11 per cent, except AM20.

Analytical accuracy was determined using the certified material NIST SRM 1648a (urban particulate matter) (Appendix 3). Recovery of most elements in NIST SRM 1648a was better with nitric acid + hydrofluoric acid digestion method. About 77 per cent of lead from NIST SRM 1648a with RSD 7 per cent (n = 5) was recovered with aqua regia digestion procedure. In comparison, 93 per cent of lead from NIST SRM 1648a with RSD 4 per cent (n = 6) (see Appendix 3 for complete results of certified reference materials).

Detection limits (three times RSD) for ICP-MS for lead and other heavy metals and metalloids were low. Detection limits (n = 18) for lead, copper, and zinc were 10 ng/mL, 90 ng/mL, and 83 ng/mL, respectively (Appendix 3). The concentrations of metals contained in all blank filters (n = 3) were lower than 178 ng/g for lead and 131 ng/g for copper, and less than the detection limits for zinc and cadmium.

2.4.2 Isotope distribution

All samples analysed for lead isotope features were conducted in the Radiogenic Isotope Facility ('RIF') at The University of Queensland. A Nu plasma highresolution MC-ICP-MS was used for high-precision, lead isotope composition measurements. About 0.1 g quantities of dry samples were leached with 1 mL of double-distilled, hydrochloric acid and 3 mL single-distilled hydrofluoric acid in sealed Teflon beakers on a hot plate (see Appendix 2 for further details). After acid leaching, the digested samples were evaporated and the lead was dissolved in a solution of hydrobromic acid and passed through an ion exchange packed column and the retained lead was then eluted with hydrochloric acid. The standard reference was prepared the same way. Before the final lead isotope analysis step, purified lead was dissolved in 1 mL of 5 ppm thallium-doped 2 per cent nitric acid. Lead concentration levels were screened using a Thermo 7 ICP-MS to make an appropriate concentration (about 15 ppb or less) for MC-ICP-MS. Total lead levels in the blank samples remained below 20 pg and were negligible.

Twenty-three NIST SRM 981 data points were obtained from inclusion in batches of sample data acquisition. During each day run, the machine drift was checked before, during and after scanning. The data were normalised with one constant ²⁰⁵TI/²⁰³TI of 2.3875 which was measured multiple times and the following means and reproducibilities were achieved:

- ²⁰⁷Pb/²⁰⁶Pb = 0.91460 ± 8
- 208 Pb/ 206 Pb = 2.1669 ± 3
- ${}^{206}\text{Pb}/{}^{204}\text{Pb} = 16.941 \pm 5 (\pm 2\sigma \text{ standard deviation}).$

These two sigma standard deviations of the mean correspond to 90 ppm, 150 ppm, and 300 ppm, respectively.

Even though ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb ratios can be measured with a higher precision than the ²⁰⁶Pb/²⁰⁴Pb ratio (Komárek et al., 2008), the ²⁰⁶Pb- based ratios have less discriminatory power, with values approximating 2 for the ²⁰⁸Pb/²⁰⁶Pb ratio and 1 for the ²⁰⁷Pb/²⁰⁶Pb ratio, compared with values of 16 to 19 in the ²⁰⁶Pb/²⁰⁴Pb ratios (Gulson et al., 2015).

- 2.4.3 Molecular properties
- 2.4.3.1 X-ray absorption spectroscopy
- 2.4.3.1.1 XANES instrument setting and data processing

Lead L_{III}-edge XANES spectra were collected at the Australian National Beamline Facility (BL-20B) Photon Factory, Tsukuba Science City, Japan (ring conditions: 2.5 GeV, 300-400 mA). BL–20B was equipped with a channel-cut Si-(111) monochromators, which was detuned by 50 per cent to reject harmonics. The spectra for samples and model compounds were recorded at room temperature and pressure in fluorescence mode, using a 36-element Ge-array detector. The data were collected over 4 beam line visits (December 2008, December 2009, February 2010, and November 2010) with scan parameters as follows:

- i. the pre-edge section, ~12.80–13.00 keV (10-eV steps)
- ii. the X-ray absorption near-edge structure (XANES) section, 13.00– ~13.10 keV (0.25-eV steps or 0.5-eV steps)
- iii. 3 the post-edge section, 13.10 13.30 keV (7 Å-1, 0.2 Å-1 steps in k-space).

A lead foil was used as an internal standard for energy calibration (calibration energy, 13,050 eV), which corresponded to the first peak of the first derivative of the foil spectrum. Solid samples were pressed into aluminium spacers between

two Kapton tape windows (window size, $2 \cdot 10$ mm). A beam size of 4.0 (horizontal) $\times 0.5$ (vertical) mm was used with nitrogen in the I0 ion chamber and krypton in the I1 and I2 ion chambers. Some XANES were collected in the region 13, 050-13,100 eV and the spectra were compared against this range only.

Data analysis, including calibration, averaging, and background subtraction of all spectra and principal component analysis ('PCA'), and target analyses of XANES spectra were performed using the EXAFSPAK software package (George and Pickering, 2000). Spectra were divided into groups based on sample characteristics. To obtain scores and loadings plots, PCA was performed on the entire data set using the program Unscrambler X 10.1. Based on the outcome of the PCA (principal components 1 vs 2; principal components 1 vs 3; and principal components 1 vs 4 (scores plots given in Appendix 4)) the following model compounds were combined because it was unlikely that the linear regression analysis would be able to differentiate between them:

- lead citrate and lead acetate
- galena from Mount Isa (Earth Science) and galena from Mount Isa (Glencore)
- lead absorbed onto goethite and lead humate
- anglesite and plumbojarosite.

Two samples of galena from Mount Isa (MIN2 and MIN3) were separated from the same geological specimen. The lead speciation of these two specimens is expected to be the same, although the crystal structures of the major minerals are galena and sphalerite, respectively, are quite different. Principal components 1 vs 3 score plots confirmed that MIN2 (galena from Mount Isa); MIN3 (galena from Mount Isa); MIN4 (galena from Mount Isa); and MC5 (purchased lead (II) sulfide, CAS 1314-87-0) were grouped closely.

Least-squares linear combination fitting ('LCF') analysis was performed in SPSS 17.0 using an energy range from 13,000 eV to 13,100 eV. Spectra were divided into groups based on the sample's source. The following criteria were used to define the components used for each model:

- i. variables were included or excluded from the model using an F probability of 0.05 for inclusion and 0.10 for exclusion
- ii. the regression coefficients for all the components in the model were positive
- iii. components contributing less than 2 per cent to the model were excluded
- iv. any component where the contribution was < 3 times the error were excluded from the model.

More details on these criteria are given in Section 3.3 (page 217).

2.4.3.1.2 Lead compounds

The XANES spectra of twenty different pure compounds and lead minerals were recorded and processed to compare with environmental samples. The majority of pure lead chemical compounds were purchased from Wako Pure Chemical Industries Ltd in Japan, including:

- lead (II) acetate (CAS 301-04-2)
- lead (II) carbonate (CAS 598-63-0, 99.999%, lead basis)
- lead carbonate basic (2PbCO₃-Pb(OH)₂, CAS 1319-46-6)
- lead (II) chloride (CAS 7758-95-4)
- lead (II) citrate (CAS 512-26-5)
- lead (II) fluoride (CAS 7783-46-2)
- lead (II) hydroxide (CAS 1319-46-6)
- lead (II) nitrate (CAS 10099-74-8, 99.5%)
- lead (II) oxide (CAS 1317-36-8, 99.9%)
- lead (II, IV) oxide (CAS 1314-41-6
- lead (II) hexafluorosilicate (CAS 25808-74-6)
- lead (II) sulfate (CAS 7446-14-2)
- lead (II) sulfide (CAS 1314-87-0, 85.0%).

Researchers from different institutes provided several lead mineral samples: galena and cerussite from Professor Sue Golding (School of Earth's Sciences, The University of Queensland); anglesite from Mount Isa Mines from Dr Stafford McKnight (School of Science and Engineering, University of Ballarat); and galena and pyromorphite from geologists at Mount Isa Mines. Six uncommon lead minerals (molybdophyllite, plumbogummite, leadhillite, plumbojarosite, mendipite, and magnetoplumbite) were provided from Professor Allan Pring at the South Australian Museum, Adelaide. Two lead compounds (lead absorbed humate and lead absorbed by goethite) were synthesised in the CMLR laboratory and in the Chemistry Laboratory at the Photon Factory, Tsukuba, Japan.

2.4.3.1.3 Spiked-lead compounds

Ground boron nitride (Sigma Aldrich, CAS 10043-11-5, powder \approx 1 µm, 98%) was spiked with different and accurately weighed (electronic balance scale, ± 0.01 mg) fractions of pure lead sulfide and lead oxide. The spiking mixtures were mixed homogeneously with an agate mortar and pestle. Two sets of mixing samples (S1O1 and S1O4) were prepared and diluted using boron nitride for uncertainty estimation.

2.4.3.1.4 Lead adsorbed by goethite

Goethite (FeO•(OH)) was synthesised the CMLR laboratory using a slightly modified procedure from Schwertmann and Cornell (2007). Ferrihydrite $((Fe^{3+})_5O_3\bullet(OH)_9)$ was precipitated by adding 180 mL of 5 M potassium hydroxide to 100 mL of 1M ferric nitrate in a 500 mL polyethylene vessel. The suspension was immediately diluted to about 2 L in the vessel with Milli-Q[®] water and kept in the oven at 70 °C for 60 hours. The brownish suspension was converted to compact, yellow-brownish goethite. After removing the goethite from the original polyethylene reaction vessel when it was completely dry, it was washed and oven dried at 60 °C for three days. The dry solid goethite was ground into fine powders and stored a new polyethylene container for future use.

The synthesised goethite powder (about 0.4 g) was dissolved in 20 mL Milli-Q[®] water and purged continuously with nitrogen gas. Concentrated nitric acid was used to adjust the pH level to 2 after 3 hours

Lead nitrate (about 0.1 g) was dissolved in 10 mL Milli-Q[®] water and purged with nitrogen gas to give 40 mM lead nitrate solution. Concentrated nitric acid was used to adjust the pH to a level of 3–4 after 3 hours to avoid the precipitation of lead II oxide and lead carbonate. Both solutions were purged with nitrogen gas for a further 7 hours before 1.1 mL of lead nitrate solution was added to the goethite suspension. The goethite suspension was centrifuged and extracted after the nitrogen gas was purged for another 18 h. An XANES spectrum of the as-prepared fresh goethite precipitate was collected and is referred to as lead adsorbed by goethite (or lead–goethite) in this study.

2.4.3.1.5 Lead adsorbed by humate

Humic acid (sodium salt, Aldrich chemicals) (CAS 68131-04-4) was used in this study. About 0.4 g of humic acid (sodium salt) was dissolved in 20 mL Milli-Q[®] water and purged with nitrogen gas for 30 minutes before the lead nitrate solution was added. The humate precipitate was centrifuged and extracted after the nitrogen gas was purged for another 25 hours. The fresh humate precipitate was scanned for XANES spectra after it was prepared and is referred to as lead adsorbed by humate (lead–humate) in this study.

2.4.3.2 X-ray diffraction

All XRD analysis was conducted in the Centre for Microscopy and Microanalysis ('CMM') at The University of Queensland, using a Bruker D8 Advance X-Ray Diffractometer, equipped with a graphite monochromator, copper target, and scintillation counter (detector). Dry solid materials were ground with micro-grinder to achieve appropriate particle size for XRD analysis. The ground samples were then exposed to a computer-controlled X-ray powder diffraction instrument. Patterns were recorded as step scans (0.02°, 20 steps 1°/min) from 4° to 60°. All raw data was analysed with the EVATM program (Bruker, 2010). The identifications of mineral forms in sample spectra were also confirmed by matching X-ray diffraction patterns of known pure mineral samples to those in EVATM database.

2.4.4 Physical properties

2.4.4.1 *Particle size*

The particle-size ('PS') analysis was conducted with a Malvern Mastersizer 2000, at the School of Chemical Engineering at The University of Queensland. The same protocol for using this instrument has been followed for all samples. The Mastersizer 2000 laser diffraction-based particle size analyser was developed to meet a growing need for global comparability of results, traceability, regulatory compliance, and efficiency in the laboratory. It incorporates a standard operation procedure and measures samples materials ranging from 0.02 μ m to 2000 μ m, with ± 1 per cent accuracy using the Malvern Quality Audit Standard as guided by ISO13320 (Malvern Instruments Limited, 2009). A small amount (approximately 0.5–1.0 g) of sample was dispersed in water until it reached the amount of light obscuration required by the Malvern Mastersizer (Malvern Instruments Limited). Particles in suspension were then measured by recirculating the sample in front of the laser beam. The scattering data was recorded and calculated to give the particle size distributions of samples.

The repeatability of particle size analysis using the Mastersizer 2000 laser diffraction-based particle size analyser was measured for seven samples with different matrices. PS1 is laboratory-synthesised goethite and PS2 is pure lead (II) sulfide (WAKO Chemicals, Japan (CAS 1314-87-0). PS3, PS4, and PS5 are the mixed samples of PS1 and PS2 with different ratios. Two ground (< 20 μ m) environmental samples collected from Mount Isa City (Noller et al., 2009) were also measured. The results of repeatability of particle size analysis are given in Section 3.8 (page 295).

2.4.4.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used for investigating the appearance and morphology of the different materials as this is the best analytical technique for obtaining high magnification, three dimensional images of small particles, together with elemental composition. Energy dispersive x-ray analysis can, simultaneously, provide semi-quantitative chemistry of individual particles. The purpose was to use SEM to give qualitative information on the morphology of air particulates compared with soil and carpet dust and the presence of heavy atoms, particularly lead. Morphology and elemental composition are key parameters for bioavailability of materials. SEM allows quick study of both morphology and composition of biological and physical materials. The image of samples can be shown directly on a computer by connecting a charge coupled device (CCD) camera to the microscopy. Such details can then be related to particle size distribution and elemental and molecular composition data, particularly for lead.

SEM investigation of HVA and city residential PM10-air samples was conducted at the Centre for Microscopy and Microanalysis at The University of Queensland using a JEOL 6460 SEM (Tungsten filament, 0-30kV, EDS, low vacuum). Samples were imaged with a beam up to a maximum level of 30 kV. The spectra were than processed with the Station program for peak identification and labelling. Air–particulate samples from Mount Isa city, were also scanned using SEM-EDS at the US Geological Survey ('USGS') in Denver, CO, USA. The SEM analysis was performed using a FEI Quanta 450 field emission gun SEM operating in low-vacuum mode. Standardless EDS analyses were acquired with an EDAX 10 mm² silicon drift detector. Data reduction was performed using the EDAX TEAM standardless analysis package, using automated background subtraction and normalisation to 100% totals.

2.4.5 Bioavailability and bioaccessibility

2.4.5.1 Bioavailability

2.4.5.1.1 Sample selection

A key challenge was to select samples for rat bioavailability that are representative of a class of samples and can be used for subsequent risk assessment for estimating of potential absorption after ingestion of lead-containing materials by human receptors in Mount Isa. The number of samples that can be processed is usually limited by the cost of undertaking animal uptake studies. A limited range of samples for bioavailability measurement are usually selected that can then be used to compare with other predictive measurements such as bioaccessibility that are more practical to undertake in larger numbers (Noller et al., 2009). The classes of samples selected for measurement of rat bioavailability are shown in Table 8. Composites were prepared by mixing equal proportions of several samples to produce a representative sample for a particular class of material. Some samples were from specific, individual samplings. All samples were shown to reflect specific kinds of samples that would be important to be characterised by measurement of rat bioavailability (Table 8).

Sample ID	Samples description	Rationale		
CS	Composite sample of garden soil from residential blocks with houses at Mount Isa	Characterise the sample matrix for lead found in soil		
RG	Composite of roof gutters from houses at Mount Isa	Characterise the sample matrix for lead found in roof gutter dust		
VD	Composite of carpet dust from houses at Mount Isa	Characterise the sample matrix for lead found in carpet dust		
SS22	Lead smelter surface dust	Single sample identified as a key source material		
SS13	Tailing Dam 5	Surface material from tailings that may become windborne		
L13	Historical river sediment west embankment Leichhardt River L13 Pb 44,944 mg/kg	Historical river sediment from Leichhardt River showing highest lead concentration (Noller et al. 2009, Sample L13)		
H2	RSL Gate adjacent to the Barkly Highway — exposed natural mineralisation	Single sample of naturally — occurring mineralisation found in town area		
SS26	Lead concentrator dust	Single sample identified as a key source material		
SS27	Copper smelter dust	Single sample identified as a key source material		
HVAP	High-volume air–particulates slurry	Composite slurry prepared from 50 air-particulate PM_{10} filters collected from 10 filters at each of five sites in Mount Isa during the period 3 July to 30 December 2008		

Table 8 Classes of samples selected for measurement of rat bioavailability

2.4.5.1.2 High volume air particulates suspension

A suspension of composite high volume air particulates of PM_{10} (HVAP slurry) was prepared from the combination of 50 air-sampling filters (20.3 x 25.4 mm filter — model EPM 2000). These filters were deployed at five sites in Mount Isa City (Figure 14, page 125) to collect atmospheric particulates during the period 3 July 2008 to 30 December 2008 (Section 2.3.6.1.1, page 127). Ten air-sampling filters at each of five sites (Kruttschnitt (K) Oval, Miles St, Racecourse, the RSL Club and BSD) were used to prepare composite slurry for the rat uptake experiment. A slurry was made because the rats could not be fed filter material directly by oral gavage.

The particulates on the surface of filters were gently brushed using a clean plastic paintbrush. The combination of dust and filter fibre was then dispersed in Milli-Q[®]
water (50%:50% in volume) in a beaker. The beaker was placed in the ultra-sonic bath for 1 hour to separate the particulates and filter fibre. The particulate matter then settled on the bottom of the beaker and filter fibre on the top was removed manually using a spatula. The separation step was repeated 3 to 5 times until most of filter fibre was removed from the suspension. The suspension was centrifuged at 910 g and the supernatant liquid was decanted. The suspension was evaporated at 50 °C in an oven until the suspension was dry and retained any soluble lead. The particulates from the 50 HVA filters were finally converted into 150 mL slurry by adding Milli-Q[®] water. The slurry was stored in a clean plastic container until required and described as HVAP slurry.

The total concentration of Pb in the slurry was measured by digesting two mL of the HVA slurry with 2mL (1+1) nitric acid and 1mL of (1+1) hydrochloric acid (using US-EPA 200.2 method) at 85°C to 95°C for gently boiling and refluxing for 30min. After allowing the beaker to cool, the sample digest solution was quantitatively transferred to a 10mL volumetric flask, made to volume with Milli-Q water, stoppered and mixed. The sample solution was analysed for Pb and other metals using ICP-MS (Section 2.4.1).

2.4.5.1.3 Rat bioavailability experimental design

Rat uptake studies were conducted at the Queensland Health and Forensic Scientific Services Biological Research Facility, Coopers Plains (Animal Ethics approval number 07P05) and the samples were analysed at Entox, a centre of The University of Queensland within the Queensland Health facility.

The 10 samples collected from the Mount Isa mine site and the city (Table 9) were used for the rat bioavailability study. A group of 65 female Sprague Dawley[®] ('SD') rats were purchased from Laboratory Animal Services at the University of Adelaide. Each rat had a body weight of about 200 g. The rats were divided into 10 groups of 5 for each mine waste treatment, with 5 for lead acetate solution i.v. dosing as the positive control (100% bioavailability), 5 for lead acetate solution oral dosing and 5 dosing of water as the negative control group. The dosing regime is detailed in Table 9.

Sample ID	Sample Description	Lead (mg/kg)	Dosage (mg/kg)	Route of administration
CS	Composite sample of garden soil from residential blocks with houses at Mount Isa	118	0.59	Oral gavage
RG	Composite of roof gutters from houses at Mount Isa	3840	19.2	Oral gavage
VD	Composite of carpet dust from houses at Mount Isa	891	4.5	Oral gavage
SS22	Lead smelter dust	44944	224.7	Oral gavage
SS13	Tailing Dam 5	2053	10.3	Oral gavage
LR13	Historical river sediment west embankment Leichhardt RL13 Pb 44, 944 mg/kg	41886	209.4	Oral gavage
H2	RSL Gate adjacent to the Barkly Highway — exposed natural mineralisation	2261	11.3	Oral gavage
SS26	Lead concentrator dust	866000	4330	Oral gavage
SS27	Copper smelter dust	500	2.5	Oral gavage
HVAP	High-volume air–particulates slurry	35.8 mg/L	0.18	Oral gavage (slurry)
Positive control	Lead acetate		1	Intravenous injection
Negative control	Water	-	-	Oral gavage
All groups	Fed wit	h normal roc	lent diet	

Table 9 Dosing regimen for the measurement of lead bioavailability in rats

2.4.5.1.4 Animal experimental procedures

The rats were housed in quarantine room for a minimum of 5 days for a general health status observation before they were released into the animal experimental room for the treatments shown in Table 9. The rats were randomly placed into their respective treatment groups. Blood samples were collected by syringe, body weights were recorded, and then rats were kept in individual metabolic cages for 24-hour urine and faeces collection. The blood samples were taken as background samples for the individual rats. Animals were fasted overnight before dosing the next morning.

Rats were given maximum amount of soil (Table 9) permissible by the Animal Ethics Committee and the amount was standardised at 1 g of soil per 200 g rat

body weight for two reasons. First is to control for amount of soil per body weight bases; and the second is aimed to get sufficient blood Pb concentrations minimising variability in low concentration measurements.

For the soil groups, each rat, under carbon dioxide:oxygen anaesthesia (50:50 mixture), was given 1 g of soil in a 3 mL slurry per 200 g body weight by oral gavage, using a flexible stomach tube. For the negative group, each rat was given an oral dose of 3 mL deionised water. Lead, as lead acetate (Unilab, Ajax Chemicals, Sydney, Australia), was used as the control compound giving 100% bioavailability. For the lead acetate positive group, each rat was injected intravenously with the measured dose in a 0.1 mL solution via the tail vein. Immediately after dosing, the rats were placed back into their individual metabolic cages for 24-hour urine and faeces collections over 10 days. The rats were given a normal rodent diet and water *ad libitum*. After this sample collection period, all animals the rats were sacrificed using an overdose of carbon dioxide:oxygen mixture.

Blood samples were collected from the orally dosed rats at 6-hours post dosing to develop a blood profile. For the rats injected with lead acetate solution intravenously, blood samples were collected at 15, 30, 60 minute and 6 hour time intervals to develop a blood profile. After the initial sampling, blood samples were collected from each rat at 24-hour intervals after dosing until necropsy. At necropsy, a final blood sample was collected in addition to a visual examination and collection of liver, kidney, and spleen samples. All samples were stored at -20 °C until analysed. Blood and urine lead measurements were used for lead bioavailability calculations. Blood and urine lead concentrations were measured using ICP-MS.

2.4.5.1.5 Rat blood samples

The alkaline method (Nunes et al., 2010) with Triton-X100 was used to digest the blood samples taken from rats. By decreasing the blood sample size (one drop ~10 μ L) and reagent (1 mL) and keeping the proportionally reduced amounts of the reagents, it was possible to collect samples from rats ethically and frequently enough to have appropriate number of samplings to establish a curve profile to calculate bioavailability. Approximately 0.05 mL blood, which is the volume of a thick drop of blood, was taken from the rat's tail vein and transferred into a 1.5 mL per weighted Eppendorf tube, which was weighed. Adding 0.1 mL of alkaline solution (5 g of EDTA + 5 mL 0.01% Triton-X100 + 25 mL ammonium hydroxide 25% in 500 mL Milli-Q[®] water), 1 mL Milli-Q[®] water and the content was weighed at each step to a 4 decimal place of accuracy, using an electronic balance. The dilution factor was noted for the final calculation of elemental concentration obtained from the ICP-MS data.

2.4.5.1.6 Rat urine samples

Urine samples (24-hour) were collected using the metabolic cages for individual rats and faeces were collected in separate tubes. The cold dilution method was used for urine digestion in this study. This method was adapted from that used at Queensland Health and Forensic Scientific Services Biological Research Facility,

Coopers Plains, a NATA-accredited trace metals laboratory (Accreditation No. 41) (Agilent Technologies, 2000). Urine samples were thawed and mixed on a roller mixer (\approx 1h) and then left upright to settle for 5 minutes before sampling. A 0.5 mL aliquot of urine and 0.25 mL of 0.001% Triton-X100 was transferred into a 5 mL polypropylene natural cap tube (Sarstedt/Banksia) and 4.25 mL of 2 per cent nitric acid was added to make the volume to 5 mL and 0.1 mL of internal standard for all tubes (Agilent Technologies, 2000). This diluted solution was mixed on the roller mixer for 1 minute and centrifuged at 910 g (Beckman Coulter, Allegra X-15R) for 10 minutes before analysis.

2.4.5.1.7 Quality control

With each batch of mine waste, blood, or urine, three certified reference materials ('CRMs') were prepared for every 100 samples (Seronorm, Sero multi-element for blood, Lyphocheck for urine, Bio-Rad, California, US). The recovery of each element within the CRM was then compared to the certified concentration after analysis (Appendix 3). Internal standards were also added to each assay solution to account for instrument drift (stability).

2.4.5.1.8 Calculation of bioavailability

Bioavailability can be measured by comparing levels in the organs, blood, or urinary excretion of an orally dosed animal to that of an animal given an intravenous dose. The intravenously dosed animal is assumed to be 100 per cent for a substance such as lead acetate, which is completely soluble in water.

The plot of blood or urine concentrations vs time gives the dose response for a particular combination of the sample ingested. The usual practice is to estimate the area under the curve ('AUC') by calculating the blood or urine concentrations on the Y-axis against collection time points on the X-axis using Graph Pad Prism statistical software. The bioavailability as ABA is then calculated by comparing the AUC of the dosed animal to the AUC of the lead acetate dosed animals that are assumed to be 100%. Complete details are given in Appendix 6.

Absolute bioavailability ('ABA') and relative bioavailability ('RBA') are calculated using Equation 5 and Equation 6, respectively. These equations are applicable to blood or urine. Similarly ABA and RBA can be calculated by comparing tissue concentration increase due to the treatment against a reference group.

ABA = (AUC_{oral-test} x Dose_{iv-reference}) x 100% / (AUC_{iv-reference} x Dose_{oral-test}) Equation 5

Where:

oral = oral gavage

iv = intravenous injection

AUC = the area of under the curve of blood or urinary concentrations of the respective test and reference items over prescribed time intervals.

The amount of soils were controlled rather the dosage (mg/kg b.w.). The latter resulted in different amounts of soils given to different groups of rats. This was also a variable and unfortunately not all the variables could be controlled.

Alternatively, specific tissue concentration for the respective treatment group has been used in lieu of AUC for estimating bioavailability.

RBA = (AUC_{oral-test} x Dose_{oral-reference}) x 100% / (AUC_{oral-reference} x Dose_{oral-test}) Equation 6

2.4.5.2 Bioaccessibility using physiologically based extraction test

The PBET test is a two-stage extraction process using various enzymes to simulate both gastric and small intestine compartments with extraction carried out in a water bath at 37 °C (Ruby et al., 1993) (Table 10). Samples were introduced into the simulated gastric solution to solubilise bioaccessible metals and metalloids. The conditions were then modified after a stomach sample was collected to simulate the small intestine. The reaction vessels for the extraction were argon-purged to keep the system under anoxic conditions. Following 2009, end-to-end rotation was used for agitation. The metal content of the extracts was determined by ICP-MS. The detailed experiment procedures are described in Appendix 2.

The analytical sequence included a 1-hour gastric phase extraction and a 2-hour intestine phase. Concentrated nitric acid was used for adjusting the pH when making the gastric solution and 10 M sodium hydroxide and sodium bicarbonate solutions were used for adjusting the pH to 7 for the intestine extraction to mimic different GI phases (Table 10).

Phases	Stomach Phase			Intestinal phase
	Fasted-solution	Mean-solution	Fed-solution	Small intestine
	1	2	3	
pН	1.3	2.5	4.0	7.0

Table 10 pH setting of PBET gastro-intestinal simulations

After the preparation was completed, samples were weighed into clean tubes and mixed in the gastric solution by gentle shaking. The tubes were then put in a water bath (37° C) and pumped with argon gas. Generally, a 1.5 mL PBET solution from each tube was used at 20-minute, 40-minute, and 60-minute intervals in the stomach phase, which took about 1 hour (to disconnect the tube, remove the lid, sub-sample 1.5 mL solution from the tube, add back 1.5 mL gastric solution, replace the lid, and reconnect the tube). Once the aliquot was picked up at the 60-minute interval, the intestinal solution (bile extract and pancreatin) was added. The pH level was adjusted with sodium hydroxide solution (or sodium bicarbonate) to 7, and the volume made up to the original

amount, which was marked on the tube (normally 30 mL for 0.3 g of soil and dust samples). The timing for the fourth phase (pH = 7) solution collection started when the sample tubes were returned to the water bath and argon gas flow recommenced. The final extracted solutions were filtered and diluted for ICP-MS to analysis concentrations of metals and metalloids.

For each batch of analysis, procedure blanks and replicates were analysed for quality control³⁰. Reproducibility of extraction analyses was based on replicates (n = 18) of the Entox in-house quality control materials (Appendix 3). Reproducibility of bioaccessibility (%) for lead is 40 per cent RSD for EnTox of inhouse quality control material (n = 18).

2.4.6 Summary of methods

A summary of preparation methods for samples for each analysis is shown in Table 11.

Technique	Sample preparation
Acid digestion for ICP-MS	US EPA Method 200.2 AS 4479.2 and laboratory-based methods
Column chemistry for lead isotope ratios analysis by MC-ICP-MS	Method adapted from Radio Isotope Facility
XAS	Samples ground to a micro scale (< 20 µm)
PBET	Homogenise sieved (< 2 mm or < 250 µm) samples
XRD	Samples ground to a micro scale (< 20 µm)
SEM-EDS	Samples rinsed in resin and gently polished
Particle size analysis	Homogenise sieved (size specified) samples

Table 11 Summary of samples preparation methods for key techniques in this study

³⁰ This study calculated the mean of BAc obtained from the four pH values over the whole gastrointestinal tract. The average pH representing the fast, semi-fed and full-fed states of the stomach and the near neutral pH of the intestine was selected to provide an intermediate pH for testing in the PBET and represents a nutritional status intermediate between fasting and fed states.

2.5 Modelling technique

Certain health effects can occur at particular levels of lead in children's blood, according to the human health risk assessment process described by enHealth(enHealth, 2012). The NHMRC has recommended a blood lead level of below 10 µg/dL for all Australians (NHMRC, 2009)³¹. This lead level, however, should be considered as the level at which sources of exposure should be investigated, rather than a simple interpretation of a 'safe' level or a 'level of concern'. Given the common concern of public health and the management goal of the NHMRC about levels of lead in the study area, prediction of blood lead concentrations in children for particular types of lead exposure from the environment is a crucial approach to enable an integrated understanding of potential community exposure to be assessed from local mining activities.

A number of models have been developed to predict human blood lead concentrations from exposure to lead (O'Flaherty, 1998, Pounds and Leggett, 1998, U.S. EPA, 2010). The Integrated Exposure Uptake Biokinetic Model ('IEUBK') model was developed by the US EPA and has been in use for about 20 years (U.S. EPA, 2010). Besides the availability and validation capability, the IEUBK model has been widely used in regulatory decision making in relation to children's health risk assessments (Díaz-Barriga et al., 1997, Dong and Hu, 2012).

The IEUBK model was designed to predict blood lead concentration for children of between 1–84 months of age (0.5–7 years) because this group are particularly sensitive to adverse health effects from lead exposure (U.S. EPA, 2010). An outline of the IEUBK model for lead is displayed in Figure 20 (page 156). Briefly, the IEUBK blood lead modelling for children in this study used a number of site-specific data. The model is designed to mimic lead exposure from air, water, soil, dust, diet, and alternative sources to predict blood lead levels in young children³². The IEUBK program used in this study is Windows version 1.1 Build 11, downloaded from the US EPA website (U.S. EPA, 2010).

The IEUBK model has four major components (U.S. EPA, 2007c):

- i. *Exposure component*: This module uses lead concentrations of environmental media to calculate the amount of lead entering a child's body. The lead input parameters are age-dependent intake via inhalation and ingestion pathways.
- ii. Uptake component: This module relates to the bioavailability of leadcontaining materials and is expressed as the gastrointestinal and lung

³¹ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

³² While the USEPA (2010) Integrated Exposure Uptake Biokinetic (IEUBK) model for blood lead prediction uses an age range of 0.5-7 years as default, the Queensland Health blood lead surveys at Mount Isa surveyed children 1-4 years of age. Thus both age groups have been considered.

coefficients to calculate the amount of lead that enters a child's bloodstream with site-specific data.

- iii. *Biokinetic component*: This module is a mathematic expression of the metabolism of lead in human body. It converts the total lead uptake rate from the uptake component into an input to the central plasma-extracellular fluid ('ECF') compartment.
- iv. *Output component* (probability variability module of exposure): This module describes the population distribution variability of a certain outcome, for example, blood lead concentrations greater than the 10 μg/dL recommended by the NH&MRC (2009)³³.

The IEUBK model inserts default values whenever site-specific information is not used. The additional site-specific parameters used for the blood lead simulation for 67 houses at Mount Isa by IEUBK win v1.1 (U.S. EPA, 2007c) are summarised in the Table 12 (page 154). The site-specific blood lead evaluation using IEUBK also required concentration data from each sampled house and these outputs are in Section 3.9 (page 301).

The main uncertainties arising from the use of the IEUBK model for site-specific blood lead level predictions are in the input values used. These are summarised as follows:

- (i) Sampling bias and measurement errors in total concentrations and bioaccessibilities
- (ii) Age-based lead exposure data, such as soil and dust ingestion rates, ventilation rate and time spent outdoors
- (iii) Food: the possibility that eating locally grown fruit and vegetables can influence the uncertainty of the site-specific IEUBK predictions
- (iv) Water: lead pipe plumbing is not widespread in Australian homes but the use of lead based solder on brass fittings and copper pipes was common up until 1989. The possibility of drinking lead contaminated water can influence the uncertainty of the site-specific IEUBK predictions.

The choice of geometric standard deviation ('GSD') is a very sensitive parameter. The IEUBK model uses a log-normal probability distribution to characterise the variability in blood lead concentrations among children having contact with the same concentrations of environmental lead. The default GSD is 1.6, which was derived from empirical studies in the USA (Midvale, Utah; Baltimore, Maryland; and Butte, Montana) with young children where both blood lead and environmental lead concentrations were measured. The US EPA documents

³³ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

state that accurate calculation of a site-specific GSD value is a complex procedure involving significantly more effort than a simple analysis of blood lead results and recommend that IEUBK model users should not substitute alternate value for the default GSD without detailed site-specific studies (U.S. EPA, 2010).

Input	Parameters	Unit	IEUBK default	Site-specific data	Site-specific data sources	Note
Air data	Indoor air–lead concentration (percentage of outdoor)	%	30	59	This study	
	Outdoor air-lead concentration	µg/m³	0.1	0.07	This study	
	Time spent outdoor	h/day	1–4	IEUBK default		Age specific
	Ventilation rate	m³/day	2–7	IEUBK default		Age specific
	Lung absorption	%	32	IEUBK default		
Dietary data	Dietary lead intake	µg Pb/day	1.95–2.26	3.2–6.7	FSANZ (2003) with conversion to µg/day using mean body weight from US EPA (2011)	Age specific
	Dietary lead bioavailability	%	50	IEUBK default		
Water	Water lead concentration	µg/L		0.6	Mount Isa Water Board (2010)	
	Water consumption	L	0.2–0.59	0.271–0.414	US EPA (2011)	Age specific
	Water lead bioavailability	%	50	IEUBK default		
Soil–dust	Soil–dust ingestion weighting factor (per cent soil)	%	45	50	enHealth (2010)	
	Outdoor soil lead concentration	µg/g	200	House-based	This study	
	Indoor carpet dust Pb concentration	µg/g	200	House-based	This study	
	Amount of soil–dust ingested daily	g/day	0.085–0.135	0.06, 0.1	NEPC (1999, 2013), enHealth (enHealth, 2012), US EPA (2011)	0–years
	Soil lead bioavailability	%	30	House-based ¹	This study	
	Indoor dust lead bioavailability	%	30	House-based ²	This study	
Maternal	Mother's blood lead concentration at childbirth	µg Pb/dL	1	1.2	Lesjak (2011)	
IEUBK output	Blood lead geometric mean	µg/dL		House-based	Predicted by IEUBK program	

Table 12 Site-specific parameters for 67 houses located in Mount Isa City by IEUBK win v1.1 (U.S. EPA, 2010)

Note: ① One house had no soil and the median lead concentration for all soil samples was applied. ② Lead levels in carpet dust were considered as indoor dust in the IEUBK program.



Figure 20 Biological structure of IEUBK model (U.S. EPA, 2007c)

The IEUBK program uses the components in Figure 20 to predict geometric mean blood lead concentrations and construct the probability distribution of children's blood lead concentrations centred on the geometric mean blood lead concentrations.

Geometric standard deviation is a measure of the relative variability in blood lead of a child of a specified age, or children from a hypothetical population whose lead exposures are known. It encompasses biological and behavioural differences, and measurement variability. (U.S. EPA, 2007c).

The recommended GSD value (1.6) is based on specific data from several neighbourhoods in Mount Isa City, with paired data for environmental lead concentration and measured blood lead levels. This recommended GSD value was used to construct the mean blood lead concentrations for children as IEUBK outputs (U.S. EPA, 2007c). The IEUBK model is not designed for the worst-case scenario, but provides an appropriate estimation of geometric mean blood lead concentrations for the children living at known exposure conditions. It represents an ongoing effort to generate the most current information on lead risk assessment science and policy³⁴. The model does not inherently implement any uncertainty or modifying factors in making lead risk estimations. By using sensitivity analyses, however, the uncertainty about the model parameters can be evaluated.

2.6 Statistical Analysis

The first step of the statistical analysis of data sets is to determine whether the data follow a normal or non-normal distribution. A normal distribution is that typically represented by a bell-shaped curve with half the data falling either side of the mean value. There are certain statistical tests that can be applied to a normal distribution to determine whether the measured differences between data sets are significant or whether they just occur by chance. These are referred to as 'parametric' tests.

A non-normal distribution is one where the shape of the curve representing the distribution is not the classic bell shape. It can be distorted or skewed in either direction. The parametric statistical tests that are used for a normal distribution cannot be used in cases where the distribution is not normal, and 'non-parametric' statistical tests must be used instead.

Therefore, it is important to examine how well the measured data can be approximated by the normal distribution before applying parametric tests. The Kolmogorov-Smirnov test, the Shapiro-Wilk test, and the Lilliefors test are commonly used as a normality test (Siegel and Castellan, 1988). The fit of the distribution for target dataset can be assessed against the theoretical normal distribution by a Quantile-Quantile plot (a 'Q-Q plot'). All statistical comparisons were evaluated against a 5 per cent significance level (p < 0.05).

The Shapiro-Wilk test and Q-Q plots were used to test for normal data distributions. The Q-Q plots display if sample concentrations for a particular metal or metalloid lie on the normal distribution line and were used to confirm the extent to which data was not normally distributed. The results of using the Shapiro-Wilk test for normality of distribution then indicated that the most of the data were not

³⁴ The revision of the National Environment Protection (Assessment of site contamination) Measure - guideline on investigation levels for soil and groundwater (NEPC, 2013) now permits using the IEUBK model to predict child blood lead level via ingestion based on soil total lead concentration. In addition, measured bioaccessibility of lead is allowed by NEPC (2013) for predicting its bioavailability in soil.

normally distributed and therefore it was considered appropriate to use nonparametric statistical tests for evaluating those data sets.

Spearman's rank correlation coefficient is a non-parametric approach to statistically measure the relationship between two variables. It gives a measure of rank order for individual groups (Siegel and Castellan, 1988). The rank value can range from -1 to +1, indicating a perfect negative correlation and positive correlation of two observations. A value of 1 represents a lack of correlation between the observed variables.

The Mann-Whitney U test is a non-parametric alternative measurement to the ttest for independent samples and based on rank sums instead of means. The rank is the order in which members of a series lie in that series such that for any two items in the series the first is ranked higher, lower or equal to the second. The assumption is that the observed variables are measured have at least a rank order. The interpretation of the result from the Mann-Whitney U test is also identical to that of a Student's t-test (which is used for a normal distribution) for paired groups. The median is a calculated value that can be used to compare values between data sets but is not the value used in the Mann-Whitney U test.

The Kruskal-Wallis test is a non-parametric alternative to one-way (betweengroups) analysis of variance ('ANOVA') for three or more independent groups. Different from the parametric one-way ANOVA, the interpretation of the Kruskal-Wallis test is based on ranks rather than means (Siegel and Castellan, 1988). The null hypothesis of Kruskal-Wallis test is that the different sets of samples are from the same distribution or from distributions with the same median (i.e. there is no statistically significant difference) and is proven when p > 0.05 (Kruskal and Wallis, 1952). However, there is a statistically significant difference between the data sets when the Kruskal-Wallis test result is p < 0.05.

Principal component analysis ('PCA') is another non-parametric test. It is a practical tool for reducing the number of dimensions of observed variables while maintaining the maximum variability of the variance-covariance structure of the data by orthogonal transformation processes into a new coordination system (Shaw, 2003). This enables associations of sets of variables to be made. The variables converted using the PCA, which have no linear correlations and contain the maximum information of the transformed dimensions, are called 'principal components'. The application of PCA helps to explore the role of the original variables and their explanation by different principal components. PCA also helps with understanding the interrelation between sample groups. Principal component analysis is a mathematical procedure that uses orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. The number of principal components is less than or equal to the number of original variables. This transformation is defined in such a way that the first principal component has the largest possible variance (that is, accounts for as much of the variability in the data as possible), and each succeeding component has the highest remaining variance possible under the constraint that it be orthogonal to (i.e., uncorrelated with) the preceding components. The principal component analysis eigenvalue scree plot gives the percentage of total variance that is assigned to each component.

An organised project needs a sound statistical approach to interpret extensive datasets. The data on the concentrations of elements in samples collected in this study were generally processed following the summary shown in Figure 21 using Microsoft Excel 2007 and the STATISTICA 11 program. The major statistical tests for other datasets, such as lead isotope ratios, XAS spectra, and particle-size data were also applied, when necessary. The results of the analyses are discussed in Chapter 3 and Chapter 4 (page 324).



Figure 21 Summary of sequence for data analysis with a statistical approach

Because the tests show that many of these data are non-normal, the discussion often uses the *median* value rather than the *mean* value.

3 RESULTS

3.1 Total concentrations of metals and metalloid

The total concentration and related data for elemental concentrations discussed in Chapter 2 (page 96) is referred to as 'metals and metalloids'. However, as there is only one metalloid (arsenic) referred to in the results, together with a range of metals, the collective expression 'metals and the metalloid' is applied to the remainder of this report.

3.1.1 Normality of elemental concentration data

The Shapiro-Wilk test was used to test the normality of metals and metalloid concentration data in this study (Section 2.6). The summary of results from the Shapiro-Wilk test is given in Table 13, Table 14, Table 15, and Table 16. Compared with natural mineralisation and mine site dust samples (Table 13 and Table 14), metals and metalloid concentrations in samples from the residential area (Table 15) are less likely to be normally distributed, except for iron, manganese, and nickel found in city fallout dust and manganese in carpet dust. Lead in most of mine dust samples shows a normal distribution pattern. Metals and metalloid concentration data in air particulates from the mine site and the city's residential area are not normally distributed either (Table 16). Therefore, nonparametric statistical tests were required to statistically test data sets. Q-Q plots were also used to assess the degree to which data sets are normally distributed. The Q-Q plots are consistent with the Shapiro-Wilk test results and indicated that the data sets of elements in most samples do not have a normal distribution. The Q-Q plots for each individual sample category and element combination are given in Appendix 5. Most data sets were not normally distributed.

Table 13 Shapiro-Wilk Test for total concentration data of metals and the metalloid in natural outcrop samples in and near Mount Isa City [natural mineralisation (NMU) and natural outcrop (BGR)]

Sample types	Metal or metalloid	W-value	p-Value	Note
	Arsenic	0.6701	0.0002	
	Cadmium	0.8508	0.2286	Normal
	Cobalt	0.8975	0.2744	Normal
Outcrops	Copper	0.6443	0.0000	
	Iron	0.8459	0.0073	
	Lead	0.59	0.0000	
	Manganese	0.7485	0.0006	
	Zinc	0.9733	0.9136	Normal

Note: 1. If the W statistic is significant (p value < 0.05), then the hypothesis that the respective distribution is normal should be rejected. 2. The p-value with bold font means the W statistic is significant — there is insufficient evidence to reject the assumption of normality

Table 14 Shapiro-Wilk Test for total concentration data of metal and the metalloid in samples from the Mount Isa mine site

Sample type	Metal or metalloid	W-value	p-Value	Note
	Arsenic	0.6342	0.0001	
	Cadmium	0.6773	0.0055	
	Cobalt	0.6949	0.0008	
Fallout dust	Copper	0.8602	0.0767	Normal
(mine site)	Iron	0.7739	0.0070	
	Lead	0.9351	0.2938	Normal
	Manganese	0.8711	0.1030	Normal
	Nickel	0.8965	0.3910	Normal
	Zinc	0.818	0.0240	
	Arsenic	0.7501	0.0054	
	Cadmium	0.9637	0.8365	Normal
Haul road dust	Cobalt	0.7401	0.0042	
	Copper	0.8661	0.1116	Normal
	Iron	0.7413	0.0043	

Sample type	Metal or metalloid	W-value	p-Value	Note
	Lead	0.9412	0.5946	Normal
	Manganese	0.8424	0.0614	Normal
	Nickel	0.9246	0.4314	Normal
	Zinc	0.8941	0.2196	Normal
	Arsenic	0.8778	0.0110	
	Cadmium	0.5	0.0000	
	Cobalt	0.4748	0.0000	
-	Copper	0.5993	0.0000	
Smelter	Iron	0.8372	0.0290	
udot	Lead	0.9165	0.0644	Normal
	Manganese	0.4664	0.0000	
	Nickel	0.6614	0.0002	
	Zinc	0.8951	0.0237	
	Arsenic	0.861	0.0016	
	Cadmium	0.2352	0.0000	
	Cobalt	0.7652	0.0000	
General	Copper	0.5304	0.0000	
source	Iron	0.8431	0.0007	
materials	Lead	0.3487	0.0000	
	Manganese	0.7417	0.0000	
	Nickel	0.9024	0.0130	
	Zinc	0.5457	0.0000	
	Arsenic	0.9305	0.5555	Normal
	Cadmium	0.88	0.2265	Normal
	Cobalt	0.848	0.1179	Normal
Tailings	Copper	0.7696	0.0202	
dam	Iron	0.8587	0.1473	Normal
materials	Lead	0.8817	0.2341	Normal
	Manganese	0.9111	0.4039	Normal
	Nickel	0.968	0.8836	Normal
	Zinc	0.8299	0.0798	Normal
Thimble	Arsenic	0.6507	0.0018	
from lead	Cadmium	0.6103	0.0006	
smelter	Cobalt	0.8879	0.3075	Normal

Sample type	Metal or metalloid	W-value	p-Value	Note
	Copper	0.9271	0.5582	Normal
	Iron	0.8424	0.1366	Normal
	Lead	0.9413	0.6698	Normal
	Manganese	0.9845	0.9717	Normal
	Nickel	0.598	0.0004	
	Zinc	0.8671	0.2151	Normal
	Arsenic	0.7633	0.0052	
	Cadmium	0.6235	0.0001	
	Cobalt	0.7796	0.0082	
Thimble	Copper	0.833	0.0364	
from copper	Iron	0.8747	0.1135	Normal
smelter	Lead	0.5633	0.0000	
	Manganese	0.7325	0.0022	
	Nickel	0.8739	0.1110	Normal
	Zinc	0.7422	0.0029	

Note: 1.) If the W statistic is significant (p value < 0.05), then the hypothesis that the respective distribution is normal should be rejected. 2) The p-value with bold font means the W statistic is significant — there is insufficient evidence to reject the assumption of normality

Table 15 Shapiro-Wilk Test for total concentration data of metals and the metalloid in samples collected from Mount Isa City

Sample type	Metal or metalloid	W-value	p-Value	Note
	Arsenic	0.568	0.0000	
	Cadmium	0.330	0.0000	
	Cobalt	0.894	0.0000	
Garden soil	Copper	0.712	0.0000	
(< 250 µm)	Iron	0.816	0.0000	
	Lead	0.799	0.0000	
	Manganese	0.538	0.0000	
	Nickel	0.907	0.0000	
	Zinc	0.826	0.0000	
PM ₁₀ extracted from	Arsenic	0.866	0.0000	
	Cadmium	0.554	0.0000	
garden soil	Cobalt	0.865	0.0000	

Sample type	Metal or metalloid	W-value	p-Value	Note
	Copper	0.761	0.0000	
	Iron	0.845	0.0000	
	Lead	0.362	0.0000	
	Manganese	0.856	0.008	
	Nickel	0.847	0.0000	
	Zinc	0.580	0.0000	
	Arsenic	0.636	0.0000	
	Cadmium	0.467	0.0000	
	Cobalt	0.619	0.0000	
	Copper	0.465	0.0000	
Roof gutter	Iron	0.524	0.0000	
uuut	Lead	0.462	0.0000	
	Manganese	0.618	0.0000	
	Nickel	0.655	0.0000	
	Zinc	0.642	0.0000	
	Arsenic	0.8775	0.0435	
	Cadmium	0.7138	0.0004	
	Cobalt	0.7793	0.0020	
	Copper	0.664	0.0001	
Fallout dust (city)	Iron	0.9071	0.1220	
(0.1)	Lead	0.8923	0.0727	
	Manganese	0.9629	0.7383	
	Nickel	0.8901	0.0672	
	Zinc			
	Arsenic	0.881	0.0000	
	Cadmium	0.469	0.0000	
	Cobalt	0.902	0.0000	
	Copper	0.649	0.0000	
Carpet dust	Iron	0.8795	0.0000	
	Lead	0.811	0.0000	
	Manganese	0.970	0.380	Normal
	Nickel	0.201	0.0000	
	Zinc	0.700	0.0000	
Carpet	Arsenic	0.243	0.0000	

Sample type	Metal or metalloid	W-value	p-Value	Note
wiper	Cadmium	0.433	0.0000	
	Cobalt	0.293	0.0000	
	Copper	0.159	0.0000	
	Iron	0.204	0.0000	
	Lead	0.180	0.0000	
	Manganese	0.293	0.008	
	Nickel	0.135	0.0000	
	Zinc	0.313	0.0000	
	Arsenic	0.274	0.0000	
	Cadmium	0.214	0.0000	
	Cobalt	0.267	0.0000	
	Copper	0.173	0.0000	
Floor wipe	Iron	0.196	0.0000	
	Lead	0.149	0.0000	
	Manganese	0.383	0.0000	
	Nickel	0.240	0.0000	
	Zinc	0.421	0.0000	
	Arsenic	0.243	0.0000	
	Cadmium	0.435	0.0000	
	Cobalt	0.329	0.0000	
	Copper	0.272	0.0000	
Roof wipe	Iron	0.5296	0.0000	
	Lead	0.291	0.0000	
	Manganese	0.413	0.0000	
	Nickel	0.280	0.0000	
	Zinc	0.209	0.0000	
	Arsenic	0.367	0.0000	
	Cadmium	0.357	0.0000	
	Cobalt	0.620	0.0000	
Window-sill	Copper	0.346	0.0000	
wipe	Iron	0.246	0.0000	
	Lead	0.235	0.0000	
	Manganese	0.469	0.0000	
	Nickel	0.252	0.0000	

Sample type	Metal or metalloid	W-value	p-Value	Note
	Zinc	0.356	0.0000	
	Arsenic	0.710	0.0000	
	Cadmium	0.514	0.0000	
	Cobalt	0.772	0.0000	
	Copper	0.697	0.0000	
Window- trough wipe	Iron	0.764	0.0000	
a cagir mpc	Lead	0.732	0.0000	
	Manganese	0.732	0.0000	
	Nickel	0.414	0.0000	
	Zinc	0.375	0.0000	
	Arsenic	0.454	0.0000	
	Cadmium	0.801	0.0000	
	Cobalt	0.855	0.0000	
	Copper	0.719	0.0000	
Veranda	Iron	0.606	0.0000	
, mpc	Lead	0.754	0.0000	
	Manganese	0.744	0.0000	
	Nickel	0.730	0.0000	
	Zinc	0.792	0.0000	

Note: 1. If the W statistic is significant (p value < 0.05), then the hypothesis that the respective distribution is normal should be rejected. 2) The p-value with bold font means the W statistic is significant — there is insufficient evidence to reject the assumption of normality

Table 16 Shapiro-Wilk Test for total concentration data of metals and the metalloid in air particulates from Mount Isa City on November 2009, November 2010, and May 2011 sampling trips

Sample type	Metal or metalloid	W-value	p-Value	Note
Air particulates (city	Arsenic	0.7574	0.0000	
outdoor)	Cadmium	0.5488	0.0000	
	Cobalt	0.8013	0.0009	
	Copper	0.8397	0.0003	
	Iron	0.5578	0.0000	
	Lead	0.7306	0.0000	
	Manganese	0.5372	0.0000	
	Zinc	0.8202	0.0002	
Air particulates (city	Arsenic	0.8171	0.0147	
indoor)	Cadmium	0.8049	0.0107	
	Cobalt	N/A	N/A	
	Copper	0.8337	0.0233	
	Iron	0.6976	0.0008	
	Lead	0.8214	0.0166	
	Manganese	0.8213	0.0165	
	Zinc	0.791	0.0074	
Air particulates (mine	Arsenic	0.5768	0.0000	
site)	Cadmium	0.3758	0.0000	
	Cobalt	0.6962	0.0000	
	Copper	0.4835	0.0000	
	Iron	0.659	0.0000	
	Lead	0.5533	0.0000	
	Manganese	0.4497	0.0000	
	Zinc	0.638	0.0000	

Note: 1. If the W statistic is significant (p value < 0.05), then the hypothesis that the respective distribution is normal should be rejected. 2. The p-value with bold font means the W statistic is significant — there is insufficient evidence to reject the assumption of normality

Because the tests show that many of these data are non-normal, the discussion often uses the *median* value rather than the *mean* value.

3.1.2 Natural outcrops near Mount Isa City

Table 17 gives the summary of total concentration data for natural outcrops (excluding the Urquhart Shale) from different geological units in Mount Isa City (BGR in Figure 6, page 68). The median concentrations for lead and other metals and the metalloid are relatively low compared with mineralised material and reflect geological sequences that do not contain base metal mineralisation. The median lead concentration for natural outcrop samples from near Mount Isa City

was 41 mg/kg, which was 2–4 times higher than the lead concentrations of 8–20 mg/kg as reported in the bulk continental crust in a previous study (Rudnick and Gao, 2003).

Metal or metalloid	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Zinc
Mean	31	N/A	116	42284	108	1368	693
SD	27	N/A	103	41046	128	1788	679
Minimum	6	N/A	22	903	8	5	213
25th percentile	16	N/A	39	15605	11	47	453
Median	21	N/A	57	26772	41	581	693
75th percentile	30	N/A	164	61806	199	2360	933
Maximum	79	N/A	325	135747	323	5350	1173

Table 17 Total concentrations (mg/kg) of natural outcrop (BGR) near Mount Isa City (n = 13)

SD: Standard deviation; N/A: data not available

3.1.3 Natural mineralisation

Table 18 gives the total concentration data for samples of natural mineralisation; this is principally from the Urquhart Shale sequence in Mount Isa city and one other exposed site on Transmission Street corresponding to the Native Bee sequence (Figure 6). The median concentrations results for arsenic, cadmium, copper, iron, lead and zinc are higher than shown in Table 17 and reflect geological sequences that contain base metal mineralisation ('NMU'). The median concentration of manganese is similar to that for data in Table 17, whereas iron is substantially higher in natural mineralisation. The differences in the median and total concentrations of Mn and Fe in outcrop samples (Table 17 and Table 18) indicated that the Urquhart Shale was a unit enriched in Fecontaining minerals, compared with other geological units under the results of XRD scans for outcrop samples from the Urquhart Shale unit (NM1, NM2, NM3, NM4, and NM5) in Table 120 (page 278) and indicated the occurrences of iron minerals, including goethite, pyrite, and hematite.

Metal or metalloid	Arsenic	Cadmium	Cobalt	Copper	Iron	Lead	Manganese	Zinc
Mean	497	2	27	629	146288	3343	1956	1484
SD	197	2	42	548	60323	1623	3261	801
Minimum	218	0.3	2	143	52175	1184	21	716
25th percentile	429	0.9	3	256	138286	2681	29	901
Median	563	1.2	8	502	168886	3587	501	1375
75th percentile	630	2	32	875	176887	4248	2428	1958
Maximum	645	4	90	1368	190204	5013	6801	2470

Table 18 Total concentrations (mg/kg) of metals and the metalloid in natural mineralisation (NMU) in Mount Isa City (n = 4)

3.1.4 Mine site samples

Different types of mine site dust samples were collected across the mine site (Section 2.3.6, page 126). The results for arsenic, cadmium, copper, iron, lead and zinc are summarised in Table 19 and Figure 22. The metals and metalloid concentrations for all mine samples covered wide concentrations ranges (Table 19). Total lead concentration ranged between 193 and 656,000 mg/kg, with a median of 7530 mg/kg, which is twice that of lead from natural mineralisation (NMU) and 180 times that of other natural outcrops. As shown in Table 18 and Table 19, apart from lead, the total concentrations compared with natural mineralisation are:

- cadmium 38 times concentrations in natural mineralisation
- cobalt 3 times that in natural mineralisation
- copper 7 times that in natural mineralisation
- nickel 2 times that in natural mineralisation
- zinc 6 times that in natural mineralisation.

The total concentrations for the other metals and the metalloid, such as iron, and manganese, are slightly lower in mine site samples than in natural mineralisation examples (Table 18 and Table 19). The total concentrations for each individual data set for the mine site can be found in Appendix 4.

Table 19 Total concentrations (mg/kg) of metals and the metalloid in samples from mine site, including thimbles (ATC and ATP) and dusts (SD) from lead and copper smelter areas, haul road dust (HR), surface tailings (TD) and general source materials (SS)

Metal or metalloid	Arsenic	Cadmium	Cobalt	Copper	Iron	Lead	Manganese	Nickel	Zinc
Mean	1323	6430	279	41875	98642	47902	605	78	29789
SD	4036	21924	448	95232	84225	113929	789	99	51795
Minimum	10.00	0.84	2	38	2010	193	5	1	122.00
25th percentile	190	22	38	1299	41393	2791	134	16	1780
Median	304	45	89	3733	65948	7530	228	34	8750
75th percentile	639	2331	317	9047	139500	31980	690	111	47733
Maximum	32000	125000	3010	576000	296000	656000	2900	464	398739

Note: SD: Standard deviation. N: Number of samples.

The ATP samples, taken from the lead smelter area, had the highest lead concentrations compared with other kinds of samples from the mine site (Figure 22). The median level of lead in ATP is 314,000 mg/kg, which is about 27 times that of fallout dust collected from the mine site ('FMM') and 500 times of that of surface tailings. Comparing lead concentrations in mine site samples using the Kruskal-Wallis ANOVA test, by rank, shows significant differences (Table 20). The sum of ranks and mean rank shown in Table 20 reveal that the highest mean rank (highest overall lead concentration group) appeared in the ATP, followed by dusts from the lead smelter areas (SDP) and FMM samples; and the lowest mean rank (lowest overall lead concentration) appeared in the copper smelter areas (SDC), which is consistent with Figure 22.

Table 20 Kruskal-Wallis ANOVA by Ranks for lead concentration in mine site samples from the Mount Isa mine site (p = 0.0000)

Sample type	Valid n	Sum of Ranks	Mean Rank
Surface tailings material (TD)	10	163	16
Thimbles from copper smelter (ATC)	10	217	22
Haul road dust (HR)	9	215	24
Fallout dust mine site (FMM)	16	641	40
Copper smelter dust areas (SDC)	2	5	2.5
Lead smelter dust areas (SDP)	19	1014	53
Thimbles from lead smelter area (ATP)	6	423	71

Note: p = 0.000 indicates that the analysed groups are significantly different



Figure 22 Total concentrations of metals and the metalloid in mine site dust

Total concentrations of arsenic are very high in particulate samples from the copper smelter area ('ATC') (Figure 22). The median level of arsenic in ATC is 5060 mg/kg, which is about 6 times that in fallout dust collected from mine site and 13 times that in surface tailings material. Total concentrations of cadmium are relatively higher in smelter dusts and particulates (SDP and ATP), particularly from the lead smelter area (Figure 22). The concentrations of copper are higher in copper smelter area samples, such as ATC, which is followed by fallout (FMM) (Figure 22). Total concentrations of iron indicated fewer variations in surface tailings (TD) and fallout dust from the mine site (FMM). Total concentrations of zinc show higher levels in ATP from the lead smelter area, followed by SDP and FMM, whereas cadmium is highest in SDP followed by ATP.

3.1.5 Mount Isa City soil and dust samples

Two types of sampling, namely conventional bulk sampling (mg/kg) of soil and carpet dust and wipe sampling (μ g/m²) for collection of surface dust samples from the city residential area, are described in Section 2.3.6 (page 126). The results for city residential samples are divided into two sections to compare the data with the same units of measurement.

3.1.5.1 *Conventional bulk sampling*

The total concentrations of metals and metalloid for soil and carpet dust materials from the city's residential area are classified and summarised as garden soil < 250 μ m fraction (Table 21), PM₁₀ fraction extracted from garden soil (Table 22), footpath samples (Table 23), fallout dust from backyard (Table 24), roof gutter dust (Table 25), and carpet dust (Table 26).

Total metals and metalloid concentrations for garden soils are compared against the Health Investigation Level (HIL) Level A criterion for houses with gardens³⁵ (Table 21). For 75 per cent of the sample population, neither the metals nor the metalloid in the soil exceed the HIL Level A criteria. Some cadmium, copper, lead, and manganese concentrations are higher than the HIL guideline at values greater than the 75th percentile concentrations.

³⁵ The revised (NEPC, 2013) HIL A (low density residential, including a sizeable garden) criteria for soil contamination (mg/kg) are: arsenic (100), cadmium (20), cobalt (100), copper (7000), iron (N/A), lead (300), manganese (3000), nickel (400) and zinc (8000).

Table 21 Total concentrations (mg/kg) of metals and the metalloid in garden soil (< 250 µm fraction) from Mount Isa City compared to Health Investigation Level A (HIL Level A)

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum	HIL level A*
Arsenic	75	92	12 (9)	2	10	15	50	100
Cadmium	75	75	4 (7)	0.3	2	4	51	20
Cobalt	75	100	13 (4)	4	12	15	27	100
Copper	75	100	442 (455)	46	288	513	2680 ³⁶	1000
Iron	75	100	28,476 (5950)	13,800	27,700	30,750	60,900	N/A
Lead	75	100	225 (214)	12	163	258	1070	300
Manganese	75	100	383 (185)	76	359	402	1747	1500
Nickel	75	100	17 (4)	4	16	19	36	600
Zinc	75	100	525 (471)	42	337	680	2310	7000

Note: * HIL Level A (NEPC, 1999d); N/A = not given by HIL Level A criteria. Bold text indicates that HIL level A is exceeded; SD: Standard deviation; n: Number of samples; LOD: Limit of detection.

Table 22 Total concentrations (mg/kg) of metals and the metalloid in soil $\rm PM_{10}$ fraction from Mount Isa City

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	74	86	39 (28)	3	34	49	130
Cadmium	74	61	8 (13)	0.2	4.5	7.9	85
Cobalt	74	91	25 (9)	12	25	29	63
Copper	74	100	877 (810)	170	571	1087	4600 ³⁷
Iron	49	100	43,863 (12288)	28,100	39,500	49,200	94,300
Lead	74	100	534 (519)	25	359	611	2550
Manganese	64	100	682 (218)	324	625	817	1320
Nickel	74	96	38 (15)	20	34	42	106
Zinc	74	100	1356 (1342)	121	788	1758	6350

Note: Bold text indicates that HIL level A is exceeded; SD: Standard deviation; n: Number of samples; LOD: Limit of detection.

 $^{^{36}}$ The revised (NEPC, 2013) HIL A for copper 7000 mg/kg.

 $^{^{37}}$ The revised (NEPC, 2013) HIL A for copper 7000 mg/kg.

Metal or metalloid	Mean (SD)	Minimum	25th percentile	Median	75th percentile	Maximum
Arsenic	9 (6)	2	4.1	7	13	21
Cadmium	0.7 (0.9)	0.1	0.3	0.4	0.5	3.1
Cobalt	12 (2)	9	11	12	14	17
Copper	235 (260)	71	107	137	162	884
Lead	88 (91)	28	41	50	66	303
Nickel	18 (3)	15	17	18	19	25
Zinc	119 (110)	44	63	74	106	394

Table 23 Total concentrations (mg/kg) of metals and the metalloid in footpath samples from Mount Isa City (n = 14)

Note: Bold text indicates that HIL level A is exceeded; SD: Standard deviation; LOD: Limit of detection.

Table 24 Total concentrations (mg/kg) of metals and the metalloid in fallout from Mount Isa City (n = 15)

Metal or metalloid	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	291(248)	24	298	376	929
Cadmium	29 (33)	4	20	29	113
Cobalt	63 (55)	10	48	70	217
Copper	20,356 (26,534)	2424	11,835	18,003	96,246
Iron	33,198 (14,390)	13,801	31,142	40,034	71,673
Lead	7511 (5974)	1200	6753	10,082	20,989
Manganese	413 (115)	172	396	479	634
Nickel	31 (17)	14	27	42	67
Zinc	5996 (7348)	754	4180	6636	30,783

Note: Bold text indicates that HIL level A is exceeded; SD: Standard deviation

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile
Arsenic	37	100	1139 (1511)	126	638	1229	3494
Cadmium	37	100	109 (197)	11	47	109	360
Cobalt	32	100	247 (329)	20	137	251	887
Copper	37	100	32,433 (61,013)	4570	12,900	20,871	130,220
Iron	37	100	153,590 (225,475)	23,112	70,601	15,1031	521,377
Lead	37	100	16,692 (29,725)	1800	7719	14,035	48,827
Manganese	32	100	921 (1087)	102	571	903	3226
Nickel	32	100	97 (117)	10	47	93	367
Zinc	37	100	31,134 (39,534)	1895	19,173	34,084	136,846

Table 25 Total concentrations (mg/kg) of metals and the metalloid in roof gutter dust from Mount Isa City

Note: Bold text indicates that HIL level A is exceeded; SD: Standard deviation; n: Number of samples; LOD: Limit of detection.

Table 26 Total concentrations (mg/kg) of metals and the metalloid in carpet dust from Mount Isa City

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	58	98	46 (26)	10	40	61	111
Cadmium	58	76	14 (18)	2	8	14	115
Cobalt	39	67	21 (9)	9	19	26	40
Copper	58	100	1816 (1193)	388	1560	2280	6300 ³⁸
Iron	58	100	19,683 (9930)	4800	17,750	22,950	50,600
Lead	58	100	891 (687)	150	721	1078	3400
Manganese	39	100	225 (73)	86	210	285	380
Nickel	39	92	77 (238)	16	34	42	1460
Zinc	58	100	3242 (3098)	470	2020	4138	14,900

Note: Bold text indicates that HIL level A is exceeded; SD: Standard deviation; n: Number of samples; LOD: Limit of detection.

Comparisons between different groups of samples from Mount Isa City are also made for arsenic, cadmium, copper, iron, lead, and zinc (Figure 23). The median lead concentration is highest in the roof gutter dust (7719 mg/kg – note not included in Figure 23) followed by fallout dust in Mount Isa city (6753 mg/kg) and then natural mineralisation, with a lead concentration of 3587 mg/kg. The median levels of lead concentration in carpet dust, soil PM_{10} fraction, and garden soil <

³⁸ The revised (NEPC, 2013) HIL A for copper 7000 mg/kg.

250 µm fraction are 721 mg/kg, 359 mg/kg, and 163 mg/kg, respectively. The median concentration of lead in the natural outcrop units (Table 17) and footpath samples (Table 23) are only 41 mg/kg and 50 mg/kg respectively.

The median arsenic concentration is highest in roof gutter dust (638 mg/kg) followed by natural mineralisation (563 mg/kg), and fallout dust in city (298 mg/kg). The median levels of arsenic concentration in carpet dust, soil PM₁₀ fraction, and garden soil < 250 μ m fraction are 40 mg/kg, 34 mg/kg, and 10 mg/kg respectively. The level of arsenic in natural outcrops (Table 17, page 168) and footpath samples (Table 23) are much lower, with median levels of 21 mg/kg and 7 mg/kg respectively.

The median cadmium concentration is highest in roof gutter dust (47 mg/kg) followed by fallout dust in city (20 mg/kg), and carpet dust, soil PM_{10} fraction, and garden soil < 250 µm fraction, with the median cadmium levels being 8 mg/kg, 4.5 mg/kg, and 2 mg/kg respectively. The median concentration of lead in natural mineralisation (Table 18) and footpath samples (Table 23) are only 1.2 mg/kg and 0.4 mg/kg respectively.

The highest concentrations of copper are in roof gutter dust (12,900 mg/kg) and fallout dust in city (11,835 mg/kg) compared with the other groups (Figure 23), followed by carpet dust, soil PM_{10} fraction, and garden soil < 250 µm fraction, with median copper levels of 1560 mg/kg, 571 mg/kg, and 288 mg/kg respectively. The median concentration of copper in natural outcrops (Table 17), natural mineralisation (Table 18) and footpath samples (Table 23) are 57 mg/kg, 502 mg/kg, and 137 mg/kg respectively.

The distribution of zinc concentrations is very similar to those for lead and cadmium (Figure 23). The median concentration of zinc is highest in roof gutter dust (19,173 mg/kg) followed by fallout dust in city, with a level of 4180 mg/kg. The median zinc concentrations in carpet dust, soil PM_{10} fraction, and garden soil < 250 µm fraction are 2020 mg/kg, 788 mg/kg, and 337 mg/kg respectively. The median concentration of zinc in samples from natural outcrops (Table 17) and natural mineralisation (Table 18) are 1173 mg/kg and 2470 mg/kg respectively. The geographical distribution of zinc in roof gutter dusts (data not shown) shows no correlation with proximity to the mine site, which does not support a mine source for all the zinc. Because galvanised iron is generally used as roofing material of houses in Mount Isa city, there is a potential contribution of zinc to roof gutter dust from this source.



Note: BGR: natural outcrops; NMU: natural mineralisation; FMT: fallout dust from Mount Isa city; CS: soil < 250 μ m fraction; PM₁₀S: PM10 fraction from garden soil; CD: carpet dust; RGD: roof gutter dust data. solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values.



The distribution pattern of iron concentrations is different from the concentrations for arsenic, cadmium, lead, and zinc (Figure 23). The overall iron concentrations in natural mineralisation (Table 18) are higher than for other groups, ranging from 52,175 mg/kg to 190,204 mg/kg with a median level of 168,886 mg/kg. The median level of iron in samples from natural outcrops (BGR), fallout dust from Mount Isa city and soils are similar, but BGR samples had a wider range of iron concentrations. Carpet dust samples had the lowest iron concentration, compared with other samples (Table 18).

Comparison of lead concentrations in soil and dust samples from the city's residential area, using the Kruskal-Wallis ANOVA test by rank, shows significant differences (Table 27). The highest mean rank (highest overall lead concentration group) appeared in the roof gutter dust, followed by FMT samples; the lowest mean rank (lowest overall lead concentration) appeared in the CS samples, which is reflected in Figure 23.

Table 27 Kruskal-Wallis ANOVA by rank for lead concentration in samples from Mount Isa City (p = 0.000)

	Valid number	Sum of ranks	Mean rank
Soil < 250 µm fraction (CS)	75	4548	61
Soil PM ₁₀ fraction (PM10S)	74	8210	111
Carpet dust	58	8798	152
Fallout from city	3	675	225
Roof gutter dust	37	8398	227

Note: p = 0.000 indicates that the analysed groups are significantly different

3.1.5.2 House wipes

The total concentrations of metals and metalloid (in units of $\mu g/m^2$) in soil and dust materials from city residential area are summarised for carpet wipes (Table 28), floor wipes (Table 29), roof wipes (Table 30), window sill wipes (Table 31), window trough wipes (Table 32), and veranda wipes (Table 33). The metals and metalloid concentrations are generally highest for wipes from window trough (WT) (Figure 24).

Comparison of the median lead concentrations shows that the highest group is window trough wipes (20,360 μ g/m²), followed by veranda wipes (1389 μ g/m²), roof wipes (1100 μ g/m²) and window sill wipes (536 μ g/m²). The median lead concentrations in carpet wipes and floor wipes is 71 μ g/m² and 92 μ g/m² (Table 28 and Table 29, respectively).

The median level of arsenic indicates the highest concentration is for window trough wipes (1119 μ g/m²) followed by roof wipes (133 μ g/m²), veranda wipes

(84 μ g/m²) and window-sill wipes (43 μ g/m²). The median lead concentration in carpet wipe and floor wipe is 4 μ g/m² and 9 μ g/m² respectively (Table 28 and Table 29). The metals and metalloid concentrations of cadmium, copper and zinc shows similar patterns to those for lead and arsenic in different wipes samples (Figure 24).

The highest iron level is found in window trough wipes (Figure 24), with a median level of 365,000 μ g/m²) and is similar to arsenic and lead for window trough wipes, followed for iron by roof wipes (6560 μ g/m²), veranda wipes (29222 μ g/m²) and window sill wipes (12500 μ g/m²). The median levels of lead concentration in carpet wipes and floor wipes are 71 μ g/m² and 92 μ g/m², respectively (Table 28 and Table 29).

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	68	99	12.8 (42.5)	1	4	7	333
Cadmium	68	76	3.4 (6.6)	0	1	3	38
Cobalt	68	93	4.8 (13.3)	0	2	3	101
Copper	68	100	645 (3243)	23	117	204	26,667
Iron	68	100	6679 (27,227)	481	1500	2685	216,667
Lead	68	100	479 (2337)	10	71	125	18,876
Manganese	68	100	61 (155)	8	26	41	1222
Nickel	68	100	29.5 (175)	1	4	6	1444
Zinc	68	100	1553 (2903)	163	1222	1333	19,259

Table 28 Total concentrations (µg/m²) of metals and the metalloid in carpet wipes from Mount Isa City

Note: SD: Standard deviation; n: Number of samples

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	176	99	17 (48)	0	9	13	500
Cadmium	178	90	4 (16)	0	1	2	167
Cobalt	109	96	6 (18)	0	2	4	167
Copper	178	100	594 (2668)	0	146	322	31,111
Iron	178	100	6315 (22,106)	286	2333	4922	263,333
Lead	178	100	380 (1801)	9	92	211	23,333
Manganese	109	100	91 (185)	8	43	81	1444
Nickel	109	100	19 (67)	1	5	9	522
Zinc	178	100	1239 (2163)	0	872	1444	19111

Table 29 Total concentrations ($\mu\text{g/m}^2$) of metals and the metalloid in floor wipes from Mount Isa City

Note: SD: Standard deviation; n: Number of samples

Table 30 Total concentrations (μ g/m²) of metals and the metalloid in roof wipes from Mount Isa City

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	47	100	1247 (5140)	5	133	320	33,333
Cadmium	47	98	14 (26)	1	4	12	130
Cobalt	37	100	30 (87)	2	8	13	433
Copper	47	100	9151 (28,006)	30	1730	3704	184,667
Iron	47	100	33,742 (65,459)	1320	6560	33148	356,667
Lead	47	100	5506 (17,292)	120	1100	3216	111,000
Manganese	37	100	110 (266)	7	21	49	1133
Nickel	37	100	20 (68)	1	3	6	367
Zinc	47	100	32348 (154,210)	200	2050	5313	1,043,333

Note: SD: Standard deviation; n: Number of samples
Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	130	100	102 (235)	1	43	92	1661
Cadmium	133	98	29 (74)	0	8	23	500
Cobalt	88	100	39 (39)	0	17	39	280
Copper	133	100	3081 (8198)	1	914	2648	63,425
Iron	133	100	30,359 (92,870)	401	12,500	23,827	942,377
Lead	133	100	2616 (9668)	19	536	1842	81,833
Manganese	88	100	267 (479)	6	132	290	3802
Nickel	88	100	54 (161)	2	22	48	1441
Zinc	133	100	5290 (12,381)	0	2273	4750	110,244

Table 31 Total concentrations ($\mu\text{g/m}^2$) of metals and metalloid in window-sill wipes from Mount Isa City

Note: SD: Standard deviation; n: Number of samples

Table 32 Total concentrations ($\mu g/m^2)$ of metals and metalloid in window trough wipes from Mount Isa City

Metal or metalloid	n	% > LOD	Mean(SD)	Minimum	Median	75th percentile	Maximum
Arsenic	134	100	2163 (2834)	1	1119	2651	16911
Cadmium	134	99	552 (1007)	0	209	500	7530
Cobalt	88	100	451 (516)	0	263	603	2475
Copper	134	100	70,714 (95,767)	33	36,491	77,544	512,527
Iron	134	100	642,836 (743,362)	687	364,866	837,923	4,077,778
Lead	134	100	45,276 (57,847)	26	20,360	54,538	251,282
Manganese	88	100	5120 (5939)	6	2786	6618	27,778
Nickel	88	100	944 (2049)	1	321	824	16,611
Zinc	134	100	98,883 (219,999)	78	41,424	82,690	2,200,000

Note: SD: Standard deviation; N: Number of samples



Note: Carpet wipes (WC), floor wipes (WF), roof wipes (WR), window sill wipes (WS), window trough wipes (WT), and veranda wipes (WV) in units of μ g/m². Solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values. The outlier and extreme points were removed based on coefficient of 1.5 for outliers and 3 for maximum cases for all elements plotted (StatSoft)

Figure 24 Total concentrations (μ g/m²) of metals and metalloid in dust materials collected by wipes

Metal or metalloid	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	Maximum
Arsenic	86	100	146 (248)	5	84	178	2111
Cadmium	86	99	26 (28)	0	14	37	133
Cobalt	73	100	39 (36)	2	28	58	167
Copper	86	100	5216 (6498)	133	3056	6750	34,222
Iron	86	100	45,442 (57,403)	1889	29,222	53,639	415,556
Lead	86	100	2630 (3137)	9	1389	3722	17,778
Manganese	73	100	457 (449)	39	306	600	2556
Nickel	73	100	32 (33)	2	21	41	189
Zinc	86	100	4749 (4564)	438	2944	6167	23,778

Table 33 Total concentrations (µg/m²) of metals and metalloid in veranda wipes from Mount Isa City

Note: SD: Standard deviation; n: Number of samples

Comparison of lead concentrations in various house wipe samples from the city's residential area using the Kruskal-Wallis test by rank shows significant differences (Table 34). The highest mean rank (highest overall lead concentration group) is for the window-trough wipes (WT); the lowest mean rank (lowest overall lead concentration) is in the carpet wipes (WC), which is consistent with the distribution shown in Figure 24.

Table 34 Kruskal-Wallis ANOVA by ranks for lead concentration in house surface wipes from Mount Isa City (p < 0.001)

Sample	Valid n	Sum of ranks	Mean rank
Carpet wipe (WC)	39	2465	63
Floor wipe (WF)	67	5427	81
Window sill wipe (WS)	67	11,178	167
Veranda wipes (WV)	58	11,435	197
Roof wipes (WR)	48	9414	196
Window trough wipes (WT)	67	20,113	300

Note: p < 0.001 indicates that the analysed groups are significantly different

3.1.6 Air particulates

3.1.6.1 *Mine site*

The total concentrations of metals and metalloid in air PM_{10} samples (in units of $\mu g/m^3$) from different mining and mineral processing locations at the mine site (Section 2.3.6, page 126) are summarised in Table 35, Table 36, and Table 37. The total concentrations of metals and metalloid in the mine site air PM_{10} indicated large variations (Figure 25). Lead concentrations ranged between 0.03 $\mu g/m^3$ and 168 $\mu g/m^3$ in 2009 and 0.13 $\mu g/m^3$ to 144 $\mu g/m^3$ in 2011 (Table 35 and Table 37). The lead concentration range is only 0.05 to 16.6 $\mu g/m^3$ from the 2010 sampling trip. The lead smelter was under maintenance and not operational during the sampling period in 2010.

Metal or metalloid	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Zinc
Mean	0.28	1.06	1.49	8.12	39	0.09	3.61
SD	0.56	2.42	3.21	10.37	69	0.13	4.22
Minimum	0.00	0.00	0.01	0.33	0.03	0.00	0.01
25th percentile	0.01	0.00	0.05	3.43	0.31	0.02	0.08
Median	0.03	0.04	0.30	3.43	2	0.06	1.44
75th percentile	0.30	0.40	0.68	13.26	33	0.08	8.11
95th percentile	1.18	5.23	6.80	25.77	167	0.31	9.45
Maximum	1.82	7.64	10.41	27.75	168	0.46	9.61

Table 35 Airborne concentrations (μ g/m³) of metals and metalloid in mine site air particulates from 2009 sampling (n = 10)

Table 36 Airborne concentrations (μ g/m³) of metals and metalloid in mine site air particulates for 2010 sampling (n = 7)

Metal or metalloid	Arseni c	Cadmiu m	Coppe r	Iron	Lead	Manganes e	Zinc
Mean	0.08	0.02	0.28	8.33	2.84	0.18	3.90
SD	0.07	0.03	0.33	19.31	6.07	0.42	9.46
Minimum	0.01	0.00	0.02	0.19	0.05	0.00	0.04
25th percentile	0.02	0.01	0.06	0.29	0.26	0.01	0.10
Median	0.05	0.02	0.12	0.47	0.53	0.01	0.15
75th percentile	0.14	0.02	0.39	2.52	1.10	0.06	0.79
95th percentile	0.15	0.06	0.80	37.32	12.00	0.82	18.0 3
Maximum	0.15	0.08	0.93	52.06	16.60	1.13	25.3 4

Metal or metalloid	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Zinc
Mean	0.27	0.29	1.05	7.36	35	0.06	2.79
SD	0.33	0.43	1.29	9.39	57	0.06	3.89
Minimum	0.01	0.00	0.02	0.33	0.13	0.00	0.02
25th percentile	0.02	0.00	0.09	1.00	0.20	0.01	0.16
Median	0.13	0.03	0.49	2.43	1.82	0.06	1.32
75th percentile	0.45	0.47	1.80	10.82	48	0.08	3.68
95th percentile	0.77	0.96	2.95	22.08	126	0.15	8.98
Maximum	0.83	1.07	3.07	25.16	144	0.17	10

Table 37 Airborne concentrations (μ g/m³) of metals and metalloid in mine site air particulates for 2011 sampling (n = 7)



Note: solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values

Figure 25 Airborne concentrations of metals and the metalloid in air PM₁₀ at the mine site

The total concentration of metals and metalloid in air PM_{10} samples from two comparative sites downwind of the mine site (Section 2.3.6.1, page 127) are summarised in Figure 26. The lead levels vary between 0.03 µg/m³ and 0.17 µg/m³.



Note: solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values

Figure 26 Total concentrations of metals and the metalloid in samples from downwind comparative sites

3.1.6.2 Mount Isa City outdoor air

Air PM_{10} samples were collected at residential outdoor area sites during the three different sampling trips: 2009, 2010, and 2011 (Section 2.3.6, page 126). The 2009 and 2010 air PM_{10} samples were collected during the dry season to estimate the worst-case scenario for dust dispersion. However, the lead smelter was under maintenance and not operational during the sampling period in 2010. The third sampling trip was conducted early in the dry season in May 2011. The air PM_{10} concentrations from the residential areas indicated fewer variations in metals and metalloid concentrations (Table 38, Table 39, and Table 40) compared with mine site samples.

Lead concentrations in air PM_{10} varied from 0.01 µg/m³ to 0.25 µg/m³ in 2009 and 0.01 µg/m³ to 0.11 µg/m³ in 2010 (Table 38 and Table 39), compared to the maximum of 0.07 µg/m³ for 2011 (Figure 27). All the results measured are within the Australian National Environmental Protection Measure (Air) ('NEPM (Air)') standard of 0.5 µg/m³ for lead in air (NEPC, 2002). The mean values of all metals and metalloid concentrations are relatively higher in samples collected in 2010 except zinc (Figure 27). The lead concentrations in air PM_{10} samples collected for this study throughout the residential area indicated that there was spatial

distribution present during each sampling trip (Figure 28). During each sampling period, the lead concentrations were higher closer to the mine site. Comparison of the total concentration of lead in air PM_{10} data between 2009 and 2010, 2009 and 2011 and 2010 and 2011, respectively, using the Mann-Whitney U test (Table 41) showed no significant differences between pairs of years. During the sampling periods, the lead smelter did not appear to be a significant contributor to airborne lead as there was no observed difference while the lead smelter was under maintenance during the 2010 sampling period (Section 2.3.6.1.1, page 127). Overall wind speed was lowest during 2010 and highest during 2011 (Figure 15). In 2009 there was $\approx 15\%$ contribution from N-direction from the mine site which could explain why the highest maximum airborne lead concentration measured during the study occurred that year.

Metal or metalloid	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Zinc
Mean	0.005	0.003	0.016	0.48	0.05	0.008	0.040
SD	0.008	0.005	0.018	0.37	0.08	0.006	0.047
Minimum	< 0.001	< 0.001	0.002	0.12	0.01	0.002	< 0.001
25th percentile	0.001	< 0.001	0.003	0.29	0.01	0.004	0.014
Median	0.001	0.001	0.011	0.40	0.02	0.006	0.022
75th percentile	0.003	0.001	0.018	0.54	0.03	0.010	0.037
Maximum	0.027	0.015	0.060	1.56	0.25	0.024	0.143

Table 38 Total concentrations (μ g/m³) of metals and metalloid in air particulates in November 2009 sampling (Mount Isa City outdoor) (n = 12)

Table 39 Total concentrations (μ g/m³) of metals and metalloid in air particulates from November 2010 sampling (Mount Isa City outdoor) (n = 11)

Metal or metalloid	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Zinc
Mean	0.007	0.002	0.025	0.21	0.06	0.004	0.041
SD	0.005	0.001	0.014	0.08	0.04	0.002	0.020
Minimum	0.001	< 0.001	0.006	0.12	0.01	0.002	0.017
25th percentile	0.003	0.001	0.015	0.16	0.03	0.003	0.026
Median	0.006	0.001	0.021	0.20	0.05	0.004	0.033
75th percentile	0.010	0.003	0.036	0.22	0.09	0.004	0.059
Maximum	0.014	0.004	0.046	0.38	0.11	0.007	0.067

Metal or metalloid	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Zinc
Mean	0.004	0.001	0.025	0.55	0.03	0.010	0.060
SD	0.004	0.001	0.028	0.70	0.03	0.014	0.053
Minimum	0.001	< 0.001	0.003	0.20	0.00	0.004	0.007
25th percentile	0.001	< 0.001	0.008	0.23	0.01	0.004	0.017
Median	0.002	< 0.001	0.011	0.29	0.02	0.004	0.052
75th percentile	0.005	0.001	0.038	0.45	0.06	0.010	0.082
Maximum	0.009	0.002	0.086	2.25	0.07	0.044	0.144

Table 40 Total concentrations (μ g/m³) of metals and metalloid in air particulates from May 2011 sampling (Mount Isa City outdoor) (n = 8)



Note: solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values



Figure 27 Total concentrations of metals and the metalloid in air $PM_{\rm 10}$ from outdoor air $PM_{\rm 10}$ in Mount Isa City

Figure 28 Spatial distribution of lead in outdoor air PM_{10} collected from the residential area

Metal or metalloid	2009 and 2010 air PM ₁₀ outdoor	2009 and 2011 air PM ₁₀ outdoor	2010 and 2011 air PM ₁₀ outdoor	2010 air PM ₁₀ outdoor and indoor
Arsenic	0.03	0.64	0.10	0.19
Cadmium	0.31	0.33	0.03	0.19
Copper	0.05	0.67	0.34	0.05
Iron	0.00	0.42	0.02	0.00
Lead	0.08	0.84	0.09	0.06
Zinc	0.19	0.39	0.84	0.16

Table 41 Summary of p value from Mann-Whitney U test in air PM10 concentration from the city's residential area

Note: Bold numbers indicate no statistically significant differences (p > 0.5).

3.1.6.3 Mount Isa City indoor air

Indoor air PM_{10} samples were also collected during the 2010 sampling trip (Table 42). Lead concentration from air PM_{10} in indoor samples ranged between 0.004 µg/m³ (minimum level) and 0.1 µg/m³ (maximum level). These levels cannot be compared directly with the standard for lead in air in the NEPM (Air) of 0.5 µg/m³, which is based on TSP collection. The air quality control ('AQC') system also includes 5 passive monitoring stations, 9 high-volume samplers for TSP and 10 dust depositional gauges for monitoring dust in the Mount Isa city air (MIM, 2012a, Wrigley, 1992). The data from these samplers show that the air quality in Mount Isa has met MIM's operating licence conditions (DEHP, 2013, MIM, 2012c). The air PM₁₀ for arsenic, cadmium, cobalt, iron, lead, and zinc concentrations are lower in the indoor compared with the outdoor air PM₁₀ samples from the same sampling trip (Figure 29).

	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Zinc
Mean	0.004	0.001	0.014	0.11	0.03	0.002	0.032
SD	0.004	< 0.001	0.011	0.07	0.03	0.001	0.024
Minimum	0.001	< 0.001	0.004	0.06	0.004	0.001	0.010
25th percentile	0.002	< 0.001	0.007	0.08	0.01	0.002	0.020
Median	0.003	0.001	0.009	0.09	0.02	0.002	0.023
75th percentile	0.005	0.002	0.018	0.11	0.04	0.003	0.037
Maximum	0.013	0.004	0.037	0.26	0.10	0.005	0.077

Table 42 Total concentrations (μ g/m³) of metals and metalloid in air particulates in 2010 sampling (Mount Isa City indoor) (n = 12)

The comparisons of the Mann-Whitney U test for indoor and outdoor air PM_{10} samples from 2010 are made in Table 41. Although the air PM_{10} concentrations are higher in outdoor samples, the Mann-Whitney U test indicates that the total concentrations for arsenic, cadmium, copper, lead, and zinc are not statistically different for indoor samples compared with outdoor samples. The total iron



Note: solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values



concentrations in the 2010 indoor air PM_{10} samples, however, show significant differences (p < 0.05) (Table 41).

3.1.7 Correlation of metals and metalloid in samples

The correlation between different sample types for total concentration data for arsenic, cadmium, copper, iron, lead, and zinc were calculated using Spearman's rank analysis (Section 2.6, page 157). The results of Spearman's rank correlation coefficient indicate the relationship between pairs of variables and are summarised for lead (Table 43), for arsenic (Table 44) for cadmium (Table 45), for copper (Table 46), for iron (Table 47), and for zinc (Table 48). Indoor air PM_{10} (IAH) and outdoor air PM₁₀ (AH) are significantly correlated for arsenic, cadmium, copper, and lead but not for iron and zinc. The correlation between soil < 250 µm fraction (CS) and soil PM_{10} fraction ($PM_{10}S$) is very significant (70–93 per cent) for most metals and the metalloid, but not for iron. Lead, arsenic, and cadmium in carpet dust samples (CD) show a positive correlation with wipes taken from roofs (WR), carpets (WC), floors (WF), window sills (WS), window troughs (WT), and the verandas (WV) of the houses. Iron and zinc in carpet dust samples, however, displayed different behaviours and are only correlated for floor wipes and window sill wipes (Table 47 and Table 48). Metals and metalloid in fallout dust from city (FMT) and roof gutter dust (RGD) are independent from other sample groups, and only zinc in roof gutter dust is correlated to floor wipes and window sill wipes (Table 48).

3.1.8 Correlation between metals and the metalloid in garden soil and carpet dust

The results of Spearman's rank correlation coefficient show the relationship between metals and the metalloid within the same type of sample (Table 49 and Table 50). The total concentrations of arsenic, cadmium, copper, lead and zinc, in garden soil < 250 μ m fraction are highly correlated (Table 49). The total concentrations data of arsenic, cadmium, copper and lead in carpet dust are also highly correlated (correlation between 0.64 and 0.87) (Table 50). Zinc levels in carpet dust are different from garden soil, but still positively correlated with arsenic, cadmium, copper, and lead, but to a lesser extent (p < 0.55). Although the correlation between iron and manganese is high in carpet dust (p = 0.85), there is less correlation with the other heavy metals and metalloid (Table 50).

Lead	IAH	АН	CD	CS	FMT	RGD	PM ₁₀ S	WR	WC	WF	WS	WТ	wv
IAH													
AH	0.82												
CD													
CS	0.67	0.42	0.23										
FMT													
RGD													
PM ₁₀ S	0.84	0.58		0.91									
WR			0.46	0.58			0.57						
WC			0.68	0.27			0.30	0.40					
WF			0.46	0.42		0.26	0.45	0.30	0.43				
WS	0.59	0.44	0.42	0.48			0.40	0.59	0.43	0.29			
WT		0.57	0.37	0.42			0.47	0.54	0.29	0.20	0.39		
WV				0.42		0.28	0.37	0.38	0.38	0.46	0.34		

Table 43 Correlation coefficient of concentration data by Spearman's rank for lead

Note: (1) **Bold** values indicate correlation between the two variables is significant at p < 0.05. *Italic* values indicate correlation is significant at p < 0.10. (2) IAH: Indoor air PM₁₀ from city residential; AH: Outdoor air PM₁₀ from city residential; CD: carpet dust; CS: garden soil < 250 µm fraction; FMT: fallout dust form city; RGD: roof gutter dust; PM₁₀S: PM₁₀ fraction from garden soil; WR: roof dust samples collected with wipes; WC: carpet dust samples collected with wipes; WF: floor dust samples collected with wipes; WT: window trough dust samples collected with wipes; WV: veranda dust samples collected with wipe.

Arsenic	IAH	AH	CD	CS	FMT	RGD	PM ₁₀ S	WR	WC	WF	WS	WT	WV
IAH													
AH	0.83												
CD													
CS	0.70	0.61	0.32										
FMT													
RGD													
PM ₁₀ S	0.72	0.56		0.71									
WR			0.31										
WC	0.82		0.45					0.52					
WF			0.37					0.33					
WS			0.38	0.25				0.67	0.44	0.28			
WT		0.58	0.33	0.26				0.57		0.25	0.49		
WV			0.27	0.36		0.33		0.43		0.36	0.28		

Table 44 Correlation coefficient of concentration data by Spearman's rank for arsenic

Note: (1) **Bold** values indicate correlation between the two variables is significant at p < 0.05. *Italic* values indicate correlation is significant at p < 0.10. (2) IAH: Indoor air PM10 from city residential; AH: Outdoor air PM₁₀ from city residential; CD: carpet dust; CS: garden soil < 250 µm fraction; FMT: fallout dust form city; RGD: roof gutter dust; PM₁₀S: PM₁₀ fraction from garden soil; WR: roof dust samples collected with wipes; WC: carpet dust samples collected with wipes; WT: window trough dust samples collected with wipes; WV: veranda dust samples collected with wipe.

Cadmium	IAH	AH	CD	CS	FMT	RGD	PM10S	WR	WC	WF	WS	WT	wv
IAH													
АН	0.90												
CD													
CS			0.34										
FMT													
RGD				0.49									
PM10S		0.70		0.70									
WR				0.50			0.42						
WC			0.39										
WF			0.47	0.39		0.36	0.40						
WS			0.52	0.31			0.34	0.47	0.50	0.33			
WT		0.59		0.36			0.35	0.54		0.28	0.28		
WV			0.33	0.34			0.42	0.32		0.48	0.34	0.27	

Table 45 Correlation coefficient of concentration data by Spearman's rank for cadmium

Note: (1) **Bold** values indicate correlation between the two variables is significant at p < 0.05. *Italic* values indicate correlation is significant at p < 0.10. (2) IAH: Indoor air PM₁₀ from city residential; AH: Outdoor air PM₁₀ from city residential; CD: carpet dust; CS: garden soil < 250 µm fraction; FMT: fallout dust form city; RGD: roof gutter dust; PM10S: PM₁₀ fraction from garden soil; WR: roof dust samples collected with wipes; WC: carpet dust samples collected with wipes; WT: window trough dust samples collected with wipes; WV: veranda dust samples collected with wipe.

Copper	IAH	AH	CD	CS	FMT	RGD	PM ₁₀ S	WR	WC	WF	WS	WT	wv
IAH													
АН	0.68												
CD													
CS	0.58		0.36										
FMT													
RGD													
PM ₁₀ S	0.69	0.50	0.33	0.87									
WR				0.29			0.36						
WC	0.68		0.67				0.34	0.41					
WF			0.24	0.48			0.37		0.38				
WS			0.50	0.31			0.31	0.57	0.42	0.26			
WT			0.30	0.30			0.43	0.45			0.44		
WV				0.39			0.27	0.40		0.48			

Table 46 Correlation coefficient of concentration data by Spearman's rank for copper

Note: (1) **Bold** values indicate correlation between the two variables is significant at p < 0.05. *Italic* values indicate correlation is significant at p < 0.10. (2) IAH: Indoor air PM₁₀ from city residential; AH: Outdoor air PM₁₀ from city residential; CD: carpet dust; CS: garden soil < 250 µm fraction; FMT: fallout dust form city; RGD: roof gutter dust; PM10S: PM₁₀ fraction from garden soil; WR: roof dust samples collected with wipes; WC: carpet dust samples collected with wipes; WT: floor dust samples collected with wipes; WT: window trough dust samples collected with wipes; WV: veranda dust samples collected with wipe.

Iron	IAH	AH	CD	CS	FMT	RGD	PM ₁₀ S	WR	WC	WF	WS	WТ	wv
IAH													
АН													
CD													
CS													
FMT													
RGD													
PM ₁₀ S		-0.58						-0.43					
WR		0.64		0.30			-0.43						
WC			0.26					0.31					
WF		-0.48	0.31	0.22			0.47						
WS				0.21			-0.21	0.39	0.32				
WT	0.54						-0.34	0.37			0.37		
WV											0.28		

Table 47 Correlation coefficient of concentration data by Spearman's rank for iron

Note: (1) **Bold** values indicate correlation between the two variables is significant at p < 0.05. *Italic* values indicate correlation is significant at p < 0.10. (2) IAH: Indoor air PM₁₀ from city residential; AH: Outdoor air PM₁₀ from city residential; CD: carpet dust; CS: garden soil < 250 µm fraction; FMT: fallout dust form city; RGD: roof gutter dust; PM₁₀S: PM₁₀ fraction from garden soil; WR: roof dust samples collected with wipes; WC: carpet dust samples collected with wipes; WT: floor dust samples collected with wipes; WT: window trough dust samples collected with wipes; WV: veranda dust samples collected with wipe.

Zinc	IAH	AH	CD	CS	FMT	RGD	PM ₁₀ S	WR	wc	WF	ws	WT	wv
IAH													
AH													
CD													
CS			0.24										
FMT													
RGD													
PM ₁₀ S				0.93									
WR													
WC	0.76												
WF			0.30	0.23		0.42			0.49				
WS	0.59	0.51	0.43	0.35			0.30						
WT						0.34							
WV		0.53		0.34			0.25	0.37		0.38			

Table 48 Correlation coefficient of concentration data by Spearman's rank for zinc

Note: (1) **Bold** values indicate correlation between the two variables is significant at p < 0.05. (2) IAH: Indoor air PM10 from city residential; AH: Outdoor air PM₁₀ from city residential; CD: carpet dust; CS: garden soil < 250 µm fraction; FMT: fallout dust form city; RGD: roof gutter dust; PM₁₀S: PM₁₀ fraction from garden soil; WR: roof dust samples collected with wipes; WC: carpet dust samples collected with wipes; WF: floor dust samples collected with wipes; WT: window trough dust samples collected with wipes; WV: veranda dust samples collected with wipe.

Metal or metalloid	Arsenic	Cadmium	Chromium	Cobalt	Copper	Iron	Lead	Manganese	Nickel	Zinc
Arsenic										
Cadmium	0.67									
Chromium										
Cobalt	0.60	0.46	0.32							
Copper	0.87	0.72		0.64						
Iron				0.39						
Lead	0.83	0.81		0.60	0.84	0.24				
Manganese	0.25	0.40	0.31	0.70	0.34	0.34	0.33			
Nickel			0.55	0.72	0.23	0.37	0.26	0.54		
Zinc	0.64	0.53		0.57	0.72		0.80	0.26	0.34	

Table 49 Correlation coefficients of concentration data by Spearman's rank for metals and the metalloid in garden soil < 250 µm fraction

Note: Bold values indicate correlation between the two variables is significant at p < 0.05

Table 50 Correlation coefficients of concentration data by Spearman's rank for elements in carpet dust

Metal or metalloid	Arsenic	Cadmium	Chromium	Cobalt	Copper	Iron	Lead	Manganese	Nickel	Zinc
Arsenic										
Cadmium	0.76									
Chromium										
Cobalt	0.79	0.87								
Copper	0.87	0.64		0.74						
Iron	0.52	0.42			0.55					
Lead	0.89	0.75		0.78	0.86	0.54				
Manganese	0.48	0.39		0.38	0.40	0.85	0.51			
Nickel						0.44		0.34		
Zinc	0.54	0.56		0.34	0.52	0.66	0.60	0.40	0.34	

Note: **Bold** values indicate correlation between the two variables is significant at p < 0.05

3.2 Lead isotope characteristics

The results of lead isotope ratios for samples are displayed as follows:

- outcrop samples from different geological units (Table 51)
- samples of ores and concentrates (Table 52), including lead ore from Black Star open cut, George Fisher and Handle Bar Hill open cut.
- mine site dust samples (Table 53, Table 54, Table 55, Table 56, Table 57, and Table 58)
- samples from Mount Isa City's residential area (Table 59, Table 60, Table 61, Table 62, Table 63, and Table 64).

Note that in these tables, the isotope ratios reported are accurate to four decimal places, based on the high precision of the MC-ICP-MS response (Section 2.4.2). It is the variation in the decimal places that is important to distinguish between samples from various origins. A difference in the third decimal can be considered a large variation in the ratio when interpreting these data.

In general, there are large variations in outcrop samples (except for outcrops in natural mineralisation) and garden soils (Table 51 and Table 59, respectively).

The lead isotope ratios for samples from the mine site and Mount Isa City residential area are broadly divided into three categories:

- i. Urquhart Shale type of lead, including natural mineralisation (NMU, Figure 6, page 68) from Mount Isa City and lead ore materials processed in the mine site
- ii. lead associated with copper mineral processing activities, mostly from Mount Isa and non-Mount Isa origin, such as Ernest Henry (Brooke et al., 2013) (Section 1.3.4, page 68)
- iii. non-lead-bearing geological sequences (BGR). The complete results for lead isotope ratios of other samples are given in Appendix 4.

Although some copper concentrate was purchased in earlier years, it was normally a relatively small proportion of the total concentrate treated. In recent years, concentrate from the Ernest Henry mine has become a significant component of the copper concentrate smelted at Mount Isa. Mount Isa produced about twice as much copper in concentrate as Ernest Henry in 2010 (Brooke et al., 2013, Magee et al., 2013).

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
NM1	36.1430	0.0015	15.4822	0.0007	16.4783	0.0007	2.1934	2.0E-05	0.9396	6.9E-06
NM2	35.8790	0.0018	15.4539	0.0007	16.1693	0.0009	2.2189	2.1E-05	0.9558	6.3E-06
NM3*	35.8816	0.0023	15.4661	0.0007	16.1479	0.0009	2.2221	3.4E-05	0.9578	1.0E-05
NM4*	35.8570	0.0033	15.4543	0.0014	16.1384	0.0009	2.2217	3.7E-05	0.9577	1.3E-05
NM5*	35.8649	0.0026	15.4618	0.0009	16.1363	0.0011	2.2226	3.2E-05	0.9582	1.1E-05
NM6	38.5114	0.0027	15.8554	0.0012	20.3621	0.0014	1.8912	4.0E-05	0.7786	1.2E-05
NM7*	35.8755	0.0033	15.4619	0.0009	16.1675	0.0008	2.2192	3.3E-05	0.9564	9.5E-06
BGR1	36.1944	0.0024	15.5052	0.0009	16.5322	0.0010	2.18934	4.7E-05	0.9379	1.3E-05
BGR2	36.0923	0.0017	15.4802	0.0007	16.3856	0.0008	2.20269	2.4E-05	0.9447	7.0E-06
BGR3	36.0722	0.0018	15.4747	0.0010	16.3721	0.0007	2.20329	2.1E-05	0.9452	6.0E-06
BGR4	36.2227	0.0017	15.4901	0.0007	16.4674	0.0007	2.19967	1.8E-05	0.9406	6.0E-06
BGR5	40.0108	0.0066	15.7249	0.0024	19.2280	0.0028	2.08082	8.6E-05	0.8178	1.4E-05
BGR6	36.3432	0.0015	15.4927	0.0006	16.5339	0.0007	2.19809	2.0E-05	0.9370	7.0E-06
BGR7	38.1342	0.0044	15.6066	0.0015	17.8818	0.0016	2.13245	4.4E-05	0.8727	1.3E-05
BGR8	36.8706	0.0025	15.5795	0.0010	17.3873	0.0011	2.12053	2.9E-05	0.8960	1.3E-05
BGR9	37.3330	0.0088	15.5997	0.0036	17.7269	0.0036	2.10597	8.2E-05	0.8800	2.2E-05
BGR10	36.4332	0.0024	15.5520	0.0009	17.0951	0.0008	2.13130	1.4E-05	0.9097	7.0E-06
BGR11	39.4037	0.0089	15.7436	0.0028	19.2862	0.0035	2.04340	5.4E-05	0.8164	1.3E-05
BGR12	35.8615	0.0017	15.4599	0.0006	16.1526	0.0008	2.22024	2.1E-05	0.9572	9.0E-06
BGR13	45.4760	0.0090	16.2945	0.0026	24.2478	0.0043	1.87548	3.5E-05	0.6720	1.6E-05
BGR14	37.3263	0.0035	15.6299	0.0015	17.9013	0.0017	2.08514	3.6E-05	0.8731	1.1E-05

Table 51 Lead isotope ratios for outcrops from different geological units from Mount Isa, including Urquhart Shale

Note: * indicates that outcrop samples were collected from natural mineralisation (Urquhart Shale). NM6 was taken from rock that was part of the Breakaway shale.

				²⁰⁷ Pb		²⁰⁶ Pb		²⁰⁸ Pb		²⁰⁷ Pb	
ID	Sample	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	/ ²⁰⁴ Pb	2σ	/ ²⁰⁴ Pb	2σ	/ ²⁰⁶ Pb	2σ	/ ²⁰⁶ Pb	2σ
SS1	Mt Haney Pb slag	35.8564	0.0045	15.4532	0.0016	16.1407	0.0010	2.2217	4.98E-05	0.9575	1.76E-05
SS2	Mt Haney Pb slag old ground	35.8555	0.0057	15.4654	0.0025	16.1272	0.0034	2.2234	5.12E-05	0.9590	1.59E-05
SS3	CuSm slag old	36.1038	0.0026	15.5053	0.0014	16.8799	0.0012	2.1389	4.38E-05	0.9186	8.73E-06
SS4	CuSm slag - RHF	35.8569	0.0020	15.4521	0.0008	16.1435	0.0007	2.2211	3.84E-05	0.9572	6.84E-06
SS5	Zn conc from Zn filter storage area	35.8850	0.0062	15.4755	0.0026	16.1358	0.0022	2.2241	4.76E-05	0.9591	1.67E-05
SS7	PAC Rim dust	35.8673	0.0067	15.4680	0.0029	16.1281	0.0030	2.2239	4.26E-05	0.9591	2.04E-05
SS8	Lead Stack	35.8639	0.0021	15.4633	0.0009	16.1363	0.0008	2.2226	3.76E-05	0.9583	6.68E-06
SS9	Sinter Plant - crusher/vibrating feeder	35.8695	0.0038	15.4619	0.0015	16.1356	0.0015	2.2229	4.20E-05	0.9582	1.49E-05
SS10	Sinter Plant - baghouse	36.0778	0.0021	15.4746	0.0008	16.3167	0.0009	2.2111	4.20E-05	0.9484	7.21E-06
SS11	Sinter Plant - sinter feed prep	36.0953	0.0040	15.4791	0.0020	16.3218	0.0019	2.2116	5.10E-05	0.9484	1.18E-05
	HBF plant, copper stacker/reclaimer,										
SS12	feed prep	35.9610	0.0036	15.4739	0.0015	16.2992	0.0016	2.2063	3.72E-05	0.9494	1.41E-05
SS13	Tailing dam 5	35.8634	0.0055	15.4651	0.0023	16.1318	0.0021	2.2230	5.50E-05	0.9586	2.40E-05
SS14	Tailing dam 7 surface	35.8510	0.0030	15.4633	0.0011	16.1503	0.0014	2.2198	3.80E-05	0.9575	5.88E-06
SS15	Tailing dam 8 surface	35.8557	0.0020	15.4656	0.0009	16.1243	0.0012	2.2238	3.36E-05	0.9592	6.89E-06
SS16	Black Star open cut ore at PAC Rim	35.8762	0.0055	15.4728	0.0022	16.1302	0.0021	2.2241	4.64E-05	0.9592	1.49E-05
SS17	George Fisher ore at PAC Rim	35.8715	0.0047	15.4708	0.0019	16.1293	0.0019	2.2240	2.86E-05	0.9592	1.29E-05
	Handle Bar Hill open cut Ore at PAC										
SS18	Rim	35.8775	0.0041	15.4732	0.0016	16.1312	0.0016	2.2240	3.80E-05	0.9592	1.52E-05
SS22	Pb smelter dust	36.0001	0.0082	15.4738	0.0032	16.2460	0.0049	2.2155	5.94E-05	0.9524	2.12E-05
SS23	P/mill (19A) Ground	36.6491	0.0056	15.5504	0.0021	16.9080	0.0024	2.1674	5.08E-05	0.9197	1.39E-05
SS24	Isa Chalcopyrite	35.7754	0.0075	15.4341	0.0045	16.1279	0.0041	2.2184	5.70E-05	0.9569	3.08E-05
SS26	Pb concentrator dust	35.9349	0.0025	15.4659	0.0010	16.2660	0.0010	2.2092	3.54E-05	0.9508	7.39E-06
SS27	Cu smelter dust	36.4617	0.0035	15.5046	0.0014	16.8551	0.0014	2.1633	5.16E-05	0.9199	1.51E-05

Table 52 Lead isotope ratios for mine site source samples

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
HR1	35.8781	0.0022	15.4600	0.0008	16.1507	0.0010	2.2214	3.82E-05	0.9572	1.08E-05
HR2	35.9430	0.0023	15.4541	0.0008	16.2143	0.0009	2.2168	3.62E-05	0.9531	1.46E-05
HR3	35.8643	0.0023	15.4506	0.0009	16.1527	0.0011	2.2204	4.86E-05	0.9566	1.15E-05
HR4	35.8697	0.0022	15.4614	0.0008	16.1497	0.0008	2.2211	3.58E-05	0.9574	1.46E-05
HR5	35.8762	0.0018	15.4634	0.0007	16.1689	0.0009	2.2189	2.84E-05	0.9564	8.30E-06
HR6	35.8636	0.0023	15.4624	0.0010	16.1397	0.0010	2.2221	3.26E-05	0.9580	1.02E-05
HR7	35.8661	0.0028	15.4637	0.0012	16.1373	0.0011	2.2226	3.30E-05	0.9583	1.15E-05
HR8	35.8848	0.0024	15.4628	0.0011	16.1608	0.0010	2.2205	3.22E-05	0.9568	1.06E-05
HR9	35.8560	0.0040	15.4621	0.0017	16.1310	0.0017	2.2228	2.74E-05	0.9585	1.11E-05

Table 53 Lead isotope ratios for haul road dust from mine site

Table 54 Lead isotope ratios for mine site fallout dust samples

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
FM11	36.0118	0.0031	15.4615	0.0013	16.2785	0.0013	2.2122	6.18E-05	0.9498	1.37E-05
FM13	36.0378	0.0037	15.4636	0.0016	16.3435	0.0018	2.2051	4.02E-05	0.9462	1.26E-05
FM15	35.9408	0.0035	15.4644	0.0013	16.2094	0.0014	2.2173	4.34E-05	0.9540	1.48E-05
FM17	36.2942	0.0028	15.4945	0.0010	16.4877	0.0011	2.2013	3.44E-05	0.9397	9.78E-06
FM19	36.1401	0.0033	15.5012	0.0013	16.2928	0.0015	2.2183	7.72E-05	0.9515	2.22E-05

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
TD5S31	35.8713	0.0110	15.4659	0.0046	16.1504	0.0047	2.22072	7.02E-05	0.95754	2.54E-05
TD5S61	35.8563	0.0088	15.4668	0.0046	16.1543	0.0047	2.21985	6.38E-05	0.95741	2.42E-05
TD7S21	35.8712	0.0109	15.4670	0.0055	16.1501	0.0050	2.22092	5.52E-05	0.95782	2.74E-05
TD7S51	35.8590	0.0060	15.4673	0.0023	16.1334	0.0028	2.22281	4.18E-05	0.95872	1.66E-05
TD8S21	35.8662	0.0065	15.4690	0.0028	16.1515	0.0025	2.22038	4.14E-05	0.95759	1.98E-05
TD8S31	35.8636	0.0036	15.4670	0.0020	16.1345	0.0020	2.22264	5.54E-05	0.95856	1.16E-05
TD8S41	35.8660	0.0045	15.4677	0.0017	16.1416	0.0016	2.22195	3.70E-05	0.95827	1.47E-05

Table 55 Lead isotope ratios for surface tailing dam materials

Table 56 Lead isotope ratios for particulate matter collected by thimbles from the copper smelter area

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
ATC1	35.8626	0.0032	15.4651	0.0013	16.3276	0.0013	2.196455	4.32E-05	0.947195	1.29E-05
ATC2	35.9076	0.0026	15.4807	0.0011	16.3531	0.0010	2.195790	3.84E-05	0.946663	1.16E-05
ATC3	35.9716	0.0025	15.5252	0.0010	16.8400	0.0012	2.136116	4.08E-05	0.921936	1.36E-05
ATC4	35.8644	0.0027	15.4782	0.0011	16.5207	0.0010	2.170750	5.82E-05	0.936864	1.37E-05
ATC5	35.9428	0.0022	15.5112	0.0008	16.7397	0.0007	2.147202	5.30E-05	0.926620	1.32E-05
ATC6	35.9485	0.0027	15.5147	0.0010	16.7751	0.0011	2.142935	4.58E-05	0.924868	1.31E-05
ATC7	35.9278	0.0019	15.5007	0.0008	16.6101	0.0008	2.162967	3.66E-05	0.933180	1.13E-05
ATC10	35.9514	0.0023	15.4862	0.0009	16.5367	0.0010	2.174063	4.64E-05	0.936455	1.42E-05
ATC11	35.8822	0.0052	15.4734	0.0017	16.4263	0.0012	2.184344	4.32E-05	0.941989	1.27E-05
ATC14	35.9377	0.0032	15.5123	0.0016	16.7956	0.0016	2.139752	4.58E-05	0.923590	1.54E-05
LEPSP01	35.9906	0.0054	15.5233	0.0013	16.8365	0.0014	2.137716	3.46E-05	0.922021	1.03E-05

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
ATP1	35.8590	0.0022	15.4659	0.0008	16.1250	0.0008	2.223871	3.78E-05	0.959125	1.19E-05
ATP3	35.9236	0.0027	15.4650	0.0011	16.1841	0.0012	2.219678	4.38E-05	0.955564	1.27E-05
ATP4	35.8491	0.0025	15.4624	0.0010	16.1213	0.0009	2.223780	4.82E-05	0.959152	1.54E-05
ATP5	35.8712	0.0023	15.4689	0.0009	16.1280	0.0009	2.224167	4.90E-05	0.959141	1.56E-05
ATP6	35.8532	0.0024	15.4633	0.0010	16.1233	0.0010	2.223708	4.78E-05	0.959076	1.59E-05
ATP7	35.8274	0.0026	15.4549	0.0011	16.1170	0.0015	2.223019	4.66E-05	0.958938	1.67E-05
ATP8	35.8537	0.0028	15.4631	0.0011	16.1236	0.0011	2.223682	4.14E-05	0.959043	1.15E-05
HMA	35.8461	0.0048	15.4610	0.0017	16.1218	0.0017	2.223483	6.22E-05	0.959037	1.67E-05

Table 57 Lead isotope ratios for particulate matter collected by thimbles from the lead smelter area

Table 58 Lead isotope ratios for air particulates from the mine site

ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
AM2	35.8225	0.0206	15.4362	0.0021	16.1230	0.0022	2.2212	6.76E-05	0.9575	2.44E-05
AM3	35.8268	0.0042	15.4544	0.0018	16.1177	0.0019	2.2228	6.58E-05	0.9588	2.12E-05
AM4	35.8529	0.0057	15.4564	0.0018	16.1370	0.0016	2.2219	3.30E-05	0.9579	1.25E-05
AM5	35.8661	0.0041	15.4669	0.0014	16.1324	0.0014	2.2232	5.02E-05	0.9588	1.41E-05
AM6	35.8395	0.0026	15.4549	0.0011	16.1243	0.0009	2.2227	2.94E-05	0.9585	1.29E-05
AM7	35.8476	0.0054	15.4601	0.0023	16.1479	0.0020	2.2201	5.80E-05	0.9575	1.90E-05
AM11	36.0418	0.0214	15.4660	0.0081	16.3319	0.0085	2.2078	1.13E-04	0.9472	2.32E-05
AM12	35.8672	0.0097	15.4574	0.0052	16.1659	0.0054	2.2187	9.76E-05	0.9562	3.80E-05

Note: Italic means the ²⁰⁸Pb ion beam intensity is between 0.3–1.0 volts relatively lower than 1–9 volts for other samples

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
CS composite	36.4069	0.0048	15.5008	0.0018	16.6880	0.0023	2.1816	3.40E-05	0.9289	1.17E-05
CS7	36.0466	0.0028	15.4747	0.0012	16.3304	0.0013	2.2073	2.68E-05	0.9476	1.32E-05
CS12	37.0145	0.0049	15.5652	0.0019	17.2905	0.0017	2.1407	4.06E-05	0.9002	1.29E-05
CS14	36.9825	0.0020	15.5510	0.0006	17.3188	0.0007	2.1353	2.52E-05	0.8979	7.43E-06
CS15	37.0950	0.0029	15.5411	0.0012	17.2849	0.0013	2.1461	3.20E-05	0.8991	1.09E-05
CS16	36.6236	0.0031	15.5103	0.0019	16.8622	0.0033	2.1717	2.60E-05	0.9197	1.47E-05
CS20	37.1014	0.0024	15.5434	0.0019	17.2879	0.0009	2.1461	4.00E-05	0.8991	2.00E-05
CS25	36.9544	0.0028	15.5320	0.0016	17.1453	0.0015	2.1553	4.26E-05	0.9059	1.16E-05
CS26	36.3663	0.0032	15.4897	0.0016	16.6215	0.0016	2.1879	3.54E-05	0.9319	9.36E-06
CS28	36.9089	0.0034	15.5316	0.0013	17.1089	0.0013	2.1573	3.52E-05	0.9078	1.12E-05
CS29	35.9700	0.0045	15.4654	0.0016	16.2542	0.0012	2.2130	3.00E-05	0.9515	9.38E-06
CS30	37.0516	0.0026	15.5438	0.0009	17.2321	0.0010	2.1502	3.12E-05	0.9020	8.42E-06
CS31	36.7297	0.0023	15.5125	0.0009	16.9584	0.0013	2.1659	3.82E-05	0.9147	1.23E-05
CS32	36.7694	0.0020	15.5235	0.0012	16.9783	0.0009	2.1656	2.52E-05	0.9143	9.10E-06
CS35	36.8400	0.0019	15.5253	0.0008	17.0660	0.0007	2.1587	3.20E-05	0.9097	9.54E-06
CS38	36.3155	0.0034	15.4927	0.0017	16.5780	0.0014	2.1905	2.56E-05	0.9345	1.00E-05
CS41	36.2648	0.0019	15.4869	0.0012	16.5191	0.0009	2.1953	3.26E-05	0.9376	7.28E-06
CS42	36.0999	0.0020	15.4740	0.0008	16.3792	0.0008	2.2040	2.80E-05	0.9447	1.13E-05
CS43	37.9162	0.0082	15.6329	0.0045	18.0235	0.0052	2.1038	3.60E-05	0.8674	1.76E-05
CS44	36.4891	0.0025	15.5063	0.0010	16.6579	0.0015	2.1906	3.10E-05	0.9309	1.30E-05
CS45	36.3522	0.0013	15.4915	0.0006	16.5830	0.0006	2.1921	3.12E-05	0.9342	8.96E-06
CS46	36.2972	0.0019	15.4810	0.0007	16.5540	0.0008	2.1927	3.40E-05	0.9352	1.17E-05
CS47	36.3668	0.0047	15.5041	0.0018	16.6068	0.0020	2.1898	3.38E-05	0.9336	1.19E-05
CS48	36.7627	0.0055	15.5278	0.0023	16.8572	0.0023	2.1806	3.74E-05	0.9211	1.83E-05
CS49	36.3726	0.0031	15.4931	0.0018	16.5987	0.0017	2.1912	4.94E-05	0.9333	1.63E-05
CS50	35.9952	0.0214	15.4528	0.0108	16.2703	0.0102	2.2127	8.52E-05	0.9499	2.32E-05
CS51	36.0088	0.0084	15.4731	0.0032	16.2823	0.0037	2.2115	3.76E-05	0.9502	1.57E-05
CS52	36.0466	0.0050	15.4720	0.0020	16.3032	0.0022	2.2110	3.60E-05	0.9490	9.46E-06

Table 59 Lead isotope ratios for garden soil from the city's residential area

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
FM21	35.8447	0.0058	15.4531	0.0022	16.1426	0.0026	2.2205	3.24E-05	0.9572	1.37E-05
FM22	35.8450	0.0069	15.4572	0.0032	16.1354	0.0032	2.2214	4.32E-05	0.9579	2.04E-05
FM22-C	35.8376	0.0033	15.4539	0.0014	16.1342	0.0014	2.2212	2.42E-05	0.9578	8.14E-06
FM23	35.8733	0.0039	15.4570	0.0015	16.1661	0.0017	2.2191	4.70E-05	0.9562	1.29E-05
FM24	35.8466	0.0042	15.4546	0.0017	16.1392	0.0016	2.2211	3.94E-05	0.9576	1.24E-05
FM25	35.8598	0.0070	15.4548	0.0030	16.1547	0.0034	2.2198	4.20E-05	0.9568	1.48E-05
FM26	35.8530	0.0051	15.4549	0.0018	16.1531	0.0019	2.2194	3.72E-05	0.9567	1.40E-05
FM27	35.8292	0.0058	15.4498	0.0026	16.1290	0.0026	2.2214	4.22E-05	0.9579	1.31E-05
FM28	35.8477	0.0046	15.4555	0.0019	16.1517	0.0021	2.2196	3.30E-05	0.9569	1.49E-05
FM29	35.8618	0.0038	15.4553	0.0015	16.1705	0.0012	2.2179	2.44E-05	0.9558	1.07E-05
FMB	35.8604	0.0086	15.4611	0.0037	16.1705	0.0039	2.2175	3.40E-05	0.9561	1.75E-05
FMK	35.8670	0.0147	15.4619	0.0062	16.1618	0.0065	2.2192	6.96E-05	0.9567	2.36E-05
FMR	35.8593	0.0049	15.4542	0.0018	16.1463	0.0018	2.2209	3.66E-05	0.9571	1.01E-05
FMRC	35.8600	0.0045	15.4535	0.0019	16.1555	0.0017	2.2196	5.14E-05	0.9566	1.52E-05
FMS	35.8266	0.0043	15.4507	0.0017	16.1272	0.0018	2.2215	2.64E-05	0.9580	9.86E-06

Table 60 Lead isotope ratios for fallout dust samples from the city's residential area

Table 61 Lead isotope ratios for roof gutter dust from the city's residential area

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
RG composite	35.8832	0.0048	15.4545	0.0019	16.1784	0.0019	2.2179	5.26E-05	0.9552	1.74E-05
RG1	35.9054	0.0048	15.4575	0.0017	16.2009	0.0015	2.2162	3.68E-05	0.9541	1.10E-05
RG2	35.9095	0.0037	15.4608	0.0012	16.2001	0.0014	2.2168	4.08E-05	0.9544	1.19E-05
RG3	35.8569	0.0034	15.4536	0.0018	16.1548	0.0017	2.2196	2.62E-05	0.9566	1.25E-05
RG4	35.8693	0.0038	15.4567	0.0018	16.1629	0.0016	2.2193	3.30E-05	0.9563	1.40E-05
RG5	35.9567	0.0035	15.4590	0.0014	16.2318	0.0015	2.2152	4.06E-05	0.9524	1.12E-05

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
PM ₁₀ S1	36.1121	0.0022	15.4745	0.0009	16.3955	0.0013	2.2025	3.10E-05	0.9438	9.22E-06
PM ₁₀ S2	36.1424	0.0039	15.4755	0.0018	16.4304	0.0017	2.1998	3.86E-05	0.9419	1.28E-05
PM ₁₀ S3	35.9308	0.0021	15.4578	0.0010	16.2270	0.0009	2.2143	3.74E-05	0.9526	1.16E-05
PM ₁₀ S4	35.9130	0.0021	15.4608	0.0008	16.2066	0.0009	2.2160	3.36E-05	0.9540	1.07E-05
PM ₁₀ S5	35.9834	0.0038	15.4562	0.0009	16.2767	0.0009	2.2106	4.06E-05	0.9496	9.70E-06
PM ₁₀ S6	36.0132	0.0026	15.4700	0.0013	16.3031	0.0014	2.2089	3.38E-05	0.9489	1.14E-05
PM ₁₀ S7	36.1242	0.0021	15.4790	0.0009	16.4062	0.0008	2.2019	3.44E-05	0.9435	1.01E-05
PM ₁₀ S8	36.9790	0.0044	15.5491	0.0016	17.1442	0.0016	2.1569	3.78E-05	0.9070	1.21E-05
PM ₁₀ S9	36.1813	0.0039	15.4904	0.0015	16.5004	0.0016	2.1927	3.36E-05	0.9388	9.18E-06
PM ₁₀ S10	36.4041	0.0030	15.5014	0.0011	16.6565	0.0010	2.1855	3.44E-05	0.9306	8.24E-06
PM ₁₀ S11	35.9662	0.0052	15.4629	0.0021	16.2391	0.0020	2.2148	3.54E-05	0.9522	1.26E-05
PM ₁₀ S13	35.9863	0.0044	15.4672	0.0009	16.2644	0.0008	2.2124	4.00E-05	0.9510	2.00E-05
PM ₁₀ S14	36.1468	0.0106	15.4796	0.0043	16.4345	0.0045	2.1995	5.78E-05	0.9418	2.42E-05
PM ₁₀ S15	35.9189	0.0029	15.4602	0.0012	16.2234	0.0012	2.2140	4.00E-05	0.9530	2.00E-05
PM ₁₀ S16	36.1315	0.0020	15.4655	0.0008	16.4096	0.0008	2.2018	4.00E-05	0.9425	0.00E+00
PM ₁₀ S17	36.0844	0.0019	15.4758	0.0008	16.3783	0.0009	2.2032	2.00E-05	0.9449	0.00E+00
PM ₁₀ S18	36.1970	0.0027	15.4829	0.0011	16.4863	0.0012	2.1956	4.00E-05	0.9391	0.00E+00
PM ₁₀ S19	36.1943	0.0029	15.4863	0.0011	16.4678	0.0011	2.1979	4.00E-05	0.9404	2.00E-05
PM ₁₀ S20	36.0233	0.0024	15.4726	0.0010	16.3116	0.0015	2.2084	4.00E-05	0.9485	2.00E-05
PM ₁₀ S21	36.1226	0.0036	15.4751	0.0014	16.3922	0.0013	2.2037	4.00E-05	0.9441	2.00E-05
PM ₁₀ S22	36.1506	0.0022	15.4794	0.0009	16.4358	0.0008	2.1995	4.00E-05	0.9418	0.00E+00

Table 62 Lead isotope ratios for soil $\ensuremath{\mathsf{PM}_{10}}$ fraction samples from the city residential area

Sample ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
VD composite	36.0053	0.0047	15.4665	0.0016	16.2765	0.0017	2.2121	3.22E-05	0.9502	1.05E-05
VD4	36.1023	0.0049	15.4760	0.0019	16.3519	0.0022	2.2078	2.58E-05	0.9464	1.26E-05
VD9	36.0475	0.0046	15.4701	0.0017	16.3044	0.0017	2.2108	3.70E-05	0.9488	1.44E-05
VD11	36.1904	0.0055	15.4774	0.0022	16.4356	0.0021	2.2019	3.82E-05	0.9417	1.29E-05
VD12	35.9755	0.0049	15.4638	0.0021	16.2440	0.0021	2.2146	4.22E-05	0.9520	1.18E-05
VD14	36.0845	0.0046	15.4705	0.0018	16.3405	0.0018	2.2083	3.78E-05	0.9468	1.19E-05
VD17	36.0869	0.0053	15.4701	0.0021	16.3529	0.0020	2.2067	3.56E-05	0.9460	8.84E-06
VD19	35.8820	0.0037	15.4439	0.0014	16.1838	0.0015	2.2170	3.64E-05	0.9542	1.37E-05

Table 63 Lead isotope ratios for carpet dust from the city's residential area

Table 64 Lead isotope ratios for air particulates from the city's residential area

ID	²⁰⁸ Pb/ ²⁰⁴ Pb	2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	2σ	²⁰⁶ Pb/ ²⁰⁴ Pb	2σ	²⁰⁸ Pb/ ²⁰⁶ Pb	2σ	²⁰⁷ Pb/ ²⁰⁶ Pb	2σ
HVA	35.9604	0.0024	15.4619	0.0010	16.2366	0.0013	2.2147	3.64E-05	0.9523	6.71E-06
HVA1	35.9228	0.0226	15.4836	0.0093	16.1829	0.0101	2.2198	9.22E-05	0.9567	5.86E-05
AH1	36.6014	0.0172	15.5440	0.0065	16.9773	0.0071	2.1561	5.66E-05	0.9155	3.84E-05
AH2	35.9431	0.0077	15.4736	0.0031	16.2526	0.0033	2.2115	4.38E-05	0.9521	2.18E-05
AH3	35.8986	0.0051	15.4698	0.0019	16.1949	0.0019	2.2167	3.16E-05	0.9552	1.60E-05
AH4	36.1249	0.0074	15.4756	0.0033	16.3907	0.0036	2.2040	5.42E-05	0.9441	1.12E-05
AH4	35.9396	0.0066	15.4696	0.0028	16.2306	0.0030	2.2143	6.12E-05	0.9531	2.20E-05
AH5	35.9269	0.0042	15.4677	0.0019	16.2210	0.0019	2.2148	3.50E-05	0.9536	1.47E-05
AH6	36.0239	0.0218	15.4777	0.0085	16.2854	0.0084	2.2124	1.31E-04	0.9505	6.72E-05
AH7	36.0825	0.0292	15.4935	0.0131	16.3231	0.0137	2.2108	1.22E-04	0.9494	7.84E-05
AH8	35.9904	0.0210	15.4667	0.0075	16.2632	0.0074	2.2130	1.15E-04	0.9511	4.88E-05
AH9	35.9426	0.0185	15.4557	0.0073	16.2370	0.0070	2.2136	9.76E-05	0.9520	4.82E-05
AH10	35.9125	0.0056	15.4682	0.0024	16.2027	0.0025	2.2164	4.28E-05	0.9546	1.27E-05
AH11	35.9611	0.0079	15.4763	0.0029	16.2486	0.0033	2.2131	4.68E-05	0.9525	2.30E-05
AH12	35.9063	0.0023	15.4712	0.0009	16.2235	0.0014	2.2132	5.78E-05	0.9536	1.93E-05
AH40	35.9748	0.0032	15.4696	0.0012	16.2543	0.0013	2.2133	4.52E-05	0.9517	6.29E-06

Note: Italic means the ²⁰⁸Pb intensity is between 0.3–1.0 volts relatively lower than 1–9 volts for other samples

The lead isotopic features for representative sample sets from the mine site and the community are displayed in Figure 30. There are three sets of data plotted in Figure 30 comprising: (a) mine site samples; (b) soil, air particulates and mineralisation; and (c) FMT, PM10S, roof gutter dust and carpet dust from houses. The data plotted in Figure 30 fall on a line, a feature seen when lead with two different origins are mixed together in the samples of soil, carpet dust and soil PM10. The line represents the mixing of different quantities of the material from the two origins, as described in Section 2.2.2 (page 98). Points clustered at the endpoints of the lines likely have a common origin. In contrast roof gutter dust and FMTshow straight lines with zero or near-zero slope indicating a common source for each kind of sample.

There are two sets of data plotted in Figure 31 for mine site, mineralisation and soil samples comprising: (a) ²⁰⁶Pb/²⁰⁴Pb mine vs ²⁰⁸Pb/²⁰⁴Pb; (b) ²⁰⁷Pb/²⁰⁴Pb mine vs ²⁰⁸Pb/²⁰⁴Pb. Figure 30 plots only ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁸Pb/²⁰⁴Pb for (a) to (c).

There are additional lead isotope ratio features associated with samples collected in the copper smelter (ATC and Isa chalcopyrite and copper slag), as indicated by Figure 30 and Figure 31. ATC samples, which include material derived from Ernest Henry copper ore, and copper smelter feed (as distinct from Isa chalcopyrite) are distinctly different from the lead ore mixing line occurring at Mount Isa (Figure 30). The source and nature of lead associated with the copper concentrate is presented in further detail in Figure 31, which shows differences for the ratios (²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb) between Isa chalcopyrite (referred to as 'Isa Cu' in Figure 31) and the Urguhart Shale type of lead ore from MIM but not copper slag which may be a mixture (Figure 31). ATC is probably more reliable in terms of indicating what has happened over a longer period of time as these samples were collected in 2010 over a few months whereas Isa chalcopyrite and copper slag were grab samples collected in 2008. In addition the copper smelter feed (SS12) collected in 2008 shows that it is a mixture of Isa chalcopyrite and Ernest Henry copper (Figure 31). Is a chalcopyrite material falls on a mixing line below the lead ore mixing line produced from the Mount Isa lead ore samples, NMU and CS (Figure 31). This further differentiates Isa chalcopyrite from lead ore mined at Mount Isa, and shows that the lead in the concentrate currently being smelted in the Mount Isa copper smelter makes no apparent contribution to the lead being measured in the city area.

Figure 30b also shows greater mixing of lead sources in the PM_{10} samples collected in the outdoor city air ('AH') than in PM_{10} samples collected from the mine site ('AM'), indicating that some of the dust contains lead from the non-Urquhart Shale source. Figure 30c shows similar behaviour in the soil PM_{10} fraction (' $PM_{10}S$ '), so it is likely that the city PM_{10} samples contain some soil PM_{10} that has been re-entrained.



Note: (a)TD: surface tailings; HR: haul road dust; ATC: thimbles from copper smelter area; ATP: thimbles from lead smelter area; FMM: fallout from mine site; FP: footpath samples; Isa Cu: Isa chalcopyrite; Cu slag: CuSm slag (SS4 in Table 52, page 204); Cu feed: SS12 in Table 52, page 204.; AH: air PM_{10} from city outdoor; (b) AM: air PM_{10} from mine site; NMU: natural mineralisation; MV: air particulates from two downwind comparative sites; and (c) FMT: fallout from city; PM_{10} S: fine fraction collected from garden soil (also called soil PM_{10}); CD: carpet dust; RGD: roof gutter dust.

Figure 30 Lead isotope ratios (²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb) for samples from Mount Isa City and the mine site



Note: CS: garden soil < 2 mm; NMU: natural mineralisation;TD: surface tailings; HR: haul road dust; ATC: thimbles from copper smelter area; Isa Cu: Isa chalcopyrite; Cu slag: CuSm slag (SS4 in Table 52, page 204); Cu feed: SS12 in Table 52, page 204.



Whisker-box plots of the lead isotope ratios ($^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$) for samples from the mine site and city residential area are given in Figure 32.The lead isotope ratios for mine site samples indicate that the lead in the copper smelter thimble (ATC) and the lead smelter thimble (ATP) samples has different isotope ratios, indicating that it has different geological origins (Table 56, Table 57, Figure 30 and Figure 31). Surface tailings material, haul road dust, and thimble samples from the lead smelter area³⁹ from the mine site have a similar ratio to crushed ore materials (Figure 31). The mean ratios of for these samples, 35.8751 ± 0.0018 (SE) for $^{208}Pb/^{204}Pb$ and 16.1302 ± 0.0006 (SE) for $^{206}Pb/^{204}Pb$,

³⁹ Thimble Sample ATP8 is identified as being collected from the flowing gas stream within the lead smelter that would be discharged via the stack exit point at the top of the smelter.

are similar to the natural mineralisation (Urquhart Shale) type of lead. The thimble samples from copper smelter area (ATC) have a unique lead isotope ratio feature (no variations in ²⁰⁸Pb/²⁰⁴Pb), which is different from other mine site samples (Figure 30).

Garden soil samples are different from mine site samples, showing a wide range of ratios (35.970-37.9162 for $^{208}Pb/^{204}Pb$ and 16.2542-18.0235 for $^{206}Pb/^{204}Pb$) (Table 59, Figure 30 and Figure 32). When plotted (Figure 30b) they fall on a line, indicating that the contained lead has two origins, with different mixing ratios in different samples. Soil PM₁₀ and carpet dust samples also fall on the same mixing line, but tend to fall closer to the cluster of points for the mine site and natural mineralisation samples (Figure 30). Soil PM₁₀ fraction samples had a range from 35.9130 to 36.9790 for $^{208}Pb/^{204}Pb$ and from 16.2066 to 17.1442 for $^{206}Pb/^{204}Pb$ (Table 62). These charts show that there is lead from some other origin as well as the Urquhart Shale present in the garden soils, soil PM₁₀ fraction and carpet dust samples.

Carpet dust samples have a lower range, from 35.8802 to 36.1904 for ²⁰⁸Pb/²⁰⁴Pb and from 16.1838 to 16.4356 for ²⁰⁶Pb/²⁰⁴Pb compared with soil PM₁₀ fraction samples (Table 63). All the roof gutter dust samples had similar lead isotopic ratios and are even lower than the garden soil PM₁₀ fraction and carpet dust samples. The mean of ²⁰⁸Pb/²⁰⁴Pb ratio for roof gutter dust is 35.8968 ± 0.03568, and ²⁰⁶Pb/²⁰⁴Pb is 16.1881 ± 0.02848 (Table 61), which are very close to the Urquhart Shale results.

The isotope ratios of fallout dust ('FMT') from the city residential area are similar to roof gutter dust, Urquhart Shale natural mineralisation, haul road dust, and tailings dam materials (Figure 30). The isotope ratios of fallout dust ('FMM') from the mine site differ from those of other mine site samples and show evidence of mixing, similar to that shown by some of the residential area soil samples (Figure 30). The comparison between mine site fallout dust ('FMM') and city fallout dust ('FMT') show a statistically significant difference (Table 54, Table 60, Figure 30 and Figure 32). The lead isotopic ratios of FMT displayed a mean of 35.8515 ± 0.01346 for 208 Pb/ 204 Pb and 16.1492 ± 0.01441 for 206 Pb/ 204 Pb (Figure 32). However, the ratios of FMM, show a wide range, from 35.9408 to 36.2942 for 208 Pb/ 204 Pb and from 16.2094 to 16.4877 for 206 Pb/ 204 Pb.

However, air PM_{10} particulates from the mine site (AM) and the city outdoors (AH), display the opposite pattern. Air-city ratios are spread from 35.8986 to 36.6014 for $^{208}Pb/^{204}Pb$ and 16.1949 to 16.3907 for $^{206}Pb/^{204}Pb$ (Figure 30). The ratios of AM indicate a mean of 35.8426 ± 0.01642 for $^{208}Pb/^{204}Pb$ and 16.1304 ± 0.01101 for $^{206}Pb/^{204}Pb$.

It is therefore not clear what the exact source of lead is in FMM excepting that it has an Urquhart Shale lead origin with some mixing in other geological sequences.



Note: ATC: thimbles from copper smelter area, ATP: thimbles from lead smelter area, CS: garden soil (< 2 mm), FMM: fallout from mine site, FMT: fallout from city, HR: haul road dust, WF: floor wipes, WS: window sill wipes, WT: window trough wipes, WV: veranda wipes, NMU: natural mineralisation, $PM_{10}S$: fine fraction collected from garden soil (also called soil PM_{10}), SSP: dust from MIM lead–zinc concentrator and lead smelter, PO: lead ore from MIM; SSC: copper ore, slag and dust from copper smelter at MIM, TD: surface tailings, CD: carpet dust; RGD: roof gutter dust, AH: air PM10 from city outdoor, AM: air PM10 from mine site, , MV: air particulates from two downwind comparative sites.

Figure 32 Lead isotope ratios (²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb) of samples from the mine site and city residential area (solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values).
3.3 X-ray absorption spectroscopy

3.3.1 Experimental validation and uncertainty of X-ray absorption near-edge spectroscopy

Samples from the mine site, natural mineralisation, natural outcrops and the city residential area were scanned for XANES analysis in December 2008, December 2009, February 2010, and November 2010 at the Australian National Beamline Facility, Photon Factory, KEK (High Energy Accelerator Research Organization), Tsukuba, Japan. The XANES spectra were normalised as described in Section 2.2.3.1 (page 100) and processed as described in Section 2.4.3.1 (page 138). The uncertainties and validation of XANES least-squares linear combination fitting ('LCF') are discussed in Section 3.3.2.

Following the completion of the data analysis, it was considered appropriate to review the data analysis process and decisions regarding the fitting of samples with the model compounds and uncertainty of fitting. Dr Jade Aitken of the University of Sydney was engaged to review all of the data analysis for the XANES spectra to confirm and validate the findings. There were some cases where it was necessary to use other techniques, such as XRD, to resolve fitting of model compounds.

In some cases, fitting occurred with model compounds that did not appear to be appropriate (for example, lead citrate in slag) but were nonetheless selected by the rigorous decision steps in the EXAFSPAK software package (see Section 2.4.3.1.1, page 138). Subsequent review has found that lead silicate (PbO.SiO₂), which was not included in the model compounds on which the analysis was based, has a very similar spectrum to that of lead citrate, and this is likely to explain the reported presence of lead citrate in slag samples (see Section 3.3.6, page 240). In some cases, the model compound was fitting to a functional group that had not been scanned as part of the group of model compounds. Such cases will be identified as they arise in the presentation of the results.

3.3.2 Uncertainty of normalisation and beam stability

The uncertainty associated with the LCF procedure was determined from the standard deviation of the fits themselves from five identical samples diluted with boron nitride (A, B, C, D, and E) of S1O1 and S1O4, as described in Section 2.4.3.1.3 (page 140). The LCF fitted results are displayed in Table 65 and Figure 33.

The dilution factors for samples S1O1 and S1O4 (diluted with boron nitride — Sigma-Aldrich Chemie GmbH, Steinheim, Germany) are 140 and 34 times boron nitride diluted respectively (Table 65). The spiked mole ratios (lead sulfide:lead oxide) are approximately 1:1 and 1:4 for the S1O1 and S1O4 samples respectively. The standard errors from LCF fitted results are very low (0.4 - 0.8 per cent) for all two sets of spiked samples (Table 65). The low magnitude of the standard error indicates that the X-ray beam was stable during the XANES

scanning and that the normalisation procedure was consistent. The significantly low residuals (< 2 per cent) (Table 65) indicate complete fittings for each group of compounds. The LCF residual for Sample S1O4B is 1.7% (Figure 33).

The relative errors, however, vary for these two sets of lead compounds (Table 65). The relative errors range from 1 per cent for lead oxide in Sample S1O4 to 37 per cent for lead sulfide in Sample S1O4. Samples with higher dilution factors, for example, 140 times for Sample S1O1 and 34 times for Sample S1O4, display a mean relative error of about 20 per cent. This is a similar finding to previous studies (Ajiboye et al., 2007), where the samples with low dilution factors had unacceptable levels of errors. A plot of 'proportion of model compound' vs 'relative error' is given in Figure 34. The lead compounds with the same spiked proportions were averaged and considered as one group in the model (Figure 34). The plot was generated using EXCEL and this was the best fit. The plot shows that relative error decreases as proportion increases. The plot shows that the relative errors for lead compound mixtures are lower when the proportion of the lead compound is high in the samples (Figure 34). A comparison of values for the plot shows that 20 per cent of a lead compound gives a relative error of 0.55 (Figure 34) whereas 11 per cent of a lead compound gives a relative error of 0.4. The data for relative error in Table 65 show that the relative error generally has a mean of 0.20 percent for a range of proportions of lead sulfide mixed lead oxide in boron nitride, except for the most dilute cases. The plot also indicates that model compounds that are not present in the samples (i.e. none were added to the calibration mixtures) are unlikely to be fitted based on the experimental data in this study (Figure 34). Comparison with the finding above (Ajiboye et al., 2007) indicates that a relative error of 0.20 is achieved for a lead compound in a mixture of 51 per cent.

The plot is described by the following function, generated using EXCEL:

$$y = 0.47e^{-1.82x}$$
 (r²=0.46) Equation 7

Sample ID	Dilution factor	Lead sulfide (49%)	Relative error	Standard error	Lead oxide (51%)	Relative error	Standard error	Residual	N _{tol}
S1O1	140	39%	20%		61%	20%		0.0054	100%
S101A		39%	20%		61%	20%		0.0052	100%
S1O1B		40%	18%		60%	18%		0.0060	100%
S101C		41%	16%		59%	16%		0.0083	100%
S101D		39%	20%		61%	20%		0.0056	100%
S101E		39%	20%		61%	20%		0.0053	100%
Overall			19%	0.4%		19%	0.4%		
Sample ID	Dilution factor	Lead sulfide (19%)	Relative error	Standard error	Lead oxide (81%)	Relative error	Standard error	Residual	Ntol

Table 65 LCF fitted results for two spiked lead compounds and their uncertainty

S104	34	17%	11%		82%	1%		0.0069	99%
S104A		15%	21%		85%	5%		0.0136	100%
S104B		17%	11%		83%	2%		0.0166	100%
S104C		15%	21%		85%	5%		0.0153	100%
S104D		12%	37%		88%	9%		0.0091	100%
S104E		15%	21%		85%	5%		0.0132	100%
Overall			20%	0.8%		5%	0.8%		



Figure 33 Lead $L_{\mbox{\scriptsize III}}$ X-ray edge XANES spectra of boron nitride spiked samples



Figure 34 Plot of relative errors of LCF results and laboratory-mixed proportion for lead compounds (dilution factors are 34–140 times for samples)



Note: Green line = LCF-fitted results. Red line = 17% lead sulfide. Pink line = 83% lead oxide

Figure 35 Lead L_{III} edge XANES spectra of boron nitrate mixed sample S1O4B Black line = the experimentally determined spectrum.

SS8 is the dust from the base of the lead stack (Section 2.3.6.2.9, page 133). It was scanned during four different beam line visits. Figure 36 compares the scans from each beam line visit. There is no significant difference in the lead L_{III} edge from all four visits (Figure 36).



Figure 36 Comparison of Lead L_{III} edge XANES spectra for SS8 from different visits to the same beam line

MC 14 is pure lead sulfate purchased from Wako Pure Chemical Industries Ltd, Japan (Section 2.4.3.1.2, page 140). The compound was diluted with boron nitrate and scanned twice: in December 2009 and November 2010. MC14 shows almost identical scan features for the lead $L_{\rm III}$ edge (Figure 37), which is similar to the findings for SS8 and indicates that, under the same beam line settings, high quality comparative spectra can be achieved between visits.



Figure 37 Comparison of lead L_{III} edge XANES spectra for pure compound lead sulfate from different visits to the same beam line (BL 20B)

In the case of SS1 (lead slag), comparison of scans from three different visits indicates different lead L_{III} edges spectra (Figure 38). All the raw spectra were normalised with the same beam line settings. The reason for the variability in the SS1 XANES spectra is not clear. A possible reason for the differences is the non-homogeneity of the samples, perhaps due to insufficient grinding. Homogeneity is important because the X-ray absorption energy points of the compounds present in the slag are very close. Figure 38 shows that the normalised absorbance ratios are slightly different between spectra recorded at different times.

The noise and variation in the measured spectra make it difficult to get a clear result using the PCA and LCF analyses of the lead and copper slag samples.



Figure 38 Comparison of lead L_{III} edge XANES spectra for lead slag (SS1) from different visits to the same beam line

3.3.3 Validation of XAS fitted results

A key approach for evaluating XANES LCF fitted results was to compare them with other molecular or elemental techniques, such as XRD and SEM-EDS. Spectra were recorded for samples MIN1 and MIN4 by XRD as well as XAS. The XANES spectra for MIN1 (cerussite from Mount Isa) and MIN4 (galena from Mount Isa), are confirmed by XRD results (Table 66). There are slight differences in the lead L_{III} edge between galena from the mine site and pure lead sulfide powder (Figure 39). However, cerussite and pure lead carbonate show visually identical normalised lead L_{III} edges from various visits (Figure 40), except for a slight offset to the XANES spectra of MIN1-2008.

Figure 39 and Figure 40 are good examples of close fits between pure laboratory samples and samples of the lead minerals.

Sample ID	Sample description	MC5 (lead sulfide)	MC17 (lead carbonate)	Residual
MIN4-2008	Galena from Mount Isa	100%	-	0.03
MIN4-201002	Galena from Mount Isa	100%	-	0.07
MIN1-2008	Cerussite from Mount Isa	-	100%	0.25
MIN1R-2008	Cerussite from Mount Isa	-	98%	0.07
MIN1-201002	Cerussite from Mount Isa	-	100%	0.02
MIN1a-201002	Cerussite from Mount Isa	-	99%	0.02

Table 66 LCF fitted results of boron nitride spiked with minerals (MIN4 and MIN1)



Figure 39 Comparison of lead L_{III} edge XANES spectra for galena (MIN4) and pure lead (II) sulfide



Figure 40 Comparison of lead L_{III} edge XANES spectra for cerussite (MIN1) and pure lead carbonate

3.3.4 Comparison of pre-edge maximum setting for background subtraction

The chemical and structural information from the XANES spectra are very subtle and can be significantly influenced by the data-reduction process. One of the crucial steps involved in processing the spectra is inaccurate extrapolation of preedge polynomial, which may introduce curvature into the edge region. Therefore, carefully normalised XANES data should be obtained for data interpretation. The Gaussian pre-edge function was used in EXAFSPAC to subtract the background signal (George and Pickering, 2000). With no objective definition of the best preedge function, the pre-edge subtraction approach was evaluated by comparing different pre-edge maximum energies for the same sample in this study so that the best normalised XANES spectra could be achieved.

The sensitivity of the spectra to the pre-edge maximum chosen during background subtraction was found to have limited effect on the calculation of the fractions of components within the sample set (Table 67). The pre-edge maximum energy of S1O1 varied from 12,900 to 13,020 eV, with 10 eV increase per step. The corresponding fitted results indicated a negligible (less than 1 per cent) standard error for each component (Table 67). The residuals have a relatively low magnitude of less than 1 per cent, except 12,910 eV and 12,920 eV.

Pre- edge	Lead sulfide (49%)	Relative error	SD	SE	Lead oxide (51%)	Relative error	SD	SE	Residual (%)	N _{tol}
12900	37%	25%			63%	24%			0.46	100%
12910	36%	27%			64%	25%			4.13	100%
12920	36%	26%			65%	27%			1.43	101%
12930	36%	26%			65%	27%			0.59	101%
12940	41%	15%			61%	19%			0.75	102%
12950	39%	21%			62%	22%			0.53	101%
12960	39%	19%			61%	21%			0.80	101%
12970	39%	19%			62%	21%			0.80	101%
12980	40%	19%			61%	21%			0.76	101%
12990	40%	18%			61%	20%			0.53	101%
13000	39%	20%			61%	20%			0.63	100%
13010	37%	24%			63%	23%			0.87	100%
13020	40%	18%			60%	18%			0.92	100%
Overall		21%	2%	0.5%		22%	2%	0.4%		

Table 67 Effects of pre-edge maximum setting to the final fits for Sample S1O1

Note: SE: Standard error – percentage lead species in boron nitride-spiked with lead compound (X140 dilution), estimated using linear combination fitting of model compound spectra. The preedge maxima of both the model compounds and boron nitride-spiked sample were changed over the range of 12,900–13,120 eV, but fitted over the range of 13,000–13,100 eV. N_{tot} is the sum of the fitted portion.

3.3.5 XANES scans for individual group

Normalised XANES edges for different groups of samples from the city's residential area and the mine site are shown in Note: AH is PM₁₀ at houses and HVA is high volume air particulate collection in city

Figure 41 to Figure 54. The XANES edges are very similar within the same sample group. It is difficult to distinguish the difference by visual comparison. The spectra were, therefore, compared using PCA, target transformation, and LCF (Section 2.4.3.1.1, page 138). The LCF results are described in Section 3.3.6 (page 240).



Note: AH is PM₁₀ at houses and HVA is high volume air particulate collection in city Figure 41 Lead L_{III} edge XANES spectra for air particulates from the city's residential area



Figure 42 Lead $L_{\mbox{\scriptsize III}}$ edge XANES spectra for air particulates from mine site





Sample Group: ATP



Figure 44 Lead $L_{\mbox{\scriptsize III}}$ edge XANES spectra for fine dust from the lead smelter area



Figure 45 Lead L_{III} edge XANES spectra for soil samples from the city's residential area

Sample Group: FM



Figure 46 Lead L_{III} edge XANES spectra for fallout dust from the city's residential area and mine site



Figure 47 Lead $L_{\mbox{\scriptsize III}}$ edge XANES spectra for haul road dust from the mine site



Figure 48 Lead L_{III} edge XANES spectra for house wipe samples from the city's residential area



Figure 49 Lead L_{\tiny\rm III} edge XANES spectra for natural mineralisation and natural outcrop samples



Figure 50 Lead L_{III} edge XANES spectra for soil PM10 fraction samples from the city's residential area

Sample Group: RG



Figure 51 Lead L_{III} edge XANES spectra for roof gutter dust from the city's residential area



Figure 52 Lead $L_{\mbox{\scriptsize III}}$ edge XANES spectra for general source samples from the mine site



Figure 53 Lead-L_{III} edge XANES spectra for tailings dam materials from the mine site



Figure 54 Lead $L_{\mbox{\scriptsize III}}$ edge XANES spectra for carpet dust from city's residential area

3.3.6 XANES least-squares linear combination fitting

According to the plot in Figure 34, the highest relative error occurs when the proportion of the lead compound in the sample (derived from Equation 7, page 218) is lowest. Based on consideration of the errors for XANES data processing, this summary only reports the lead model fittings > 15 per cent. For a conservative estimation, the LCF fitting is rejected when the fitted abundance of lead species is < 15 per cent, unless the fitting occurs over a 50 per cent proportion of the sample group and XANES spectra are not excessively noisy.

A feature of the XANES fitting process (Section 2.4.3.1.1, page 138) using model lead compounds is the occasional selection of compounds that do not appear logical. This occurs when the chemical structure of a missing model compound is similar to one that is used. For example, although lead silicate (PbO.SiO₂) was not available as a model lead compound, it has a similar spectral feature to those of lead citrate and acetate, which has likely resulted in the observation of lead citrate peaks in samples where this is more likely to be lead silicate. Examples where this may have occurred include, but are not limited to, smelter slag samples, tailings dam samples and air–particulate samples(Table 69, Table 71 and Table 76) (Witkowska et al., 2005, Witkowska et al., 2000). The XANES fitting process is mathematical not judgemental, so from time to time apparently anomalous fits are produced. Manual exclusion of models was not used.

3.3.6.1 *Natural outcrops*

This group of samples (Figure 49) included natural mineralisation samples from Urquhart Shale and one sample from a non-Urquhart Shale unit (NM6 from Breakaway Shale) in the city's residential area. The dominant components for the outcrop samples were lead–goethite, the anglesite–plumbojarosite grouping, plumbogummite, and molybdophyllite (Table 68). The numbers in brackets in Table 68 represent the standard errors.

Sample ID	Lead– goethite	Lead sulfate	Plumbogummite	Molybdophyllite	Residual
NM1	0.75 (1)				8.70E-04
NM2	0.80 (1)	0.21 (1)			3.80E-05
NM3	0.63 (1)	0.12 (3)	0.25 (3)		5.98E-05
NM4	0.59 (2)	0.22 (1)	0.07 (1)	0.12 (1)	1.30E-05
NM5	0.55 (4)		0.29 (2)	0.14 (3)	1.21E-04
NM6			0.99 (1)		9.81E-05

Table	68 Summary	of XANES	fittings	for outcrop	samples
		•••••			

3.3.6.2 *Mine site*

There are significant differences in lead speciation in various samples from the mine site, and lead, zinc, and copper mineral processing sites in the general source group (Figure 52 and Table 69). Galena and anglesite are commonly found in this group. Lead slag samples (SS1 and SS2) have a mean of 37 per cent of the total lead as metallic lead. SS5, which is from the zinc filter plant shed

area, showed 77 per cent of the lead as anglesite. This material is likely to be old dust accumulated and the galena oxidised to the sulfate by weathering or some other mechanism. Samples associated with lead mining and mineral processing activities are dominated by galena. Dust collected from the inside base of the lead smelter stack (SS8) shows evidence for the complexity of chemical reactions of the metallurgical processes at a relatively high temperature and produced reaction products, such as leadhillite $[Pb_4(SO_4)(CO_3)_2(OH)_2]$ or mendipite $(Pb_3O_2Cl_2)$, in dust materials. Some of these compounds are generated from the gas phase during cooling of hot gases.

Results of the XANES LCF for air PM_{10} samples (Figure 42) from the mine site are shown in Table 70, including from the lead smelter area and tailings, and two downwind comparative sites (AM9 and AM10) (Section 2.3.6.1.1, page 127). The majority of lead species in this group are lead sulfate, lead sulfide, and lead oxide.

Lead species in air–particulate samples collected with thimbles from the copper and lead smelter areas (Section 2.3.6.1.1, page 127) show different features from other mine site samples (Table 71 and Table 72), which is a result of the reaction conditions in the metallurgical furnaces. Thimble samples of particulates from the copper smelter area are primarily anglesite, rather than galena (Table 71), most likely due to the reaction of lead oxide with sulfur trioxide in the copper smelter furnace off-gases (Davenport et al., 2002, Sarkar, 1992, Fountain et al., 1993). Thimble samples from the lead smelter area are similar to lead smelter area dust and characterised by the presence of lead sulfide (Table 72) in the samples taken close to the sinter plant feed system.

Haul road dusts on the mine site are notable, primarily for having large proportions of lead–goethite and lead chloride and relatively small percentages of lead sulfate (Table 73). Groundwater waters extracted during dewatering operations at MIM are used for haul road dust control and have a similar composition to tailings seepage water and dry-season river water. These water had high salinity, mainly from sulfate (range 436–8300 mg/L) and chloride (range of 604–880 mg/L) (Noller et al., 2012). The quantity of salinity in the mine water used for haul road dust control is significant as the solution and evaporates become incorporated in fine particles formed on the haul road surface. Calculations based on the lead concentration show that approximately 3 L of road watering per 10 m² of road surface is needed to produce the lead chloride measured in the road dust (Figure 22, page 171). The median bioaccessibility of lead in the haul road dusts is 42 per cent (see Table 90, page 259), which is the highest measured, indicating that the solubility of lead in these dusts is higher than most locations.

Lead sorption onto iron oxides and hydroxides results in the formation of leadgoethite (Bargar et al., 1998), which is commonly found in the XANES analyses of Mount Isa environmental samples (Section 3.3.6.3, page 242). In the presence of dilute sodium chloride solution, the lead sorption onto iron oxides and hydroxides is enhanced (Bargar et al., 1998). Studies of the hydro-chemical conversion of galena in ferric chloride–potassium chloride solution (Long et al., 2009) show that lead chloride is easily precipitated and that increased chloride concentration accelerates the dissolution of lead chloride. Dissolution of galena– pyrolusite in sodium chloride is also enhanced with increasing sodium chloride concentration (Long et al., 2010). The literature reports of lead–goethite and lead chloride formation collectively support the observations of the XANES analysis of haul road dusts.

Various reviews show that haul road dust is a major source of fine particles at mine sites (Cox and Isley, 2012). Wheel generated dust (mainly from trucks travelling on unsealed haul roads) was identified as the primary source of TSP and PM₁₀ (52% and 39%, respectively) at mine sites and the second highest contributor to PM_{2.5} emissions of about 23% (Katestone, 2011). Unsealed haul roads at mine sites generally consist of a graded and compacted roadbed and may be topped with hard surface materials. When a vehicle travels an unpaved road, the force of the wheels on the road surface causes pulverisation of surface material (U.S. EPA, 2006). Particles are lifted and dropped from the rolling wheels, and the road surface is exposed to strong air currents in turbulent shear with the surface. The turbulent wake behind the vehicle continues to act on the road surface after the vehicle has passed (U.S. EPA, 2006). The silt content of the road surface material is usually reduced by vehicle traffic, leaving a high percentage of coarse particulates. The amount of dust that is liberated from a road surface depends on a number of factors, including (Foley et al., 1996): (i) airflow at the road surface, which is proportional to the speed of the vehicles, vehicles aerodynamic shape (lower vehicles with many wheels tend to increase dust) and ambient wind speed; (ii) number of vehicles; (iii) vehicle weight; (iv) number of wheels per vehicle; (v) particle size distribution of the surface material; (vi) restraint of the surface fines, which is related to compaction of the road surface, bonding of the surface material, and durability of the material; and (vii) weather, particularly humidity, which is influenced by the amount of precipitation and evaporation. In addition, road watering for dust control is undertaken with recycled mine water including groundwater and recovered seepage. Thus, it can be expected that fine particles can easily be generated on haul roads and that the mixture of particles, high salinity dewatering for dust control and high ambient temperature at MIM mine site will give specific chemical features that may be distinct from other mineral and processed lead forms on the mine site.

Tailing samples were collected from the three main tailings dams (known as Number 5 ['TD5'], Number 7 ['TD7'] and Number 8 ['TD8'] tailings dams), of which TD7 and TD8 are currently operating. All tailings have a high proportion of lead–goethite, ranging from 26 per cent to 98 per cent. Both surface tailings (0–2 cm) and deeper tailings (2–10 cm) were collected. The XANES scan data indicates that deeper tailings normally show a higher proportion of lead–goethite but less lead sulfate (Table 74). Apart from lead–goethite, there is also about a 20 per cent contribution from anglesite and plumbojarosite. The fitting for the tailings materials is very similar to haul road dust (Table 73 and Table 74). The main lead species in fallout dust collected at mine site are galena and anglesite (Table 75).

3.3.6.3 *City residential area*

Air PM_{10} samples Note: AH is PM10 at houses and HVA is high volume air particulate collection in city

Figure 41) in the city are characterised by the presence of lead–goethite, galena, and lead citrate (Table 76⁴⁰). The XANES process cannot distinguish between lead citrate and lead acetate, so these two compounds were grouped together in reporting (see Section 2.4.3.1.1, page 139). The citrate is a model for the structure of lead silicate (Witkowska et al., 2005, Witkowska et al., 2000). Such fitting of model compounds occurs when there is similarity of chemical structure with a missing model compound as described in Section 3.3.6 (page 240). Surface soil samples from house gardens consist of a mean of 87 per cent lead–goethite and small portions (about 10 per cent) of molybdophyllite (Table 77).

Fine fractions extracted from garden soils ($PM_{10}S$) (Figure 50) are very similar to the bulk surface soil samples, with a mean of 86 per cent lead–goethite (Table 78). Fallout dust samples from the city show lead–goethite and galena (Table 79). Anglesite and pyromorphite are also common (Table 80). Compared with fallout dust from the mine site, more lead–goethite, but less galena, is found in the fallout dust samples from the city. The majority of lead in roof gutter dusts is lead–goethite, sometimes up to 100 per cent (Table 80). It seems very likely that other deposited lead forms such as lead sulfide or lead sulfate have been converted to lead–goethite upon standing or the latter was the deposited form. Lead sulfide is a photoactive compound and its reaction might be accelerated by ultraviolet light.

Carpet dusts are different from soil and roof gutter dusts (Table 77, Table 80, and Table 81). The two major lead species in the carpet dust samples are lead–goethite (about 50 per cent) and galena (about 20 per cent).

Bulk ghost wipe samples (Section 2.3.6.2) from three houses in the city's residential area primarily consist of high portions of lead-goethite (37–90 per cent) and lead sulfide, and are similar to the fallout dust from the community (Table 82). The veranda wipes from House 2, which is about 0.7 km south-east of the lead stack (Figure 13a), contained over 61 per cent lead sulfide, but no lead–goethite as normally detected in this group of samples.

⁴⁰ Table 76 also indicates that HVA1 (Station Street-MIM TEOM) and HVA2 (K-Oval) show the presence of lead sulfide and are closer to the lead smelter facility than HVA4 (RSL-MIM TEOM). HVAP slurry composite used as a sample to dose rats for bioavailability measurement also did not contain lead sulfide. Refer to Fig. 57 for location of HVA samplers or MIM annual report.

Sample ID	Sample description	Lead total (mg/kg)	Residual	Lead sulfide	Lead sulfate	Lead– goethite	Mendipite	Lead citrate	Magnetoplumbite	Lead metal	Molybdophyllite	Leadhillite
SS1	Lead slag	30673	7.67E-06	6 0.07(1)			0.23(1)		0.17(1)	0.36(1)	0.17(2)	
SS2	Lead slag old	24882	5.91E-06	0.13(1)			0.38(1)	0.07(1)		0.38(1)	0.04(1)	
SS3	Copper slag	3919	1.21E-05	0.06(1)	0.45(1)	0.27(3)			0.15(3)	0.05(1)		
SS5	Zinc concentrator dust	21834	2.40E-05	0.05(1)	0.77(2)			0.18(2)				
SS6	Copper concentrator dust	337	7.60E-05	0.33(2)		0.58(1)				0.10(2)		
SS7	Lead ore stockpile dust	1756	4.13E-06	0.79(1)	0.180(1)							
SS8	Lead stack	656000	1.04E-05	6 0.21(1)	0.34(2)	0.12(1)	0.14(2)					0.18(3)
SS9	Lead smelter area dust	126432	5.91E-06	0.49(4)	0.38(1)							0.12(1)
SS10	Lead smelter area dust	61568	6.86E-06	0.69(4)	0.02(1)		0.17(2)					0.10(3)
SS11	Lead smelter area dust	68645	2.18E-06	0.49(1)	0.14(1)		0.34(1)					
SS12	Copper smelter area dust	599	9.13E-04	0.23(4)	0.60(3)							
SS16	Stockpile lead ore from Black Star open cut	22307	1.40E-05	0.48(1)		0.22(1)		0.29(1)				
SS17	Stock pile lead ore from George Fisher	39304	7.91E-06	0.67(1)	0.05(1)	0.07(1)		0.20(2)				
SS18	Stock pile lead ore from Handle Bar Hill	3956	3.63E-05	0.06(1)	0.92(1)							

Table 69 Summary of XANES fittings for general source samples from the mine site

Sample ID	Sample description	Lead total (mg/kg)	Residual	Lead sulfide	Lead sulfate	Lead– goethite	Mendipite	Lead citrate	Magnetoplumbite	Lead metal	Molybdophyllite	Leadhillite
SS19	Lead mine non- acid waste	771	1.73E-05	0.18(1)		0.50(1)		0.28(1)				
SS20	Lead ore potential acid forming	1210	2.24E-05	0.33(1)		0.61(2)		0.07(1)				
SS21	Stockpile composite	9269	1.05E-05	0.67(1)		0.33(1)						
SS22	Lead smelter area dust	44944	5.43E-06	0.60(1)	0.09(1)	0.06(1)					0.22(1)	
SS26	Lead concentrator dust	19064	5.90E-06	0.88(1)	0.05(1)							
TV1	XZn concentrate	26164	4.03E-05	,	0.99(1))						
TV7	XZn lead dross	43098	1.79E-04				0.32(3)				0.66(3)	

Note: the numbers in brackets are standard errors.

Sample ID	Residual	Lead sulfate	Lead sulfide	Lead oxide	Pyromorphite	Molybdophyllite	Lead citrate	Leadhillite	Mendipite	Magnetoplumbite	Lead– goethite
AM1	3.91E-05	0.17(2)	0.07(2)								0.68(2)
AM2	1.80E-04	0.72(2)	0.14(3)	0.12(2)							
AM3	6.71E-05	0.54(2)	0.12(2)	0.15(1)	0.19(4)						
AM4	4.86E-05	0.44(3)	0.13(1)			0.15(2)	0.29(4)				
AM5	6.36E-05	0.21(2)	0.30(2)		0.29(4)	0.23(2)					
AM6	1.94E-06	0.10(1)	0.31(1)	0.13(1)				0.14(1)	0.17(1)	0.13(1)	
AM7	4.23E-06	0.14(1)	0.53(3)			0.09(1))					
AM9	1.69E-04	0.15(4)					0.33(7)				0.52(4)
AM10	3.74E-05	0.38(1)	0.49(1)	0.11(1)							

Table 70 Summary of XANES fittings for air particulates from the mine site

Table 71 Summary of XANES fittings for air particulates samples from the copper smelter area

Sample ID	Residual	Lead sulfate	Lead sulfide	Lead chloride	Lead–goethite	Magnetoplumbite	Lead citrate	Molybdophyllite
ATC1	3.67E-05	0.72(6)	0.26(1)					
ATC2	1.48E-04	0.66(1)	0.30(1)					
ATC3	2.22E-04	0.94(1)						
ATC4	6.85E-04	0.48(5)			0.40(5)			
ATC5	1.05E-04	0.88(1)	0.08(1)					
ATC6	4.62E-04	0.72(5)				0.19(5)		
ATC7	2.95E-04	0.42(6)					0.48(6)	
ATC8	1.44E-04	0.64(2)						0.39(2)
ATC9	1.17E-03	0.26(4)	0.39(4)					
ATC10	9.59E-06	0.64(3)		0.23(1)				
ATC11	2.62E-05		0.15(1)	0.15(2)		0.47(2)		0.11(1)
LPC01	9.03E-05	0.90(1)	0.28(2)	0.07(1)				
LPC01F	8.58E-05	0.92(1)		0.08(1)				

LPESP01 3.84E-05 0.99(1)

Sample ID	Residual	Lead sulfide	Lead chloride	Lead sulfate	Leadhillite	Mendipite
ATA1	2.16E-06	0.19(3)	0.09(1)	0.47(1)		0.098(8)
ATB1	8.15E-05	0.29(2)				0.72(2)
ATP1	3.10E-05	0.84(4)			0.16(2)	
ATP2	7.40E-05	0.73(2)			0.26(2)	
ATP3	1.60E-05	0.55(3)	0.12(2)		0.32(2)	
ATP4	5.15E-05	0.85(5)	0.15(2)			
ATP5	7.08E-06	0.41(1)				0.592(5)
ATP6	4.21E-06	0.29(3)	0.22(1)	0.45(1)		0.027(7)
ATP7	1.74E-04			0.22(1)		0.81(1)
ATP8	4.97E-06	0.18(1)	0.25(1)	0.30(1)	0.26(1)	
ATS1	3.03E-06	0.52(1)	0.10(1)	0.05(3)	0.177(9)	
ATS2	1.21E-05	0.74(1)			0.257(8)	
HMA	5.90E-06	0.48(3)	0.26(1)	0.25(8)		

Table 72 Summary of XANES fittings for air–particulates samples from the lead smelter area

Table 73 Summary of XANES fittings for haul road dust samples from the mine site

Sample ID	Residual	Lead– goethite	Lead sulfate	Lead chloride	Pyromorphite	Magnetoplumbite
HR1	2.02E-05	0.66(1)		0.17(1)		
HR2	2.52E-05	0.31(1)	0.13(1)	0.582(9)		
HR3	2.66E-05	0.43(1)	0.15(1)	0.423(9)		
HR4	2.45E-05	0.57(1)	0.15(1)	0.292(9)		
HR5	1.34E-05	0.38(3)		0.17(1)	0.16(2)	0.19(4)
HR6	1.67E-05	0.42(1)	0.11(1)	0.34(1)	0.14(2)	
HR7	1.45E-05	0.52(1)	0.228(9)	0.11(1)	0.16(2)	
HR8	2.59E-05	0.46(1)	0.12(1)	0.428(9)		
HR9	3.19E-05	0.53(1)	0.14(1)	0.35(1)		

Sample ID	Residual	Lead– goethite	Lead sulfate	Lead chloride	Pyromor phite	Lead citrate	Magnetoplumbite
SS13	1.01E-05	0.78(3)		0.10(1)	0.04(1)		0.10(3)
SS14	2.41E-05	0.67(1)	0.13(1)	0.213(9)			
SS15	1.74E-05	0.65(1)	0.20(1)	0.07(1)	0.10(2)		
TD5S31	9.66E-06	0.82(2)	0.04(1)				0.15(2)
TD5S61	1.53E-05	0.67(1)	0.06(1)	0.155(8)		0.13(2)	
TD5S62	7.56E-06	0.98(1)			0.026(8)		
TD7S21	2.45E-05	0.44(1)	0.56(4)				
TD7S22	8.17E-06	0.59(1)	0.26(2)			0.16(2)	
TD7S51	3.81E-05	0.65(1)	0.14(1)	0.21(1)			
TD8S21	2.51E-05	0.62(1)	0.17 (1)	0.21(1)			
TD8S31	2.43E-05	0.38(2)	0.04(1)	0.38(1)		0.20(3)	
TD8S41	3.06E-05	0.46(1)	0.21(1)	0.34(1)			
TD8S71	1.01E-05	0.67(1)	0.26(3)		0.08(1)		
TD8S72	7.02E-06	0.71(2)	0.04 (1)		0.14(1)		0.11(2)
TD8S81	2.06E-05	0.44(2)	0.14(1)	0.20(1)		0.22(3)	

Table 74 Summary of XANES fittings for tailings dam materials from the mine site

Table 75 Summary of XANES fittings for fallout dust samples from the mine site

Sample ID	Residual	Lead sulfide	Lead sulfate	Pyromor phite	Mendipite	Magneto plumbite	Lead– goethite
FM3	1.40E-05	0.516(6)	0.179(8)				0.30(1)
FM4	2.55E-05	0.379(8)	0.267(8)				0.36(1)
FM7	1.29E-05	0.68(3)			0.13(1)	0.200(8)	
FM8	1.17E-05	0.59(4)	0.12(1)		0.28(1)		
FM11	6.51E-06	0.55(3)	0.27(1)	0.10(1)	0.089(8)		
FM12	4.72E-06	0.48(4)	0.18(1)	0.07(1)	0.082(9)	0.18(2)	
FM13	9.87E-06	0.49(1)	0.160(9)	0.09(2)	0.038(9)	0.23(1)	
FM14	1.33E-05	0.50(1)	0.16(1)	0.06(2)		0.30(1)	
FM15	1.27E-04		0.40(2)				0.63(2)
FM17	3.31E-06	0.524(6)	0.292(4)		0.123(5)		0.064(5)
FM18	3.94E-06	0.557(6)	0.264(5)		0.070(5)	0.108(8)	
FM19	7.98E-06	0.419(9)	0.134(8)	0.16(2)		0.16(2)	0.14(2)
FM20	1.33E-05	0.396(8)	0.22(1)			0.22(1)	

Sample ID	Residual	Lead– goethite	Lead sulfide	Lead citrate	Magneto- plumbite	Pyro- morphite	Molybdo- phyllite
AH1	1.24E-04	0.59(3)	0.21(2)	0.18(4)			
AH2	2.13E-04			1.06 (1)			
AH3	9.99E-05	0.55(3)		0.47(3)			
AH4	2.71E-04	0.79(5)		0.17(5)			
AH5	1.63E-04	0.33(4)		0.69(4)			
AH6	3.83E-03		0.727(8)				
AH7	6.07E-04		0.58(4)		0.30(4)		
AH8	2.98E-04	0.63(3)	0.31(3)				
AH9	1.47E-04	0.31(4)		0.71(4)			
AH10	2.05E-04	0.76(2)	0.21(2)				
AH11	1.37E-04	0.25(8)		0.27(6)	0.37(9)	0.13(6)	
AH12	1.73E-04			1.01 (1)			
HVA1	1.34E-05	0.12(2)	0.375(8)		0.30(3)	0.22(1)	
HVA4	5.11E-05	0.70(2)		0.31(2)			
HVA2	4.11E-04		0.53(4)				0.36(4)
HVAPslurry	1.09 E-04	0.27(3)					0.72(3)

Table 76 Summary of XANES fittings for air particulates from the city's residential area

Sample ID	Residual	Lead– goethite	Molybdophyllite
CS	3.09E-05	0.84(3)	0.11(2)
CS7	4.34E-05	0.82(2)	
CS16	3.57E-05	1.004(1)	
CS17	2.78E-05	0.93(2)	0.10(2)
CS20	7.17E-05	1.018(1)	
CS22	6.75E-05	1.017(1)	
CS23	4.81E-05	1.012(1)	
CS24	4.94E-05	0.91(2)	0.10(2)
CS25	2.96E-05	1.007(1)	
CS26	9.36E-05	0.83(3)	0.17(3)
CS27	6.86E-05	0.74(2)	0.27(2)
CS28	5.99E-05	0.76(2)	0.25(2)
CS29	4.78E-05	0.83(2)	0.18(2)
CS30	6.49E-05	0.79(2)	0.23(2)
CS31	1.02E-04	0.66(3)	0.33(3)
CS32	3.24E-05	0.96(2)	0.06(2)
CS33	2.37E-05	0.91(1)	0.09(1)
CS34	2.86E-05	0.96(2)	0.05(2)
CS35	2.17E-05	0.95(1)	
CS37	4.71E-05	0.74(5)	0.14(2)
CS38	2.39E-05	0.51(3)	0.36(2)

Table 77 Summary of XANES fittings for soil and footpath samples from the city's residential area

Sample ID	Residual	Lead– goethite	Lead sulfate	Cerussite	Molybdo- phyllite	Plumbo- gummite	Magneto- plumbite	Lead citrate
$PM_{10}S1$	2.75E-05	0.876(8)	0.14(1)					
PM ₁₀ S2	5.12E-05	0.76(2)						0.27(2)
PM ₁₀ S3	5.68E-05	0.87(2)			0.11(2)			
PM ₁₀ S4	1.12E-05	0.867(5)	0.08(1)			0.06(1)		
$PM_{10}S5$	5.80E-05	1.026(1)						
$PM_{10}S6$	4.70E-05	0.87(2)			0.14(2)			
PM ₁₀ S7	5.29E-05	0.91(2)		0.11(2)				
PM ₁₀ S9	6.06E-05	0.86(2)		0.12(2)				
PM ₁₀ S10	6.13E-05	0.93(1)			0.08(1)			
PM ₁₀ S11	1.09E-05	0.74(2)	0.10(1)		0.17(1)			
PM ₁₀ S12	1.07E-05		0.15(1)	0.07(1)		0.40(1)	0.377(7)	
PM ₁₀ S13	5.07E-05	0.77(2)	0.06(1)	0.05(2)	0.13(1)			
PM ₁₀ S14	1.46E-05	0.83(2)	0.07(1)		0.11(1)			
PM ₁₀ S15	1.39E-05	0.96(1)		0.05(1)				
PM ₁₀ S16	1.96E-05	0.925(7)				0.099(7)		
PM ₁₀ S17	2.95E-05	0.90(2)			0.11(2)			
PM ₁₀ S18	1.76E-05	0.81(1)	0.05(1)					
PM ₁₀ S19	7.49E-05	0.75(6)					0.27(6)	
PM ₁₀ S20	1.70E-05	0.80(2)	0.07(2)		0.04(1)	0.10(1)		
PM ₁₀ S21	2.20E-05	0.80(2)				0.09(1)		
PM ₁₀ S22	3.43E-05	1.00(1)						

Table 78 Summary of XANES fittings for soil $\ensuremath{\mathsf{PM}_{10}}$ samples from the city's residential area
Sample ID	Residual	Lead– goethite	Lead sulfide	Lead sulfate	Pyro- morphite	Magneto- plumbite
FM21	8.63E-06	0.294(9)	0.37(1)	0.055(8)	0.17(2)	
FM22	4.01E-05	0.91(1)	0.11(1)			
FM22C	5.86E-05	1.020(1)				
FM23	8.46E-06	0.468(8)	0.307(8)	0.115(7)	0.12(2)	
FM24	9.33E-05	1.015(1)				
FM25	1.70E-05	0.34(3)	0.14(2)		0.29(2)	0.18(4)
FM26	1.64E-05	0.67(1)	0.286(7)	0.062(8)		
FM27	5.03E-06	0.17(2)	0.327(8)	0.073(6)	0.25(1)	0.10(3)
FM28	1.03E-05	0.528(9)	0.383(5)	0.099(5)		
FM29	6.63E-06	0.44(2)	0.230(8)	0.079(7)	0.18(1)	0.08(2)
FMB	6.94E-06	0.343(8)	0.322(7)	0.144(7)	0.20(1)	
FMK	1.48E-05	0.45(3)	0.329(8)	0.047(7)		0.18(3)
FMR	9.03E-06	0.321(9)	0.334(8)	0.213(8)	0.15(2)	
FMRC	6.62E-06	0.347(9)	0.334(7)	0.055(8)	0.19(2)	
FMS	5.52E-06	0.171(8)	0.358(8)	0.266(9)	0.11(2)	

Table 79 Summary of XANES fittings for fallout dust from the city's residential area

Table 80 Summary of XANES fittings for roof gutter samples from the city's residential area

Sample ID	Residual	Lead-goethite	Magnetoplumbite
RG	1.35E-05	0.87(2)	0.14(2)
RG1	2.50E-05	1.012(1)	
RG2	5.55E-05	1.021(1)	
RG3	3.55E-05	1.023(1)	
RG4	3.79E-05	1.020(1)	

Sample ID	Residual	Lead– goethite	Lead sulfide	Cerussite	Lead sulfate	Lead hexafluorosilicate	Lead citrate
VD	7.95E-06	0.593(9)	0.217(5)	0.135(9)	0.060(8)		
VD1	6.26E-05	0.60(3)	0.30(1)			0.11(3)	
VD2	7.04E-06	0.455(8)	0.308(4)	0.166(9)	0.069(8)		
VD3	1.84E-05	0.53(2)	0.333(7)			0.15(1)	
VD4	1.01E-05	0.58(1)	0.304(5)	0.118(7)			
VD5	1.96E-05	0.68(1)	0.126(7)	0.20(1)			
VD6	1.18E-04	0.60(3)	0.24(2)	0.13(3)			
VD7	1.23E-05	0.55(1)	0.191(5)				0.28(1)
VD8	1.65E-05	0.11(2)	0.157(9)	0.11(2)	0.21(2)	0.19(3)	0.24(5)
VD9	1.14E-05	0.55(1)	0.260(6)	0.15(1)		0.05(1)	
VD10	2.05E-05	0.89(1)		0.12(1)			
VD11	2.14E-05	0.74(1)	0.139(6)	0.13(1)			
VD12	1.46E-05	0.46(2)	0.079(8)	0.31(1)			
VD13	1.12E-05	0.66(1)	0.210(5)	0.135(8)			
VD14	1.31E-05	0.64(1)	0.186(6)	0.178(8)			
VD15	1.55E-05	0.23(1)	0.325(7)	0.06(1)	0.30(1)	0.06(2)	
VD16	2.48E-05	0.70(2)	0.245(8)	0.05(1)			
VD17	1.04E-05	0.67(1)	0.165(5)	0.11(1)	0.05(1)		
VD18	1.58E-05	0.66(1)	0.170(7)	0.175(9)			
VD19	8.80E-06	0.55(1)	0.279(5)	0.102(9)		0.07(1)	

Table 81 Summary of XANES fittings for carpet dust samples from the city's residential area

Sample ID	Residual	Lead– goethite	Lead citrate	Lead sulfide	Pyro- morphite	Leadhillite	Magneto- plumbite
HW1F1	4.07E-05	0.72(1)		0.28(1)			
HW1S1	2.95E-05	0.65(2)	0.31(2)	0.048(9)			
HW1T1	6.77E-06	0.71(2)	0.17(1)	0.037(5)			
HW1V1	1.04E-05	0.60(2)	0.24(1)	0.110(7)			
HW2F1	1.84E-05	0.41(1)	0.13(3)	0.33(1)	0.15(3)		
HW2F2	8.04E-06		0.16(2)	0.445(5)			0.34(1)
HW2S1	9.76E-06	0.45(3)	0.19(2)	0.19(1)	0.10(2)		0.10(3)
HW2T1	1.10E-04	0.90(3)	0.13(3)				
HW2V1	1.76E-05			0.61(5)	0.10(1)	0.29(2)	
HW3C1	2.27E-04	0.80(2)		0.16(2)			
HW3F1	1.35E-04	0.74(3)			0.33(3)		
HW3S1	9.79E-04		0.4(1)				0.7(1)
HW3T1	1.34E-05	0.62(1)	0.27(2)		0.13(2)		
HW3V1	1.40E-05	0.37(2)		0.50(3)			

Table 82 Summary of XANES fittings for large house wipe samples from three Mount Isa City houses

3.4 Bioaccessibility

Bioaccessibility estimation of lead and other heavy metals and arsenic for samples in this study was conducted using PBET analysis and has been in use for over ten years. The results of bioaccessible metal and metalloid concentrations (mg/kg) and bioaccessibility (%) are detailed in the following sections. Bioaccessibility estimate have been made for both arsenic and lead. Comparative studies on bioaccessibility estimates of other metals have be undertaken in the authors laboratories but are not yet accepted nationally or internationally⁴¹.

3.4.1 Natural outcrops near Mount Isa City

The results of bioaccessibility for outcrops from different geological units are summarised in Table 83 and Table 84. Total concentrations of these samples are in Table 17 (page 168). Because the total concentrations for arsenic, cadmium,

⁴¹ The Lead Pathways Study – Extension Report on Arsenic and Cadmium Studies gives comparative study data on arsenic and cadmium.

copper, lead, and zinc are low, the bioaccessible fractions of these metals and the metalloid are sometimes lower than their detection limits. The bioaccessible lead concentrations detected for these outcrop samples were a maximum of 51 mg/kg and a minimum of 20 mg/kg (Table 83). In terms of human health, the bioaccessibility adjusted concentration is much more relevant than the total concentration.

Table 83 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, con	oper,
lead, and zinc in natural outcrops (BGR) near Mount Isa City	

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
n > LOD	5	0	5	4	1
n	13	13	13	13	13
% > LOD	38	0	38	31	8
Mean	3	N/A	28	30	51
SD	2.1	N/A	28	14	N/A
Minimum	0.9	N/A	6	20	N/A
Median	2.2	N/A	14	25	N/A
75th percentile	5	N/A	35	33	N/A
Maximum	5.5	N/A	74	51	N/A

LOD: Limit of detection; SD: Standard deviation; n: Number of samples; N/A: data not available.

Table 84 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in natural outcrops (BGR) near Mount Isa City

	Arsenic	Cadmium	Copper	Lead	Zinc
n > LOD	5	0	5	4	1
n	13	13	13	13	13
% > LOD	38	0	38	31	8
Mean	9	N/A	16	11	4
SD	6	N/A	8	4	N/A
Minimum	2	N/A	11	7	N/A
Median	6	N/A	11	10	N/A
75th percentile	10	N/A	17	12	N/A
Maximum	18	N/A	29	29	N/A

LOD: Limit of detection; SD: Standard deviation; n: Number of samples; N/A: data not available.

3.4.2 Outcrops from natural mineralisation

The results of bioaccessibility-adjusted concentrations for natural mineralisation outcrops (NMU) from different geological units are summarised in Table 85 and Table 86. The mean bioaccessible fractions of Urquhart Shale samples were 2 per cent for lead and 5 per cent for copper (Table 86).

Table 85 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in natural mineralisation outcrops (NMU) in Mount Isa City

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
n > LOD	1	3	3	1	3
n	4	4	4	4	4
% > LOD	25	75	75	25	75
Mean	7	0.21	37	27	43
SD	N/A	0.11	31	N/A	18
Minimum	N/A	0.12	20	N/A	24
Median	N/A	0.18	21	N/A	48
75th percentile	N/A	0.26	47	N/A	53
Maximum	N/A	0.33	73	N/A	58

LOD: Limit of detection; SD: Standard deviation; n: Number of samples; N/A: data not available.

Table 86 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in natural mineralisation outcrops (NMU) in Mount Isa City

	Arsenic BAc (%)	Cadmium BAc (%)	Copper BAc (%)	Lead BAc (%)	Zinc BAc (%)
n > LOD	1	3	3	1	3
n	4	4	4	4	4
% > LOD	25	75	75	25	75
Mean	1	24	5	2	3
SD	N/A	18	2	N/A	0.15
Minimum	N/A	4.6	3	N/A	2.4
Median	N/A	15	4	N/A	2.4
75th percentile	N/A	33	5.8	N/A	2.6
Maximum	N/A	40	6	N/A	2.7

LOD: Limit of detection; SD: Standard deviation; n: Number of samples; N/A: data not available.

3.4.3 Mine site samples

Bioaccessibility of lead and other heavy metals and the metalloid in the mine site samples was also estimated. The median bioaccessibility-adjusted concentration

for lead levels in mine site general source samples (SS) is 2414 mg/kg, and 19 mg/kg for As (Table 87). The bioaccessibility, which considered both the total and bioaccessible concentrations of the same sample, indicated a median level of 19 per cent for lead in general source samples, but less than 10 per cent for arsenic, cadmium, copper, and zinc (Table 88).

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
n > LOD	16	16	16	17	17
n	28	28	28	28	28
% > LOD	57	57	57	61	61
Mean	25	53	667	5333	2922
SD	23	112	1406	8320	4481
Minimum	2	0	1	31	25
Median	19	4	48	2414	1007
75th percentile	42	29	328	4842	3875
95th percentile	64	292	3313	26,416	10,312
Maximum	68	390	5066	26,428	15,894

Table 87 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in mine site general source samples

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

Table 88 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in mine site general source samples

	Arsenic BAc (%)	Cadmium BAc (%)	Copper BAc (%)	Lead BAc (%)	Zinc BAc (%)
n > LOD	16	16	16	17	17
n	28	28	28	28	28
% > LOD	57	57	57	61	61
Mean	8	11	4	22	9
SD	6	12	4	14	7
Minimum	1	0	0	1	0
Median	6	9	2	19	9
75th percentile	11	11	5	32	14
95th percentile	19	31	11	44	20
Maximum	23	46	12	51	21

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

The median bioaccessibility-adjusted concentrations for haul road dusts (HR) are 1820 mg/kg for lead and 20 mg/kg for arsenic (Table 89). The median bioaccessibility for lead in haul road dusts is 42 per cent and that for arsenic is 10 per cent (Table 90). The median bioaccessibility-adjusted concentration of samples of surface tailings dam materials (TD) is 1415 mg/kg for lead, but higher for arsenic (74 mg/kg) than in haul road dust (Table 89 and Table 91). The

median bioaccessibility for lead and arsenic in surface tailings dam materials is 31 per cent and 15 per cent, respectively (Table 92).

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
Mean	32	14	673	1969	1749
SD	27	8	429	657	498
Minimum	8	6	151	1240	1292
Median	20	13	685	1820	1577
75th percentile	64	21	996	2623	2062
95th percentile	69	25	1206	2880	2547
Maximum	71	26	1332	3010	2698

Table 89 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in haul road dusts (HR) (n = 9)

Table 90 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in haul road dusts (HR) (n = 9)

	Arsenic BAc (%)	Cadmium BAc (%)	Copper BAc (%)	Lead BAc (%)	Zinc BAc (%)
Mean	11	48	22	43	22
SD	4	26	10	13	4
Minimum	5	20	11	26	15
Median	10	40	19	42	23
75th percentile	14	68	29	52	24
95th percentile	16	86	37	62	27
Maximum	16	94	43	62	28

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
Mean	112	6	687	1371	1526
SD	96	2	1009	683	749
Minimum	23	3	146	493	606
Median	74	7	206	1415	1217
75th percentile	119	8	607	1672	1922
95th percentile	261	8	2303	2274	2618
Maximum	313	8	2881	2461	2750

Table 91 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in surface tailings dam materials (TD) (n = 7)

Table 92 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in surface tailings dam materials (TD) (n = 7)

	Arsenic BAc (%)	Cadmium BAc (%)	Copper BAc (%)	Lead BAc (%)	Zinc BAc (%)
Mean	31	39	26	33	23
SD	28	14	25	8	10
Minimum	6	25	7	23	10
Median	15	35	13	31	25
75th percentile	47	45	32	37	30
95th percentile	74	60	67	45	36
Maximum	79	63	77	46	39

The median bioaccessibility-adjusted concentrations of thimbles from the lead smelter area (ATP) are 17,664 mg/kg for lead and 125 mg/kg for arsenic (Table 93). The bioaccessibility indicates a median level for lead and arsenic in surface tailings dam materials of 6 per cent and 25 per cent, respectively (Table 94). The median bioaccessibility-adjusted concentration of thimbles from the copper smelter area (ATC) is 1063 mg/kg for lead. The median bioaccessibility-adjusted concentration of arsenic in ATC samples, however, is much higher than ATP samples (1679 mg/kg) (Table 93 and Table 95). The median bioaccessibility-adjusted concentrations for lead and arsenic in surface tailings dam materials are 26 per cent and 28 per cent, respectively (Table 96).

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
Mean	138	917	120	17,738	1561
SD	57	1138	132	9846	1065
Minimum	93	200	10.1	4482	263
Median	125	547	76	17,664	1577
75th percentile	142	651	161	25,958	2248
95th percentile	220	2579	313	28,753	2854
Maximum	246	3213	357	28,896	3020

Table 93 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in thimbles from lead smelter area (ATP) (n = 6)

SD: Standard deviation; n: Number of samples

Table 94 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in thimbles from lead smelter area (ATP) (n = 6)

	Arsenic BAc (%)	Cadmium BAc (%)	Copper BAc (%)	Lead BAc (%)	Zinc BAc (%)
Mean	32	8	2	6	5
SD	24	3	2	3	5
Minimum	11	2	0.4	2	1
Median	25	8	1	6	3
75th percentile	29	9	4	9	4
95th percentile	68	12	5	9	12
Maximum	80	13	6	10	15

SD: Standard deviation; n: Number of samples

Table 95 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in thimbles from copper smelter area (ATC) (n = 10)

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
% > LOD	90	89	90	90	90
Mean	2852	29	8376	1294	233
SD	3192	26	6401	1052	134
Minimum	40	6	3501	528	94
Median	1679	18	5954	1063	193
75th percentile	5239	38	7168	1292	273
95th percentile	7843	70	19,735	3054	456
Maximum	9568	87	22,185	3854	526

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

	Arsenic BAc (%)	Cadmium BAc (%)	Copper BAc (%)	Lead BAc (%)	Zinc BAc (%)
% > LOD	90	80	90	90	90
Mean	29	40	5	24	18
SD	15	21	5	7	11
Minimum	14	19	1	13	7
Median	28	38	4	26	15
75th percentile	36	62	6	27	20
95th percentile	53	64	13	34	37
Maximum	61	64	16	35	39

Table 96 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in thimbles from copper smelter area (ATC) (n = 10)

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

The median bioaccessibility-adjusted concentrations of lead in smelter area dust (ATP) are 11,601 mg/kg for lead and 13 mg/kg for arsenic (Table 97). The bioaccessibility indicates median levels for lead and arsenic in lead smelter area dust of 43 per cent and 6 per cent respectively (Table 98).

Table 97 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in lead smelter area dust (SD) (n = 22)

	Arsenic	Cadmium	Copper	Lead	Zinc
	BAc	BAc	BAc	BAc	BAc
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
% > LOD	100	95	95	91	100
Mean	30	3634	171	14,044	1471
SD	42	8582	293	12,021	1517
Minimum	1	1	1	296	17
Median	13	351	22	11,601	809
75th percentile	31	1229	263	24,537	2499
95th percentile	114	26,896	694	34,228	4204
Maximum	165	28,964	1154	34,702	4453

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

	Arsenic BAc (%)	Cadmium BAc (%)	Copper BAc (%)	Lead BAc (%)	Zinc BAc (%)
% > LOD	100	91	91	91	100
Mean	8	14	4	47	8
SD	5	11	5	26	7
Minimum	0.32	0.34	0.04	6	0.35
Median	6	12	1	43	5
75th percentile	12	19	8	70	14
95th percentile	16	28	14	83	20
Maximum	18	45	16	92	21

Table 98 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in lead smelter area dust (SD) (n = 22)

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

Fallout samples from the mine site were also collected (Section 2.3.6, page 126) and processed for bioaccessibility-adjusted concentrations using PBET. Since limited samples were collected from each site, the PBET analysis is only presented for lead. The summary of lead bioaccessibility in fallout dust from the mine site is given in Table 99. The median bioaccessible lead in fallout dust from the mine site is 1149 mg/kg.

Table 99 Summary of bioaccessibility (%) and bioaccessibility-adjusted concentration for lead in mine site fallout samples

	Lead BAc (%)	Lead BAc (mg/kg)
n	10	10
Minimum	7	304
25th percentile	8	499
Median	13	1149
75th percentile	30	1611
Maximum	55	4784

The bioaccessibility-adjusted concentrations for all mine site samples are summarised in Table 100. The median bioaccessibility-adjusted concentrations for mine site samples were 2017 mg/kg for lead and 36 mg/kg for arsenic (Table 100). The bioaccessibility for different groups of mine site samples varies (Table 88, Table 90, Table 92, Table 94, Table 96, and Table 98), depending on the source of the samples and their particle size. Generally, haul road dust, surface tailings, and smelter dust show higher bioaccessibility than other mine site samples (Table 90, Table 92, and Table 98). Bioaccessibility-adjusted lead concentrations and bioaccessibility (%) from the PBET analysis for mine site dust

samples were summarised in Table 100 and Table 101. The summary of bioaccessibility (%) given in Table 99 indicates a median bioaccessibility of 13 per cent for lead in fallout dust samples collected from the mine site. This is compared with a median lead bioaccessibility of 29 per cent for lead in all samples collected from the mine site.

Table 100 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc for samples from mine sites, including thimbles (ATC and ATP) and dusts (SD) from lead and copper smelter areas, haul road dust (HR), surface tailings materials (TD), and general source samples (SS) and fallout dust

	Arsenic BAc (mg/kg)	Cadmium BAc (mg/kg)	Copper BAc (mg/kg)	Lead BAc (mg/kg)	Zinc BAc (mg/kg)
n	82	81	81	88	82
% > LOD	84	81	83	84	85
Mean	415	1204	1508	7113	1713
SD	1451	4930	3611	9804	2488
Minimum	1	0.02	1	31	17
25th percentile	10.5	5.2	20.5	1001	165
Median	36	14	182	2017	1027
75th percentile	97	298	975	8551	2188
95th percentile	1754	2824	6363	28,308	5339
Maximum	9568	28,964	22,185	34,702	15,894

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

Table 101 Bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc for samples from the mine site, including thimbles (ATC and ATP) and dusts (SD) from lead and copper smelter areas, haul road dust (HR), surface tailings materials (TD), and general source samples (SS) and fallout dust

	Arsenic BAC (%)	Cadmium BAC (%)	Copper BAC (%)	Lead BAC (%)	Zinc BAC (%)
N	82	82	82	82	82
% > LOD	84	80	82	83	85
Mean	15	23	9	32	13
SD	16	21	13	21	10
Minimum	0.32	0.01	0.03	0.50	0.30
25th percentile	5.4	8.6	0.8	15.9	3.5
Median	11	17	4	29	12
75th percentile	18	32	12	43	19
95th percentile	53	64	29	79	30
Maximum	80	94	77	92	39

3.4.4 Mount Isa city samples

3.4.4.1 Garden soil less than 250 µm

The bioaccessibility-adjusted metal and metalloid concentrations (mg/kg) and bioaccessibilities (%) in garden soil (< 250 μ m fraction) are summarised in Table 102 and Table 103. The median bioaccessibility-adjusted concentrations in garden soil (< 250 μ m fraction) are 43 mg/kg for lead and 1 mg/kg for arsenic (Table 102). The maximum bioaccessibility-adjusted concentrations of arsenic, cadmium, copper, and lead are 9 mg/kg, 18 mg/kg, 562 mg/kg, and 292 mg/kg, respectively (Table 102). The median level for lead and arsenic bioaccessibilities for garden soil (< 250 μ m fraction) are 22 per cent and 13 per cent, respectively (Table 103).

Elements	% > LOD (n = 76)	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	92	2 (2)	0.18	1	2	4	9
Cadmium	72	1 (2)	0.08	1	1	3	18
Cobalt	100	2 (1)	0.40	2	2	3	5
Copper	99	73 (89)	4	46	87	256	562
Lead	99	57 (59)	0	43	70	187	292
Manganese	100	94 (42)	15	86	111	159	288
Nickel	30	6 (9)	0.02	3	6	20	44
Zinc	99	182 (218)	3	100	205	570	1305

Table 102 Bioaccessibility-adjusted concentrations (mg/kg) of metals and the metalloid in garden soil (< 250 µm fraction)

Table 103 Summary statistics for bioaccessibility (%) of metals and the metalloid in garden soil (< 250 µm fraction)

Elements	% > LOD (n = 76)	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	92	15 (8)	4	13	18	26	49
Cadmium	70	36 (17)	2	35	44	65	80
Cobalt	100	15 (5)	6	14	18	23	34
Copper	99	16 (8)	3	15	19	27	60
Lead	99	24 (12)	1	22	29	45	65
Manganese	100	26 (9)	9	24	30	41	65
Nickel	28	21 (18)	0	17	27	49	75
Zinc	99	30 (12)	5	28	35	53	70

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

3.4.4.2 PM₁₀ fraction from garden soil

The bioaccessibility-adjusted metal and metalloid concentrations (mg/kg) and bioaccessibilities (%) in the soil PM_{10} fraction are summarised in Table 104 and Table 105. The median bioaccessibility-adjusted concentrations of lead and arsenic in the soil PM_{10} fraction are higher than those in the garden soil < 250 µm fraction, at 117 mg/kg for lead and 8 mg/kg for arsenic (Table 104). The maximum bioaccessibility-adjusted concentrations of arsenic, cadmium, copper, lead and zinc are 70 mg/kg, 43 mg/kg, 3219 mg/kg, 1727 mg/kg, and 4034 mg/kg,

respectively (Table 104). The median lead and arsenic bioaccessibilities for soil PM_{10} are 28 per cent and 27 per cent, respectively (Table 105).

Elements	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	74	99	11 (11)	1	8	13	29	70
Cadmium	74	86	3 (6)	0	2	3	11	43
Cobalt	74	100	8 (4)	2	7	9	14	23
Copper	74	99	336 (458)	23	187	388	1086	3219
Lead	74	100	206 (311)	0	117	193	735	1727
Manganese	64	98	287 (106)	97	269	363	454	558
Nickel	74	88	6 (10)	1	4	6	25	64
Zinc	74	99	557 (718)	5	334	601	1799	4034

Table 104 Summary statistics for metals and the metalloid bioaccessibility adjusted concentrations (mg/kg) in soil PM₁₀ fraction

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

Table 105 Summary statistics for bioaccessibility (%) of metals and the metalloid in soil $$\rm PM_{10}\ fraction$

Elements	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	74	85	28 (15)	6	27	34	53	90
Cadmium	74	59	44 (15)	18	41	54	69	86
Cobalt	74	91	31 (12)	10	31	39	48	73
Copper	74	99	35 (18)	9	31	41	68	91
Lead	74	100	34 (20)	0.5	28	49	72	83
Manganese	64	98	43 (13)	17	43	50	66	74
Nickel	74	84	16 (22)	3	11	16	34	160
Zinc	74	99	38 (15)	3	39	46	64	81

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

3.4.4.3 Footpath samples

The bioaccessibility-adjusted metal and metalloid concentrations (mg/kg) and bioaccessibilities (%) in footpath samples are summarised in Table 106 and Table 107. The median bioaccessibility-adjusted concentrations of lead and arsenic in footpath samples are lower than in soils, at 7 mg/kg for lead and

1.9 mg/kg for arsenic (Table 106). The maximum bioaccessibility-adjusted concentrations of arsenic, cadmium, copper, lead, and zinc are 3.2 mg/kg, 1.9 mg/kg, 229 mg/kg, 54 mg/kg, and 69 mg/kg, respectively (Table 106). The median bioaccessibilities for lead and arsenic for footpath samples are 15 per cent and 23 per cent, respectively (Table 107).

	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	57	1.9 (0.9)	0.6	1.9	2.3	3.0	3.2
Cadmium	43	0.7 (0.7)	0.2	0.3	0.8	1.7	1.9
Copper	100	55 (64)	6	32	54	188	229
Lead	100	13 (15)	0.1	7	17	40	54
Zinc	57	20 (23)	1.5	13	24	58	69

Table 106 Bioaccessibility-adjusted concentrations (mg/kg) of arsenic, cadmium, copper, lead, and zinc in samples from Mount Isa City's footpaths (n = 14)

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

Table 107 Summary statistics for bioaccessibility (%) of arsenic, cadmium, copper, lead, and zinc in samples from Mount Isa City's footpaths (n = 14)

	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	57	27 (14)	11	23	41	46	48
Cadmium	43	61 (18)	29	66	75	76	76
Copper	100	25 (12)	7	24	35	41	45
Lead	100	16 (11)	0.1	15	25	33	37
Zinc	57	12 (8)	3	13	17	23	26

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

3.4.4.4 Fallout dust from the city's residential area

The bioaccessibility-adjusted metal and metalloid concentrations (mg/kg) and bioaccessibilities (%) in fallout dust from the city's residential area are summarised in Table 108 and Table 109. The median bioaccessibility-adjusted concentrations in fallout dust were 1641 mg/kg for lead and 126 mg/kg for arsenic respectively (Table 108) and both values were higher than the concentrations found in soil (Table 102). The maximum bioaccessibility-adjusted concentrations of arsenic, cadmium, copper, lead and zinc for fallout dust from the city's residential area are 42 mg/kg, 24 mg/kg, 747 mg/kg, 516 mg/kg, and 5756 mg/kg, respectively (Table 108). The median lead and arsenic bioaccessibilities for fallout dust from the city's residential area are 19 per cent and 21 per cent, respectively (Table 109).

Elements	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	87	130 (90)	24	126	202	260	263
Cadmium	27	13 (19)	2	5	15	36	41
Copper	100	1101 (748)	313	892	1434	2324	3025
Lead	100	1560 (1093)	304	1641	2026	3177	4341
Zinc	100	761 (863)	152	461	694	2697	3140

Table 108 Summary statistics for metals and the metalloid bioaccessibility-adjusted concentrations (mg/kg) in fallout from city (n = 15)

Table 109 Summary statistics for bioaccessibility (%) of metals and the metalloid in fallout from the city (n = 15)

Elements	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	87	47 (23)	17	38	56	83	87
Cadmium	27	54 (12)	36	59	60	61	61
Copper	100	10 (5)	2	8	13	18	19
Lead	100	23 (8)	14	21	25	39	41
Zinc	100	15 (7)	6	12	19	26	29

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

3.4.4.5 Roof gutter dust

The bioaccessibility-adjusted metal and metalloid concentrations (mg/kg) and bioaccessibilities (%) in roof gutter dust are summarised in Table 110 and Table 111. The median bioaccessibility-adjusted concentrations of lead and arsenic in roof gutter dust are higher than in soils, at 699 mg/kg for lead and 34 mg/kg for arsenic (Table 110). The median bioaccessibilities of lead and arsenic in roof gutter dust are 12 per cent and 7 per cent, respectively (Table 111).

Elements	n	% > LOD	Mean (SD)	Minimum	Median	75th percentil	95th percentil	Maximu m
Arsenic	18	100	52 (54)	6	34	71	132	228
Cadmium	18	100	3 (2)	1	2	3	6	7
Cobalt	13	100	2.6 (1.9)	0.4	2.1	3.3	6.0	7.1
Copper	18	100	1371	6	1132	2011	3438	3617
Lead	18	100	721 (383)	147	699	953	1214	1704
Manganes	13	100	22 (15)	8	16	23	53	58
Nickel	13	100	1.5 (0.9)	0.4	1.4	2.1	2.9	3.3
Zinc	18	100	959 (1148)	249	641	905	3512	4647

Table 110 Summary statistics for metals and the metalloid bioaccessibility-adjusted concentrations (mg/kg) in roof gutter dust.

Table 111 Summary statistics for bioaccessibility (%) of metals and the metalloid in roof gutter dust

Elements	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	18	100	11 (10)	0.18	7	11	25	46
Cadmium	18	100	8 (6)	0.35	6	10	19	22
Cobalt	13	100	3 (3)	0.05	2	3	7	12
Copper	18	100	10 (11)	0.09	6	10	30	46
Lead	18	100	16 (14)	0.31	12	19	44	53
Manganes	13	100	6 (8)	0.31	3	5	18	32
Nickel	13	100	4 (4)	0.10	2	4	11	15
Zinc	18	100	7 (5)	0.42	7	9	17	22

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

3.4.4.6 Carpet dust

The bioaccessibility-adjusted metal and metalloid concentrations (mg/kg) and bioaccessibilities (%) in carpet dust are summarised in Table 112 and Table 113. The median bioaccessibility-adjusted concentrations of lead and arsenic are 96 mg/kg and 7 mg/kg, respectively, in carpet dust (Table 112) and are higher than in soils. The maximum bioaccessibility-adjusted concentrations of arsenic, cadmium, copper, lead, and zinc are 42 mg/kg, 24 mg/kg, 747 mg/kg, 516 mg/kg, and 5756 mg/kg, respectively (Table 112). The median bioaccessibilities for lead and arsenic in for carpet dust are 19 per cent and 21 per cent respectively (Table 113).

Elements	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	60	98	9 (7)	1	7	10	22	42
Cadmium	60	85	3 (4)	0	2	3	9	24
Cobalt	41	85	2 (1)	0	1	2	4	5
Copper	60	98	141 (128)	23	96	194	293	747
Lead	60	98	133 (116)	17	96	162	399	516
Manganese	41	100	38 (24)	10	29	55	76	108
Nickel	41	51	4 (2)	1	4	5	9	10
Zinc	60	98	745 (851)	106	565	800	1729	5756

Table 112 Summary statistics for metals and the metalloid bioaccessibility-adjusted concentrations (mg/kg) in carpet dust

Table 113 Summary statistics for bioaccessibility (%) of metals and the metalloid	d in
carpet dust	

Elements	n	% > LOD	Mean (SD)	Minimum	Median	75th percentile	95th percentile	Maximum
Arsenic	60	92	22 (10)	8	21	29	42	47
Cadmium	60	67	31 (18)	8	26	38	65	77
Cobalt	41	73	9 (5)	3	8	11	19	24
Copper	60	98	11 (7)	2	9	14	24	37
Lead	60	95	22 (18)	6	19	24	55	93
Manganese	41	100	16 (10)	3	14	24	31	36
Nickel	41	51	14 (10)	4	13	17	24	49
Zinc	60	88	30 (16)	4	27	41	59	69

LOD: Limit of detection; SD: Standard deviation; n: Number of samples

3.4.4.7 Summary of city samples

The bioaccessibilities of lead and other metals and the metalloid for different groups of samples collected from Mount Isa City are summarised in Table 103, Table 105, Table 107, Table 109, Table 111, and Table 113. The bioaccessibility-adjusted lead concentrations and bioaccessibility of lead in samples from Mount Isa City samples are summarised in Table 114. The median lead bioaccessibility is 21% for samples from the residential area.

	Lead Total (mg/kg)	Lead BAc (mg/kg)	Lead BAc (%)
n	242	242	242
Mean	1569	265	25
SD	4160	504	16
Minimum	12	0.12	0.3
5th percentile	56	9	6
25th percentile	186	40	14
Median	427	97	21
75th percentile	969	208	31
95th percentile	6739	1217	58
Maximum	47306	4341	0.83

Table 114 Total concentration (mg/kg) and bioaccessibility of arsenic, cadmium, copper, lead, and zinc for samples from the city residential area

3.5 Bioavailability

The calculated absolute bioavailability (ABA) from the rat uptake study (detailed in Section 2.2.5.1, page 107) for the 10 samples from the mine site and the city's residential area is given in Table 115. The curve profile for lead uptake was used to estimate the area under the curve to calculate ABA for blood and urine, respectively (Appendix 4). Similarly, ABA can be calculated by comparing tissue concentration increases due to treatment, against an untreated reference group.

Sample ID	Sample Description	Lead concent ration (mg/kg)	AUC (arbitrary units)	Dosage (mg/kg)	% ABA (area under urinary curve)	% ABA (area under blood curve)
CS	Composite of community soils	118	124	0.60	1.20	1.20
RG	Composite of roof gutter dust	3840	2354	19.20	0.80	1.00
CD	Composite of carpet dust	891	1432	4.50	2.00	1.10
SS22	Lead smelter area dust	44,944	44,459	224.70	1.20	0.40
SS13	Tailing dam 5 (surface material)	2053	634	10.30	0.36	3.00
LR13	Historical river sediment (Noller et al., 2009)	41,886	3599	209.00	0.10	0.20
H2	RSL Gate adjacent Barkly highway exposed natural mineralisation (NMU)	2261	567	11.30	0.30	1.20
SS26	Lead concentrate	19,064	6945	4330.00	0.01	1.00
SS27	Copper smelter area dust	500	186	2.50	0.44	1.10
HVAP	High volume air–particulate PM ₁₀ slurry	35.8 (mg/L)	554	0.54	6.10	6.2

Table 115 Bioavailability of lead calculated from the area under the curve (AUC) for blood and urine

The results in Table 115 show that the bioavailabilities for the samples from the mine site and from the city residential areas are all very low, with all samples being < 5 per cent (mean 1.47 per cent) except for the urinary curve (HVAP), which is 6.1 per cent. Comparing the results for the area under the HVAP with blood, shows that most results are within an order of magnitude of each other. The very low values of both fits are probably associated with larger errors resulting from the low magnitude of the values. Similar low results have been found for other lead bioavailability (ABA) measurements in other Australian lead mine wastes (Bruce et al., 2007, Diacomanolis et al., 2007).

The bioavailability (BA) of lead covers the range 1.0–14.0 per cent (mean 10 per cent) (Owen, 1990), which is indicative of the generally low absolute bioavailability of lead compounds. Measurements of lead relative bioavailability are often low, with ranges from as low as 6 per cent observed in New Zealand white rabbits fed contaminated soils (Davis et al., 1992), and 20 per cent observed in rats, also fed contaminated soils (Freeman et al., 1992). The US EPA assumed 30 per cent of ingested lead in soil would be bioavailable (absolute bioavailability) when assessing the health risk of contaminated sites (U.S. EPA, 1994a). However, these recent studies using animal models demonstrated that the BA of lead from some soils and mine waste materials may be considerably lower (Bruce et al., 2007, Diacomanolis et al., 2007). BA is generally dependent on the solubility of the materials. Mineral composition is also a key factor in influencing the BA of a particular element. A report by the US EPA (2007b) showed the BA by category, as general guide, with galena having a relatively low value compared to lead oxide, and with cerrusite, the mineral form of lead carbonate, having the highest BA. BA data for lead are variable and can be influenced by a number of factors, including the sample matrix (food, water), dietary factors, particle size, and pH conditions of the gastrointestinal tract. Thus the bioavailability (ABA) of soil and mine waste samples from this study appear to be much lower than found overseas.

The ABA of samples tested in this study (Table 115) range from 0.01–6.1 under the urinary curve and 0.01–6.2 for the area under the blood curve. There is a good correlation relationship between these two targeted sample types. The correlation of BA (AUC-blood) and BA (AUC-urine) (Table 115) is shown in Figure 55 with a correlation coefficient (r) of 0.827. The equation for the prediction of BA (blood) from BA (urine) is shown in Equation 8 (Figure 55). The high r^2 value ($r^2 = 0.68$) suggests that BA obtained from urine excretion can be used for predicting BA obtained from the area under the blood curve. BA obtained from urine extraction is more ethically acceptable because the collection of urine samples is considered to be less invasive to the test animals.



Figure 55 The correlation of BA (AUC-blood) and BA (AUC-urine)

Equation 8 for the prediction of BA (blood) from BA (urine):

It is acknowledged that the correlation is influenced by the HVAP sample and gave an r^2 =0.9898. However, for a relative small data set comprising representative samples and for completeness there is no justification to eliminate any datum point.

Based on available literature about on lead in humans, the Integrated Exposure Uptake Biokinetic Model for Lead (IEUBK model in Section 2.5), used by the US EPA, estimates that the ABA of lead from water and diet is usually about 50 per cent in children (U.S. EPA, 1994a). Therefore, when a reliable site-specific relative bioavailability ('RBA') value for soil is available, it may be used to estimate a site-specific absolute bioavailability in that soil using Equation 9. Conversely, RBA can be calculated from the ABA, using Equation 10.

$$ABA_{soil} = 50\% \times RBA_{soil}$$
 Equation 9

From Equation 6, the maximum RBA of the test samples is 12.4 per cent, which places the RBA of < 25 per cent or low bioavailability category as indicated in Table 116 (e.g. galena material).

In the absence of site-specific data, the absolute absorption of lead from soil, dust, and other soil-like materials is set at a default value of about 30 per cent (U.S. EPA, 1994a). Therefore, the default RBA used by US EPA for lead in soil and dust compared to lead in water is 30%/50% or 60 per cent. This estimate illustrates the value of having site-specific data, because the default value would overestimate the risk for Mount Isa materials.

Table 116 Relative bioavailability (RBA) ranking order found in various soil and soil-like materials obtained from juvenile swine dosing experiments (from US EPA, 2007a)

Low Bioavailability RBA< 25%	Medium Bioavailability RBA = 25–75%	High Bioavailability RBA > 75%
Iron sulfate	Lead phosphate	Cerussite (lead carbonate)
Anglesite	Lead oxide	Manganese oxide
Galena (PbS)		
Lead oxide		
Iron oxide		

Although bioaccessibility (BAc) was adopted as an alternative means to predict bioavailability (Ng et al., 2010), using PBET to measure BAc of lead is a more conservative estimate compared to ABA measured using rat animal uptake as

discussed in Section 2.4.5 (page 143). The Phase I study (Noller et al., 2009) used the more conservative BAc estimate of the potential intake of lead. A more accurate, site-specific determination of exposure for lead was obtained by using the linear regression of measured bioavailability (%ABA) and bioaccessibility (%BAc) data (Noller et al., 2009, Bruce et al., 2007, Diacomanolis et al., 2007).

The linear fitting results and 95 per cent confidence level bands for %ABA were calculated as shown in Table 117 and were plotted (Figure 56) to give the 95 per cent confidence intervals of the data set on ABA and BAc. The more conservative upper interval level of 0.17 was used (Equation 11, page 277) to give the linear relationship between %ABA and %Bac without elimination of any datum point. The lack of a strong correlation with this data set arises because the measured ABA values are very low and have higher errors than high ABA samples.

The %BAc for the HVAP PM_{10} slurry is shown in Table 118. Because a slurry of PM_{10} air particulates was prepared for the practical need of oral gavage, it was necessary to use a volume basis to present its concentration and bioacessibility data. The weight of lead and other metals and metalloids could be measured accurately from calibration lines of ICP-MS in a dispensed volume of slurry and allow the final concentration to be presented in weight/volume. The slurry was the actual form of sample dispensed to rats. The composition of HVAP from XANES fitting (Table 76) is 27% lead-goethite and 72% molydophyllite and therefore similar to soil, including for % BAc (Table 114).

Sample ID	%ABA (blood)	%BAc	Slope (Ratio ABA/BAc)
CS	1.20	9.80	0.12
RG	1.00	15.40	0.06
CD	1.10	5.60	0.20
SS22	0.40	19.90	0.02
SS13	3.00	14.40	0.21
LR10	0.20	24.00	0.01
H2	0.20	3.80	0.05
SS26	0.01	25.40	0.00
SS27	1.40	9.36	0.15
HVAP PM ₁₀ (mg/L)	6.20	20.50	0.30
Mean	1.47	14.82	0.11
SD	1.78	7.19	0.10
Median	1.05	14.90	0.07
95% confidence interval	1.10	4.45	0.06
Upper interval level	2.57	19.27	0.17
Lower interval level	0.37	10.36	0.05

Table 117 Confidence intervals of slope values for plot of %ABA versus % BAc

Category	ID	Arsenic	Cadmium	Copper	Lead	Zinc
Total (mg/L)	Total (mg/L)	3.4	1.6	42.2	38.5	15.7
Bioaccessibility (%)	PBET (%)	39.1	42.1	12.7	20.5	5.8
Bioaccessible concentration (BAc mg/L)	BAc (mg/L)	1.3	0.7	5.4	7.9	0.9

Table 118 Table for high volume air (HVA) PM₁₀ composite slurry from Mount Isa City



Figure 56 Confidence interval plot of %ABA against %BAc

Measured %BAc values for soil and dust at the 67 houses from Mount Isa City were then converted to the predicted %ABA using Equation 11 and used as input values for the IEUBK prediction of blood lead (Section 3.9.3, page 315).

What the data indicate is that there is no predictive relation between the BAc and ABA (r^2 value of .0096). The assessment shows that BAc x 0.17 is the conservative "bounding" value to use, based on the limited available data set for ABA and BAc.

3.6 X-Ray diffraction

Samples from natural outcrops, the mine dust, mineral-processing materials, and samples from the city's residential area were scanned by XRD to determine the mineralogy of these samples. The results are summarised in Table 119 and Table 120. The XRD scan data is given in alphabetical order in Appendix 4.

Four city samples were scanned by XRD (Table 119). The results of the XRD scans indicate two groups: major fitting minerals and minor fitting minerals. Quartz appears as a major mineral in the samples from the city's residential areas. Goethite is likely to exist in all four residential samples, supported by the fact that goethite appears as the dominant iron oxide in soils from the Mount Isa region (Rossel et al., 2010).

Sample	Site information	Major	Minor
CS	Composite garden soil	quartz	plagioclase, microcline, illite,
RG	Composite roof gutter	quartz	muscovite, kaolinite,
RG4	Roof gutter dust from	quartz	albite, illite, muscovite,
VD	Composite carpet dust	quartz,	dolomite, goethite, calcium

Table 119 Summary table of XRD analysis for samples from Mount Isa City

Samples from natural outcrops, mine site dust, and mineral processing materials were also scanned by XRD (Table 120). Quartz is a common major mineral in outcrops from different sites (BGR1–BGR14 in Table 120). The lead species in different mineral samples from Mount Isa are confirmed by XRD (MIN1–MIN6, MIN13, and MIN14 in Table 120). Most of the natural mineralisation (NMU) samples from Urquhart Shale (MIN7, MIN12, NM1–NM5 in Table 120) indicate the presence of goethite, manganese oxide, and hematite. Mine site dust samples have large variations in mineralogy (SS2–SS27 in Table 120), depending on the nature and location of the sampling sites. For lead mining and mineral processing associated samples, galena and anglesite frequently occur. Lead in samples from the city's residential area, copper-associated activities and mine tailings is not detected by XRD in this study. This result confirmed the importance of XANES as a crucial tool to estimate the complex lead-containing samples in an environmental study that may be present at concentrations < 0.1% (10,000 mg/kg).

Table 120 Summary of XRD analysis for natural outcrops, natural min	eralisation and
mine site samples	

Sample ID	Site information	Major	Minor
BGR1	May Downs site outcrop	quartz	
BGR2	Magazine shale outcrop	quartz	illite
BGR3	Magazine shale outcrop	quartz	muscovite, kaolinite
BGR4	Kennedy siltstone outcrop	quartz, plagioclase	dolomite
BGR5	Spear Siltstone outcrop	quartz	muscovite, kaolinite, goethite

Sample ID	Site information	Major	Minor
BGR6	Urquhart Shale outcrop	quartz	hematite, illite, kaolinite, calcite
BGR7	Kennedy Siltstone outcrop	quartz	chalcopyrite, anglesite, muscovite, kaolinite
BGR8	Native bee Siltstone outcrop	quartz, dolomite, calcium carbonate	illite, kaolinite,
BGR9	Native bee Siltstone outcrop	quartz, calcite, ankerite	muscovite, (hematite)
BGR10	Moondarra Siltstone outcrop	quartz, dolomite	muscovite, kaolinite, goethite
BGR11	Outcrop from Cromwell member of ECV	quartz	illite, dolomite, pyrite, richterite, albite, goethite, (hematite)
BGR12	Judenan beds outcrop	quartz	
BGR13	outcrop from Amphibolite in ECV W MIF	quartz, albite	richterite, calcium silicate, kaolinite, dolomite
BGR14	Breakaway shale outcrop	quartz	muscovite, kaolinite
MIN1	Cerussite from Mount Isa	quartz, cerussite	sodium calcium silicate, kaolinite,
MIN2	Galena from Mount Isa	quartz, galena, sphalerite	ankerite, kaolinite, calcite
MIN3	Sphalerite from Mount Isa	sphalerite	dolomite, galena, quartz, dolomite, calcite,
MIN4	Galena from Mount Isa	galena, sphalerite ferrous, quartz	muscovite, microcline
MIN6	Pyromorphite	pyromorphite	
MIN7	Urquhart Shale outcrop	quartz	goethite, hematite
MIN12	Urquhart Shale outcrop	quartz	kaolinite, natroalunite, (manganese copper oxide)
MIN13	Anglesite	anglesite	
MIN14	Mineral from MIM	smithsonite	
NM1	ANZAC Hill ore deposit halo	goethite, quartz	sillimanite(alumina- silicate Al ₂ SiO ₅ .)
NM2	Outcrop from RSL Gate adjacent Barkly highway	calcium magnesium carbonate, quartz	chalcopyrite, pyrite, hematite
NM3	Outcrop from U-Shale site 1	quartz, goethite	kaolinite
NM4	Outcrop from RSL gate	quartz	kaolinite, hematite, muscovite
NM5	Outcrop from ANZAC Hill	quartz	goethite
NM6	Transmission St outcrop	quartz	kaolinite, muscovite

Sample ID	Site information	Major	Minor
SS2	Mount Haney Pb slag old	wüstite	calcium silicate, rutile,(galena, mendipite)
SS3	Copper slag old site	quartz	calcium magnesium silicate, calcite, fayalite
SS4	Copper slag	quartz, magnesium iron manganese silicate	magnesioferrite, calcite
SS8	Lead stack	galena, Pb	anglesite, pyrite, vaterite
SS13	Tailings dam 5	quartz, calcium magnesium carbonate	pyrite, chalcopyrite, hematite,
SS22	Lead smelter area dust	galena	pyrite, chalcopyrite, feldspar, quartz
SS26	Lead concentrator dust	galena	anglesite, pyrite
SS27	Dust from copper smelter area	cuprite	barite

Note: The minerals are given in the brackets are possible matches.

3.7 SEM-EDS

Samples from city residential area and mine site were scanned by SEM-EDS analysis (Section 2.3.5). To evaluate the general morphology of the particles, each sample was scanned for more than 10 images at a particular step size (1 mm) across a 1.5–2.0 cm size filter stick to the SEM sample holder. EDS was conducted concurrently, whenever possible, to record semi-quantitative elemental composition for particles.

Blank filters (Whatman EPM2000 and 25 mm PALL PVC membrane filter) were also scanned with SEM-EDS. Blank Whatman EPM2000 filters show the main background elements are silicon (38%), oxygen (41%), aluminium (2%), potassium (<2%), calcium (5.5%), sodium (11%) and magnesium (2%). Blank PALL PVC membrane filters had no detectable elements, except carbon and chlorine. It is difficult to confirm the existence of sulfur when lead is present in the sample because of the close energies for lead M and sulfur K α . The samples were analysed at USGS, Denver, US, using an Oxford ISIS standardless analysis package with automated correction procedures (Section 2.4.4.2, page 142) and provided matching scans with, and without sulfur, to compare the occurrence of the lead–sulfur bond in the city's residential samples.

High-volume air (HVA) particulate samples (air- PM_{10}) from five historical monitoring sites (Figure 57), and soil and carpet dust samples from the city's residential area (Section 2.3, page 117) were analysed by SEM-EDS (Figure 58). A summary of the frequency with which particles are present in the HVA samples is shown in Table 121, based on the SEM images for these samples. Although more particles were captured from Site RC (Racecourse), the site with highest

frequency of heavy metal containing particulates presence is the RSL Club, followed by BSD (Table 121).



Figure 57 Spatial distribution of high-volume air samples from Mount Isa City

Table 121 Rank of the frequency of presence for high-volume air particulates (PM₁₀)

Site	Rank of all particles (geogenic and metal containing)	Rank of heavy-metal containing particles (copper, lead, and zinc only)
BSD	2	2
КО	4	4
Miles	5	2
RC	1	5
RSL	3	1

Note: Rank values are based on the SEM-EDS results. Lower rank values indicate higher frequency of particles found in the sample.

3.7.1 High-volume air samples

3.7.1.1 Base Supply Depot

The Base Supply Depot (BSD) sampling site is located beside the acid plant car park. The SEM-EDS images indicate that silicate, iron, iron–manganese, silicon, and iron–sulfur (Fe–S) are common, but there are a large number of irregular lead $(1 - 5 \mu m)$, zinc–sulfur (Zn–S) $(3 \mu m)$, copper–zinc–sulfur (Cu–Zn–S) (6 μm), Cu–copper–iron–sulfur (Cu–Fe–S) (1 μm) particles (Figure 58) It is easy to find zinc–sulfur (Zn–S) minerals in each SEM scan.

3.7.1.2 Kruttschnitt Oval

Kruttschnitt Oval (KO) is about 1 kilometre south-east of the lead smelter and 0.6 kilometres north-east of the BSD (Figure 57). Small numbers of particles are present in the sample from Kruttschnitt Oval, including mixed metal–silicon features (Si–Al–O–Na–Mg–Ca–K–Fe–Cu),), iron–sulfur (Fe–S) (10 µm) particles, zirconium–hafnium–silicon (Zr–Hf–Si) (2-4 µm), titanium–iron–manganese Ti–Fe–Mn (2–4 µm), and Zn–S (2–4 µm), mass ratio = 2 confirms the presence of zinc–sulfur (Zn–S). Lead-containing particles are found as 1–3 µm size, but most particles are silicon-containing particles, which normally indicate a geogenic origin.

3.7.1.3 RSL

Table 121 and Figure 58 show that more heavy-metal containing particles are found at the RSL site than the other four sites, including iron–copper–sulfur (Fe–Cu–S) (2–8 μ m), copper–sulfur (Cu–S) (4 μ m), lead (2–5 μ m), and zinc–lead (Zn–Pb) (2–5 μ m, linear or irregular). Barium–sulfur (Ba–S) (1–2 μ m) particles are also occasionally present.

3.7.1.4 Miles St

The Miles Street site shows a high frequency of zinc–sulfur (Zn–S) (8–10 μ m, linear irregular shape), iron–copper–sulfur (Fe–Cu–S), and lead–sulfur (Pb–S) (1–3 μ m) particles present in the filter. Barium–sulfur (Ba–S) (5–10 μ m) and titanium–iron (Ti–Fe) (2 – 4 μ m) particles are also detected.

3.7.1.5 Racecourse

Table 121 and Figure 58 show that geogenic silicon-containing particles $(2-3 \mu m)$ are the most common minerals at the Racecourse (RC) site. Less common particles are iron-titanium (Fe-Ti) (generally 1–2 µm), barium–sulfur (Ba–S) (2–3 µm), zirconium–yttrium–gadolinium–terbium (Zr–Gd–Y–Tb) (5 µm), titanium–manganese–iron (Ti–Mn–Fe) (2–3 µm), iron–copper (Fe–Cu), iron–copper–sulfur (Fe–Cu–S) (2–3 µm), zinc–sulfur (Zn–S) (3 µm). Few lead minerals are detectable. This indicates that PM₁₀ from the RC site is more likely to be influenced by natural phenomenon such as wind, or artificial procedures, such as car parking, rather than being influenced by the mine site. Spatial differences

among the five high-volume air sites were recorded. More site details are given in Appendix 4.



Site BSD-012008-02

Site BSD-012008-04



Site KO-012008-15

Site KO-012008-22



Site RSL-012008-02

Site RSL-012008-08

Figure 58 SEM-EDS results for high-volume air PM_{10} samples from five monitoring sites in Mount Isa City. VD and CS are carpet dust and garden soil from residential houses in Mount Isa City



Site Miles-012008-04

Site RC-012008-18



Site VD19-02

Site CS31-05



Site CS31-07



Figure 58 SEM-EDS results for high-volume air PM₁₀ samples from five monitoring sites in Mount Isa City. VD and CS are carpet dust and garden soil respectively from residential houses in Mount Isa City (continued)

3.7.2 Air PM₁₀ samples

Air PM_{10} filters (Sites B54 and B50) from two houses of different distances from the mine site were scanned for SEM-EDS analysis



Site B54

Site B50



Site B54-01-002

(

Site B50-01-002

Figure 59). House B54 is approximately 1.5 kilometres south-east of the lead processing facilities and House B50 is approximately 3 kilometres east of the

lead processing facilities. Based on a visual comparison of



Site B54





Site B54-01-002

Site B50-01-002



Site B54





Site B54-01-002

Site B50-01-002

and
Figure 59b, there are relatively more heavy metal-containing particles in the B54 f $\hfill -S)$



Site B54

Site B50



Site B54-01-002

(

Site B50-01-002



Site B54

F

(



-S)



Site B54-01-002

Site B50-01-002

Figure 59d) in those two filters with clear isometric crystal structures that are characteristic of galena (Vaughan, 2006).



Site B54

Site B50



Site B54-01-002

Site B50-01-002

Figure 59 Backscattered SEM images of air particulates (PM¹⁰) from two houses in Mount Isa City. The bright dots in (a) and (b) are heavy metal-containing particles

3.7.3 Soil and carpet dust

Components such as mixed metal–silicon–chloride (Fe–Ca–K–Na–Mg–Ti–Si–Cl) (50 μ m – 0.1 mm), calcium–carbon–oxygen (Ca–C–O) particles (100 μ m), iron–copper (Fe–Cu) (40 μ m), titanium–iron (Ti–Fe) (50 μ m), iron–sulfur (Fe–S) (40 μ m), copper–sulfur (Cu–S) (40 μ m) in the soil samples are very common. Zinc–sulfur (Zn–S) and lead–sulfur–oxygen (Pb–S–O) particles also have a high chance of appearing, but particle size is usually larger than 10 μ m and can be up to 50 μ m. Lead silicate is also detected (≈ 20 μ m) (CS31 in Figure 58).

Silicate minerals (Si–Al–O–Fe–K–Ca–Cl–S) in carpet dust are common (CD19 in Figure 57). Other materials, such as calcium–carbon–oxygen (Ca–C–O) (not found in PM_{10} and soil), and barium–sulfur–oxygen (Ba–S–O), lead–copper (Pb–Cu) are also found. The major difference between the soil CS31 and carpet dust CD19 is the size of the particulates. The particle sizes in the soil samples are much larger than for the carpet dust sample (Figure 57).

3.7.4 Mine site samples

Air PM_{10} samples from three sites (lead ore open pit, lead smelter, and lead slag stockpile) were scanned for SEM-EDS analysis (Figure 60). The sample from the lead ore open pit generally contains a large amount of lead sulfide, as well as quartz and other silicate minerals (Figure 60a). The sample from lead smelter, however, is dominated by heavy metal–containing particulates (Figure 60b). The shapes of the particulates from each of these sites are also characterised by SEM images. Particles from the lead ore open pit are irregular and less than 4 μ m (Figure 60c). The surface of samples from the blast furnace (Figure 60d–f) have smooth and aggregated features, compared with the sample from the mining process. The SEM-EDS mapping view (Figure 61) for the air particulates collected from the lead ore open cut at the mine site confirm extensive lead-containing particles, which correlate with other elements, such as zinc, iron, silicon, calcium, and aluminium.



Site C11-02-005 (lead smelter area) Site B9 (lead slag stockpile)

Figure 60 Backscattered SEM images of Air PM10 samples collected from the mine site.



Figure 61 SEM/EDS mapping for Site B11 (lead ore Black Star open cut)

3.8 Particle size

3.8.1 Repeatability of particle size analysis

The repeatability of particle size analysis using the Mastersizer 2000 laser diffraction-based particle size analyser (Section 2.4.4.1, page 142) was measured for seven samples with different matrices. The relative standard deviations ('RSD') for triplicates are lower than 10 per cent for most samples (Table 122), including ground (< 20 μ m) environmental samples collected from Mount Isa City (L1 and L13). The RSD values are higher in sample PS2, which is pure lead (II) sulfide.

Sample ID	10 percentile*	50 percentile*	90 percentile*	Note
PS1 (n = 3)	12	3	4	Laboratory synthesised goethite
PS2 (n = 3)	18	24	15	Purchased pure lead (II) sulfide
PS3 (n = 3)	15	15	6	Mixture of PS1 and PS2
PS4 (n = 3)	8	8	10	Mixture of PS1 and PS2
PS5 (n = 3)	4	3	2	Mixture of PS1 and PS2
L1 (n = 3)	9	8	3	Ground sediment samples from Leichhardt River
L13 (n = 3)	4	2	1	Ground sediment samples from Leichhardt River

Table 122 Repea	atability (RSD	(%) of	particle	size anal	vsis
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Note: * corresponds to a certain percentage of the cumulative distribution in the sample, as described in ISO 13200 (2009) (Section 2.4.4.1, page 142)

3.8.2 Overall characteristics of particle size distributions

Samples from the mine site and the city's residential area were analysed to estimate the size distribution of different types of particles (Section 2.3.6, page 126). The median particle size range for each sample group is shown in Figure 62. Mine site dust materials are finer than dust and soil collected in the city's residential area (Figure 62). The size distributions — from fine to coarse — were listed in the following order:

- for mine dust (surface tailings, fallout from the mine, general mine source dust, smelter area dust, and haul road dust)
- for city dust (roof gutter dust, fallout from the city, carpet dust)
- for soil samples (soil < 250 μm fraction, and soil < 2 mm).

The particle size range for $PM_{10}S$ samples is close to the size of dust samples from the mine, which were artificially extracted from soil < 250 µm fraction (Section 2.3.6.1.2, page 129).

Of all the sample groups, surface tailings are the finest, with three unique peaks (0.1 μ m, 0.65 μ m, and 10 μ m). This is in part due to the fine grinding of the ore

and the weathering of the particles, which may include alteration by chemical reaction, on the surface of the tailings dams.

Particles less than 250 μ m represent over 90 per cent of all particles in all the samples from the mine site and the city.



Figure 62 Summary of particle size distribution of samples from the mine site and the city's residential area as volume (%) and cumulative (%)

3.8.2.1 *Mine site samples*

Dust samples from the various sites at the mining and mineral processing facilities were collected and analysed for the range of particle sizes (Section 2.3.6, page 133). The details of the general source samples are listed in Table123 and the results of size distribution are plotted in Figure 63. Particle size distributions for other groups collected from the mine site, such as haul road dust, surface tailings, and smelter dust are plotted in the Figure 64 for comparison.

Most mine site samples, such as smelter area dust and surface tailings materials, have bi-modal or even tri-modal distributions of particle size volume (Figure 64). The first significant peak is about 10 μ m size, followed by a large second peak at about 800 μ m. Surface tailings has distinct peaks and the finest particle size of all the mine site samples (Figure 64), which is similar to Figure 62. The samples from Number 5 tailings dam, which is older than Numbers 7 and 8, tend to be coarser, reflecting earlier production when the lead–zinc ore was not ground as fine as in recent times (Young et al., 1997).

Note that smelter slags were sieved to -2 mm before the particle size distributions were determined. Most of the slag was coarser than 2 mm. The samples of mine site material were grab samples, not fallout dust or high-volume samples.

Sample ID	Sample description	Sample ID	Sample description
SS1	Lead slag	SS10	Sinter plant
SS2	Lead slag old	SS11	Sinter plant
SS3	Copper slag	SS22	Lead smelter area dust
SS7	Lead ore stockpile dust	SS26	Lead concentrator dust
SS8	Lead stack	SS27	Copper smelter area dust
SS9	Sinter plant		

Table123 Summary of source samples collected from the mine site for particle size analysis



Figure 63 Summary of particle size distribution of dusts from various sources from the mine site



Figure 64 Summary of particle size distributions of samples from different locations at the mine site

3.8.2.2 Mount Isa City samples

The cumulative particle size distributions of samples from the city's residential area are plotted in Figure 65. Figure 65 shows size distributions by volume for five different categories of sample. There were more samples in the first three categories for which particle size analysis was undertaken, and so they occupy a larger proportion of the x-axis. Each point on the x-axis represents one sample, arranged in order of increasing PM₁₀ fraction particle size within each category. About 10 per cent of particles in the city's samples are in < 10 μ m range, which is the size fraction normally absorbed via the human respiratory system (Figure 9, page 75) and ingestion when agglomeration of particles occurs. More than 80 per cent of particles in the city's samples are in the size range of 10–250 μ m. These particles are easily ingested via hand-to-mouth behaviour (Figure 9).



Figure 65 Cumulative percentage of particle size distributions, by volume, for samples from the city's residential area. (i) Soil fine fraction (soil PM10), (ii) soil < 250 µm fraction, (iii) carpet dust, (iv) roof gutter dust, (v) fallout dust from city

Particle size distributions for individual sample groups from the city are shown in Figure 66. Garden soil samples (< 250 μ m) and fine fraction extracted soils from garden soil indicates the mono-modal feature at 100 μ m and 20 μ m size points respectively. However, the particle size patterns of carpet dust were significantly different from garden soil, showing bimodal peaks (Figure 66) with the main peak similar to the PM₁₀ extracted soil samples (also called 'soil PM₁₀'). Most of the roof gutter dust samples also showed the mono-modal feature, but the particles were finer than for garden soil samples. Fallout dust samples from the city indicated bimodal peaks, with finer particles than those found in fallout dust samples from the mine site (Figure 64). Roof gutter dust and fallout dust from the city showed similar ranges of particle size (Figure 66).



Figure 66 Summary of particle size distribution for samples from the city's residential area



Figure 66 (continued) Summary of particle size distribution for samples from the city's residential area

3.9 IEUBK model

The IEUBK model was used to estimate children's blood lead concentrations from ingestion and inhalation of lead-containing matrices to assist with the health risk assessment for the study area (Section 1.7.6, page 94). The default values used in the model are summarised in Table 12 (page 154). The site-specific parameter settings are detailed in this Section 3.9.1.

3.9.1 Site-specific parameters

3.9.1.1 Air input

The IEUBK model considers lead sources mainly from two exposure pathways: inhalation of lead in air and ingestion via diet, water, soil, dust, and other materials.

The site-specific estimation of an inhalation pathway in Mount Isa City needed an input of reliable air lead concentration data. Indoor and outdoor air particulates (< 10 μ m) from eight houses were collected from different locations in Mount Isa City (Section 2.3.6.1.1,page 127). The median ratio of lead levels in indoor and outdoor air particulates (59 per cent) was applied in the IEUBK program (Table 124).

The monitoring data for lead concentrations from total suspended particulates (TSP) at the five high-volume air-monitoring sites (Figure 13, page 125) in Mount Isa City are summarised in Table 124. The data have a median value of $0.07 \ \mu g/m^3$ during 2005–2010. This median value was used in the IEUBK program as the input for the air module because the data do not have normal distributions (see Section 3.1.1, page 160).

	Ratio of indoor lead/outdoor lead (%) ①	Historical lead concentration in TSP (µg/m³) ②
n	8	1353
Mean	58	0.39
SD	24	0.86
Minimum	21	0.001
25th percentile	39	0.03
Median	59	0.07
75th percentile	74	0.35
80th percentile		0.50
95th percentile		1.98
Maximum	93	11.48

Table 124 Summary table of lead in air particulates in Mount Isa City

Notes: ① Indoor/outdoor air PM₁₀ on 2010 field trip (Section 2.3.6.1); ② Historical HVA monitoring data during 2005–2010 (MIM, 2011, DEHP, 2013)

3.9.1.2 Soil and dust input

Detailed requirements for the input data to the IEUBK model are summarised in Table 12 (page 154). House-based total lead concentration and lead bioaccessibility (% BAc) from the Mount Isa City data were applied (Table 21 [page 173] and Table 26 [page175] in Section 3.1.5.1 for total concentrations and Table 102 [page 266] and Table 113 [page 271] in Section 3.4 for lead bioaccessibility). One dwelling was sampled without collecting a soil sample. In that case, the median value of the total lead concentration and lead bioaccessibility (%) for all sampled houses was used.

Different types of house dust materials were collected (Section 2.3.6, page 126). Indoor dust is an important pathway for lead absorption into the body. It should be considered as an input for consistent and robust IEUBK model prediction (U.S. EPA, 2001). Nearly all houses had carpets. Carpet dust materials were collected at all houses, except the eight that did not have carpets (Table 125). A

basis for estimating an appropriate lead concentration in dust was developed for these eight houses to provide input values for the IEUBK model, as discussed below.

House ID	Floor wipe total median lead (µg/m ²)
1	40
2	339
14	99
16	96
34	244
35	47
51	3056
62	189
75	144
n	8
Mean	514
SD	1032
Minimum	40
25th percentile	84
Median	144
75th percentile	268
95th percentile	2105
Maximum	3056

Table 125 Comparison of data for houses without carpet dust samples

There are similarities between carpet dust and floor wipe concentration data for lead when data for samples of floor wipes and carpet dust were compared using both lead isotope ratios and lead speciation fitting by the XANES LCF technique (Figure 67 and Figure 68). A method was devised to use common data features correlating lead concentrations in carpet dust (mg/kg) for those eight houses against the lead concentrations in floor wipes (μ g/m²) for each house (Figure 69). All sampled houses were further divided into two groups: (i) low loadings; (ii) high loading, as displayed in Figure 70 and Table 127.

House ID	House location	Lead in hand wipe (n = 27) (µg/wipe)		Lead in floor wipe (n = 15) (µg/wipe)		Transfer rate (%)		Lead in blank wipes (n = 18) (µg/wipe)	
		Median	SD	Median	SD	Median	SD	Median	SD
House W1	Central south of Mount Isa City	38	23	190	45	18	14		
House W2	East of Mount Isa city	7.0	1.1	35	8	19	5	0.23	0.17
House W3	North of Mount Isa city	1.8	1.4	2	1.4	61	69		

Table 126 Transfer rate of lead from floor wipes to hand wipes (wipe area 0.09 m²)



Figure 67 Comparison of lead isotope ratios for floor wipes and carpet dust with soil and mine dust



Figure 68 Comparison of lead speciation from XANES fitting for floor wipes, carpet dust, soil, and mine dust. The mean relative error of XANES fitting is 20% (Section 3.3.2)

A detail that supported the assignment of low and high loading groups is the apparent division into two parts of the data set. The division occurred in the cumulative plot of the total lead concentration in floor wipes for all 67 houses in Mount Isa City and the floor wipes and hand wipes from three representative houses (different locations in the residential area Table 126) with different lead loadings (Figure 69 and Table 127). The houses in the high group (Houses W1 and W2 in Table 126) have the same transfer rates of lead from floor-to-hand wipes, but the rates are very different from House W3.



Lead distribution in floor wipes from 69 houses

Note: The intersection for high and low groups is House 23, the intersection of high and low data linear regression equations and giving a floor wipe concentration of 66 μ g/m²

Figure 69 Lead cumulative plot and total concentrations in floor wipes for houses in Mount Isa City (precluding the maximum and minimum values)

The low group included houses for the lead concentrations in floor wipes that are < 66 μ g/m², and the high group is comprised of the remaining houses (Figure 69). The statistical summary of lead concentrations in carpet dust for all available

houses is shown in Table 127 and Figure 70. The median lead levels in carpet dust for both groups were calculated for input into the IEUBK model for site-specific blood lead prediction, namely 520 mg/kg and 885 mg/kg for the low and high group respectively.

	Low group	High group
n	19	39
Mean	536	1065
SD	228	767
Minimum	150	210
25th percentile	359	540
Median	520	885
75th percentile	665	1300
95th percentile	870	2871
Maximum	1040	3400

Table 127 Summary of predicted lead concentrations (mg/kg) in carpet dust for low and high groups



Note: solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values

Figure 70 Lead concentrations in carpet dust for all sampled houses in Mount Isa City

3.9.1.3 *Maternal data*

The lead accumulated in the tissues of a newborn child is calculated by entering the maternal lead blood concentration of the child at the time of delivery in the IEUBK model. This study used the maternal default data (default = $1.0 \mu g/dL$) used in IEUBK model. These default data are based on the Technical Review Workgroup analysis of 1999–2002 NHANES data (U.S. CDC, 2005). This report suggested that women aged 20-59 years in the USA had a mean blood lead level of 1.2 µg/dL and 0.3 per cent of women had blood lead levels above 10 µg/dL during the 1999 and 2002 sampling period (1999–2002 NHANES data). Another study on umbilical cord blood screening at Broken Hill, NSW indicated a level of 1.2 µg/dL for a population of 171 in 2011 (Lesjak, 2011). The Broken Hill study showed more similarity to the lead exposure scenario of Mount Isa, compared with other studies, particularly urban studies in the US. Since this current Mount Isa study focused on children in the 0-7 year old for the IEUBK model age range or 1-4 years age range for the Queensland Health survey, instead of newborn babies, a maternal lead concentration of 1.2 µg/dL was used as the default input for the IEUBK model. Sensitivity testing showed that this was a relatively minor contributor to the predicted blood lead levels in children. Increasing the maternal blood lead level from 0.1 µg/dL to 10 µg/dL changed the predicted childhood blood lead level from 2.7 to 2.9 µg/dL, when all other contributing intakes remain at minimum levels.

3.9.1.4 *Food and water input*

The IEUBK prediction of blood lead in this study was calculated based on a national intake average reported in the Australian dietary survey (2003). This survey indicated that the diet of Australians overall is very consistent and largely derived from supermarket food. For this reason it is considered appropriate to use FSANZ (2003) data here as the food input for the IEUBK model. For children who regularly consumed food grown from the local yard where the lead concentrations in soil were elevated, the lead exposure risk from the dietary route could be higher than the findings in this study. Home-grown food items including vegetables and fruit are not commonly featured in Mount Isa city. There was one study conducted on total concentrations of heavy metals in home-grown vegetables (3 lettuces and 2 cabbages) at Mount Isa city in 1990 (Sadler et al., 1990). The total concentrations for lead ranged between 1.2 and 2.8 mg/kg in the lettuces and 1.0 to 4.4 in cabbages, as reported by Sadler et al. (1990). Since leaded petrol was still used in early 1990 in Australia and lead-containing particulates were more frequently deposited, the total lead concentration of lead in those home grown vegetables from the 1990 study (Sadler et al., 1990) might not be directly applicable in the current study. Home-grown vegetables were not tested during the current study; however, they can be considered should the residential setting change in the future.

Site-specific lead concentration in drinking water based on the measured concentration in potable water being reticulated to Mount Isa city (0.6 μ g/L) (MIWB, 2010) was applied in the IEUBK calculation in this study. The Australian Drinking Water Guidelines (ADWG, 2011) requires no exceedance of 0.01 mg/L

(10 μ g/L) of lead in drinking water. Regular tap water testing by Mount Isa Water Board indicated a 99.99% compliance rate to ADWG guideline during 2011–2012 (MIWB, 2012). The preliminary comparison of using 0.6 μ g/L compared with 0.01 mg/L as an input value in the IEUBK model gave negligible changes in children's blood lead prediction (< 0.01 μ g/dL).

3.9.2 Children's blood lead prediction using bioaccessibility

While using bioavailability is the gold standard for lead uptake assessment (see Section 2.2.5, page 107), such as inputs into the IEUBK model, ethical and other practical considerations limited the number of bioavailability tests that could be undertaken. Consequently, most of the data available were obtained using bioaccessibility tests.

The output of the IEUBK model is a distribution of blood lead levels predicted using a physiologically-based pharmokinetic model and incorporating a Monte-Carlo simulation, which provides frequency and probability. The model calculates the geometric mean associated with the curve and the probability of exceeding a designated level (5 or 10 μ g/dL in this study⁴²).

The predicted blood lead concentrations using the IEUBK model with bioaccessibility values for soil and dust as inputs for children living in 67 houses in Mount Isa City's residential area are summarised in Table 128, Figure 71 and Figure 72. Of all the age groups considered in the model (A. 0.5–7 years and B. 1-4 years), the 1–3 year age group is the most vulnerable population group. The IEUBK modelling indicated that the blood lead level for one house located on the Urquhart Shale that exceeded the 10 μ g/dL NHMRC recommended level (NHMRC, 2009) for all age groups, except the 5–7 year old age group (



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 μ g/dL Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 μ g/dL.

⁴² 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.



Figure 71) and all age groups for 1-4 year old age groups exceeded the 5 µg/dL NHMRC recommended level⁴³. The geometric mean of predicted blood lead

B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 µg/dL.

Figure 72. The house exceeding NHMRC recommended level of < 10 µg/dL, had a 52%, probability of exceeding 10 µg/dL, which means that 52 of 100 children living in the same house under the same lead exposure scenario might exceed NHMRC recommended the (



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 µg/dL.

⁴³ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

Figure 72). However, the 16 houses exceeding NHMRC recommended level of < 5 μ g/dL, had a 52%, probability of exceeding 5 μ g/dL, which means that 52 of 100 children living in the 16 houses under the same lead exposure scenario might exceed the NHMRC 2016 recommended maximum blood lead level (



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 μ g/dL Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 μ g/dL.

Figure 72).

Table 128 Summary of IEUBK predicted blood lead level (µg/dL) for different age groups in Mount Isa City using bioaccessibility-adjusted data for soil and dust

	Blood lead geometric mean (µg/dL)	Exceedance	0.5–1 У	1–2 y	2–3 У	3–4 y	4—5 У	5– 6 y	6– 7 у
n	67	67	67	67	67	67	67	67	67
Mean	3.8	5%	4.1	4.6	4.4	3.8	3.5	3.4	3.2
SD	1.8	0.10	1.6	2.0	1.9	1.9	1.8	1.7	1.6
Minimum	1.5	0.000	1.9	1.9	1.8	1.3	1.1	1.1	1.1
25th percentile	2.6	0.2%	3.0	3.2	3.1	2.5	2.3	2.2	2.1
Median	3.4	1%	3.7	4.2	3.9	3.4	3.1	3.0	2.8
75th percentile	4.6	5%	4.8	5.5	5.2	4.6	4.3	4.1	3.9
Maximum	10.2	52%	10.1	11.9	11.2	10.6	10.2	9.7	9.1

A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 $\mu\text{g/dL}$

B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

	Blood lead geometric mean for 1-4y (μg/dL)	Blood lead geometric mean for 1-4y (µg/dL)		2-3 у	3-4 у
n	67	67	67	67	67
Mean	4.2	5%	4.6	4.4	3.8
SD	1.9	0.10	2.0	1.9	1.9
Minimum	1.6	0.00	1.9	1.8	1.3
25th percentile	2.9	0.2%	3.2	3.1	2.5
Median	3.8	1%	4.2	3.9	3.4
75th percentile	5.1	5%	5.5	5.2	4.6
Maximum	11.2	52%	11.9	11.2	10.6



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 µg/dL

Note: The red line indicates the NHMRC (2009) recommended maximum level of 10 μ g/dL.



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 µg/dL.

Figure 71 IEUBK predicted BLL (µg/dL) for different age groups in Mount Isa City. Mean BLL: geometric mean of blood lead level



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 µg/dL

Note: The red line indicates the NHMRC recommended maximum level of 10 µg/dL.



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 μ g/dL.

Figure 72 IEUBK predicted blood lead level geometric mean (μ g/dL) and the predicted probability of exceedance for 67 houses in Mount Isa City. The red line indicates the blood lead level of concern (5 or 10 μ g/dL)

3.9.3 Children's blood lead prediction using bioavailability

The results for absolute bioavailability (ABA) of lead from the rat uptake study for the 10 samples from the mine site and the residential area are given in Section 3.5 (page 272). The linear regression relationship of lead bioaccessibility and bioavailability data for the upper interval of the 95 per cent confidence interval gives a slope of 0.17 (Equation 11, see page 277), which was used to calculate the predicted %ABA in each case of soil and dust values as input values for the IEUBK prediction of blood lead.

The predicted blood lead concentrations using the IEUBK model with bioavailability values for soil and dust as inputs for children living in 67 houses in Mount Isa City's residential area are summarised in Table 129,

Of all the age groups, the 1–3 years age group is the more vulnerable population group, as identified in Section 3.9.2. The IEUBK modelling of the estimation for all houses indicated that no houses exceeded the NHMRC guideline for blood lead level of both 5 and 10 μ g/dL (NHMRC, 2009⁴⁴). For 10 μ g/dL the house showing the highest predicted blood lead of 2.8 μ g/dL, the probability of exceedance is 0.37% whereas at 5 μ g/dL the house showing the highest predicted blood lead was 3.4 μ g/dL. These values show the significant effect of using the actual bioavailability data, as compared with using bioaccessibility to give predicted values.

⁴⁴ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

Table 129 Summary of IEUBK predicted blood lead level (µg/dL) for different age groups in Mount Isa City using bioavailability-adjusted data for soil and dust

	Blood lead geometric mean (0.5-7y)	Exceedance	0.5–1 У	1–2 y	2–3 у	3–4 y	4–5 y	5–6 y	6–7 y
n	67	67	67	67	67	67	67	67	67
Mean	1.5	0.01%	1.9	1.9	1.8	1.3	1.2	1.1	1.1
SD	0.3	0.05%	0.3	0.4	0.4	0.4	0.4	0.3	0.3
Minimum	1.1	0.00%	1.5	1.4	1.3	0.9	0.7	0.7	0.8
25th percentile	1.3	0.00%	1.7	1.6	1.6	1.1	0.9	0.9	0.9
Median	1.4	0.00%	1.8	1.8	1.7	1.2	1.1	1.1	1.1
75th percentile	1.6	0.01%	2.1	2.1	2.0	1.5	1.3	1.3	1.3
Maximum	2.8	0.37%	3.2	3.5	3.3	2.8	2.5	2.4	2.3

A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 $\mu\text{g/dL}$

B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 $\mu\text{g/dL}$

	Blood lead geometric-mean (1-4y)	Exceedance	1-2 y	2-3 у	3-4 y
n	67	67	67	67	67
Mean	1.7	0.01%	1.9	1.8	1.3
SD	0.39	0.05%	0.4	0.4	0.4
Minimum	1.18	0.00%	1.4	1.3	0.9
25th percentile	1.41	0.00%	1.6	1.6	1.1
Median	1.54	0.00%	1.8	1.7	1.2
75th percentile	1.83	0.01%	2.1	2.0	1.5
Maximum	3.19	0.37%	3.5	3.3	2.8



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 µg/dL



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 73 ABA approach predicted blood lead levels for children of different age groups and exceedance



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 $\mu g/dL$



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 74 IEUBK model predicted blood lead level geometric mean (μ g/dL) and exceedance for 67 houses in Mount Isa City using the ABA approach

3.10 Summary of results

Total concentration of metals and metalloid are outlined in Section 3.1 (page 160). The Q-Q plots and Shapiro-Wilk Tests (Section 3.1.1, page 160) indicate non-normal distributions of elements in most samples. Because of these non-normal distributions, non-parametric tests were used in this study.

Statistical summary tables of total concentrations for metals and the metalloid and the results of Kruskal-Wallis ANOVA tests are detailed in Section 3.1.4 (page 169), Section 3.1.5 (page 172), and Section 3.1.6 (page 184). The Kruskal-Wallis ANOVA tests show statistically significant differences in total lead concentrations within the samples from the mine site (Section 3.1.4, page 169). Similarly, there were statistically significant differences in lead concentrations within the soil and dust samples from the city's residential area (Section 3.1.5 [page 172] and Section 3.1.6 [page 184]). The Mann-Whitney U test indicates that the total concentrations of lead in indoor and outdoor air PM₁₀ samples are not statistically different. Also the differences in the total concentrations of lead are not statistically significant for outdoor air PM₁₀ samples between each individual sampling trip (Table 41, page 192).

Total concentrations of metals and the metalloid for outcrops from non-Urguhart Shale units are lower than samples from the Urguhart Shale and from the mine site, except for manganese and iron (Section 3.1.2 [page 167] and Section 3.1.3 [page 168]). Metal and the metalloid concentrations for mine samples vary over three orders of magnitude (Table 19, page 170). The median level of total lead concentration in mine site sample is 7530 mg/kg, twice the level for outcrops from Urguhart Shale and even more than other geological units. In addition to lead levels, the total concentrations for cadmium, cobalt, copper, nickel, and zinc in mine site samples are all higher than the background rock samples and natural mineralisation outcrops. The median total concentrations of arsenic, iron, and manganese in mine site samples (Table 19, page 170) are lower than those from Urquhart Shale (Table 18 [page 169]). Statistical summary tables of total concentrations for metals and the metalloid in samples from the city's residential area are detailed in Section 3.1.5 (page 172). Total elemental concentrations for garden soils were compared with HIL Level A criteria⁴⁵ (Table 21, page 173) and there are various levels of exceedances for metals and the metalloid. The arsenic, cadmium, copper, iron, lead, and zinc concentrations in samples from the city's residential area were compared (Figure 23, page 174). The median level of lead for Mount Isa City samples shows the highest concentration (6753 mg/kg) in fallout dust samples from the city. The distribution pattern of iron is different from arsenic, cadmium, lead, and zinc (Figure 23, page 174). Total concentrations for metals and the metalloid were also summarised, and generally show the highest levels in wipes from window troughs (Figure 24, page 174).

⁴⁵ The revised (NEPC, 2013) HIL A (low density residential, including a sizeable garden) criteria for soil contamination (mg/kg) are: arsenic (100), cadmium (20), cobalt (100), copper (7000), iron (N/A), lead (300), manganese (3000), nickel (400) and zinc (8000).

Total concentrations for air particulates from the mine site and the city's residential area (indoor and outdoor) from three different sampling periods are detailed in Section 3.1.6 (page 184). Total concentrations of metals and the metalloid for air PM₁₀ from the mine site have large variations (Figure 25, page 187). The air PM₁₀ samples from the city's residential area have fewer variations in concentrations of metals and the metalloid and show spatial distribution for each sampling trip (see Section 3.1.6.2, page 187 and Figure 28). Although the lead concentrations are lower for indoor air PM₁₀ compared with outdoor air PM₁₀, the Mann-Whitney U test indicates that the total concentrations for arsenic, cadmium, cobalt, lead, and zinc are not statistically different between indoor air PM₁₀ and outdoor samples. The correlation of different sample sets from the city's residential area and the metals and metalloid in garden soils and carpet dust were tested using Spearman's Rank Test (Section 3.1.7 [page 194] and Section 3.1.8 [page 194]). The results showed several correlated data pairs that support the findings of other statistical tests, but are not definitive as standalone tests.

The results of lead isotope ratio measurements for outcrop samples from different geological units, mine site dust samples and samples from the city's residential area are summarised in Section 3.2 (page 202). The lead isotope ratios for mine site samples indicate different features for copper- and lead-associated specific categories of samples (Table 56 [page 206], Table 57 [page 207] and Figure 30 [page 213]). Surface tailings material, haul road dust, and thimble samples from the lead smelter area have similar isotope ratios similar to crushed ore materials. Isa chalcopyrite is differentiated from lead ore mined at Mount Isa, and the copper smelter ATC samples show clear mixing with lead from a different source (i.e. the Ernest Henry concentrate being mixed with the Isa chalcopyrite smelted in the Mount Isa copper smelter makes no apparent contribution to the lead being measured in the city area.

Garden soil samples are different from mine site samples, showing a wide range of ratios (Table 59 [Page 208] and Figure 30 [page 213]). Soil PM_{10} and carpet dust samples also fall on the same mixing line, but tend to fall closer to the cluster of points for the mine site and natural mineralisation samples (Figure 30). There is lead from some other origin as well as the Urquhart Shale present in the garden soils, soil PM_{10} fraction, city air PM_{10} fraction and carpet dust samples.

The isotope ratios of fallout dust ('FMT') from the city residential area are similar to roof gutter dust, Urquhart Shale natural mineralisation, haul road dust, and tailings dam materials (Figure 30). The isotope ratios of fallout dust ('FMM') from the mine site are different from those of other mine site samples and show evidence of mixing, similar to that shown by some of the residential area soil samples (Figure 30). The comparison between mine site fallout dust ('FMM') and city fallout dust ('FMT') show a statistically significant difference (Table 54, Table 60 and Figure 30). The lead isotopic ratios of FMT displayed a mean of 35.8515 ± 0.01346 for 208 Pb/ 204 Pb and 16.1492 ± 0.01441 for 206 Pb/ 204 Pb (Figure 32). However, the ratios of FMM, show a wide range, from 35.9408 to 36.2942 for 208 Pb/ 204 Pb and from 16.2094 to 16.4877 for 206 Pb/ 204 Pb. However, it

is not clear what the exact source of lead is in FMT excepting that it has an Urquhart Shale lead contribution with some mixing in of other geological sequences.

Lead composition and chemical forms were given by the XANES LCF process and the uncertainties of the process are detailed in Section 2.4.3.1 (page 138). The LCF results of spiked pure lead compounds show the relative errors for lead compounds are lower when the portion of the species is high in the samples (Figure 34, page220). Differences in the normalised XANES scans are difficult to distinguish by visual comparison. Therefore, LCF results are given in Section 3.3.6 (page 240) to quantify the goodness-of-fit of various lead species in the samples. Lead species in natural mineralisation outcrop samples are mainly lead-goethite + plumbogummite (Section 2.4.3.1, page 138). There are some differences in lead species in samples from the mine site and the copper, lead, and zinc mineral processing sites. Galena and anglesite were common in most lead smelter area sites⁴⁶. Haul road dusts from the mine site are primarily characterised by large portions of lead-goethite and small percentages of lead chloride and lead sulfate (Table 97, page 262). The LCF results from the tailings material samples are very similar to the haul road dust samples (Table 73 [page 248] and Table 74 [page 249]). Lead-goethite is the primary lead species in all the samples from the city's residential areas on which the XANES scans were run, with galena sometimes also occurring in low proportions in these samples. No galena or lead sulfide was detected in soil samples.

The composition of HVAP from XANES fitting (Table 76)⁴⁷ is 27% lead-goethite and 72% molydophyllite and therefore similar to soil, including for % BAc (Table 114). The XANES analysis of PM₁₀ air particulates exiting from the Mount Isa lead smelter stack contained negligible lead sulfide whereas near surface samples of dust and fallout from the lead smelter/ sinter plant area collected at the surface or at 2-3m above ground usually contained lead sulfide. Roof gutter dust did not contain lead sulfide. In addition, PM₁₀ samples obtained during a period in 2010 when the lead smelter was shut down for maintenance showed no apparent difference in lead concentrations from those taken in 2009 and 2011. This implies a minimal contribution from the lead smelter operations to these samples to the 2009 and 2011 samples, when the smelter was operating together with re-entrainment of deposited smelter dust. Further, PM10 particles obtained in the lead smelter and from the lead slag stockpile showed smoother features than those from the city samples or the mining samples.

⁴⁶Thimble Sample ATP8 identified as being collected from the flowing gas stream within the lead smelter that would be discharged via the stack exit point at the top of the smelter and showed only 18% lead sulfide which is negligible.

⁴⁷ Table 76 also indicates that HVA1 (Station Street-MIM TEOM) and HVA2 (K-Oval) show the presence of lead sulfide and are closer to the lead smelter facility. HVAP slurry composite used as a sample to dose rats for bioavailability measurement did not contain lead sulfide.

Thus, lead isotope ratios can show origin of lead regardless of chemical or mineral form while XANES analysis gives the chemical form. XANES analysis may show differences even when lead isotope ratios are shown to be the same.

Estimations of bioaccessibility were conducted for different samples sets from natural outcrops, natural mineralisation, the mine site and the city's residential area, as summarised in Section 3.4 (page 255). There are some variations in bioaccessibility for the mine site samples. The median bioaccessibility for samples from the mine site is higher than those from the city's residential area, with a median of 29 per cent for mine site dust, compared with 21 per cent for city soil and dust samples (Table 101, page 265 and Table 114, page 272). The mean bioaccessibility (BAc) of lead in natural mineralisation in Mount Isa city was 2% compared with 24% in garden soil samples tested in this study and about an order of magnitude lower than the often-adopted default value of 100%. The actual individual % BAc value obtained from each house specific dust sampling program was used in the IEUBK modelling of blood lead level.

The calculated absolute bioavailabilities from a rat uptake study for 10 samples from the mine site and the city's residential area are given in Section 3.5 (page 272) and show similar values for blood and urine. Generally, lead bioavailabilities from a range of mine site and city samples are all very low, with all samples < 5 per cent, except for the HVAP PM_{10} urinary and blood curves, which were 6.1 per cent and 6.2 per cent, respectively. The very low values of both fits are probably associated with large errors and the low magnitude of values found for other lead bioavailability measurements of lead mine wastes. The linear fitting results and 95 per cent confidence level bands were calculated and the upper limit of the 95 per cent confidence interval was used to give a more conservative slope of 0.17. This is more conservative than using the slope given by the best fitted line.

XRD analysis details in Section 3.6 (page 278) indicate that quartz is the major mineral in the samples from the city residential areas. Goethite is in all four city samples, including three composite samples, determined from XRD scan fitting. SEM-EDS information (Section 3.7, page 280) for samples from the city residential area indicates spatial differences across the city. More metal-containing particulates were captured from sites closer to the mine site. The lead particles found in filters from a residential house show clear isometric crystal structures of galena, but most of the lead-containing particles are irregular. Particle-size distributions from the lead ore open pit in the mine site were irregular (Figure 60c, page 293). The surfaces of samples from the blast furnace (Figure 60d–f) have smooth and aggregated features, in contrast with the sample from the mining process. Mine site dust materials are finer than dust and soil collected in the city's residential area (Figure 62, page 296). The particles in the < 250 µm fraction represent over 90 per cent of all particles in < 2 mm fraction of the samples (Section 3.7, page 280).

Using the US EPA's IEUBK model, a site-specific parameter was set to predict the blood lead concentrations for children living in a statistically representative set of houses in Mount Isa City's residential area. These results are summarised in Section 3.9 (page 301). Whereas one house exceeded NHMRC recommended level of < 10 µg/dL, with a 52%, probability of exceeding 10 µg/dL, 16 houses might exceed the NHMRC recommended maximum blood lead level of < 5 µg/dL. When the input data for soil and dust are based on bioavailability, rather than bioaccessibility, the IEUBK model gave lower predicted blood lead levels, with a maximum geometric mean of 2.8 µg/dL for a 10 µg/dL level and 3.4 µg/dL at 5 µg/dL. Using the bioavailability data, which is regarded as the gold-standard approach of lead uptake, no predicted blood lead levels exceeded the Australian NHMRC recommended blood lead level of either 5 or 10 µg/dL⁴⁸. The data obtained from bioaccessibility and bioavailability for 10 samples confirm that bioaccessibility gives a conservative estimate of bioavailability for lead in environmental samples.

 $^{^{48}}$ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

4 DISCUSSION

The results of various analyses are outlined in Chapter 3 (page 160). Chapter 4 interprets the results and integrates data from different analyses following the human health risk assessment approach (Figure 1, page 61). The air–dust pathway of lead from mining and mineral processing activities into the city's residential area was characterised using data from the integrated methods. The potential impact of the lead air–dust pathway on the Mount Isa residential area was assessed using the risk assessment approach. The aims and objectives described in Section 1.1 (page 59) and Section 1.2 (page 61) are achieved in this chapter.

4.1 Issue identification

The issue identification step of the health risk assessment framework involves investigating and identifying potential sources of environmental hazards (enHealth, 2012). People living and working in Mount Isa City, particularly young children, can potentially be exposed to hazardous materials, where lead and other heavy metals and metalloids may be released from outcrops of natural mineralisation, as well as from mining and mineral processing activities. A good understanding of the characteristics of the pathway of lead-containing materials and their potential health risks is required to help avoid elevated blood lead levels and subsequent health effects in the population of Mount Isa (Chapter 1, page 59). The issue identification step (Figure 1, page 61) of this study was to identify the potential sources of lead to provide a basis to undertake the (next) hazard assessment step. The issues may be mining, non-mining, historical mining, historical residues from lead paint, leaded petrol, aviation gasoline, vehicle oil residues. lead-acid batteries. lead extrusion chemicals. lead-soldered food and drink cans, lead-based pesticides, and other sources such as lead sinkers. There may also be an issue from social perceptions regarding effects from lead-containing materials.

4.2 Hazard assessment

Hazard assessment (Figure 1, page 61) involves obtaining and interpreting sound data from various techniques and measurements to evaluate the environmental context and determine what type of adverse health effects might be caused. Potential health risks associated with exposure to compounds containing various heavy metals and arsenic, with a particular focus on lead, were estimated by measuring their lead bioaccessibilities, which gives a prediction of their bioavailabilities. The chemical and physical properties of samples help to explain their bioaccessibilities and bioavailabilities and potential risks to be explained. Based on the results of Chapter 3 (page 160), the hazard assessment data are interpreted and discussed in the following sections.
4.2.1 Assessment of physico-chemical features

Hazard assessment is simplified where guidelines exist and metal and metalloid concentrations in environmental media can be compared directly with the guidelines.

4.2.1.1 *Comparison with guidelines*

4.2.1.1.1 Soil

Elemental concentrations in all garden soil samples were summarised and compared against the NEPM Level A criteria (NEPC, 1999d⁴⁹) given in Table 21 (page 173). The HIL Level A criteria are set for soil within residential gardens or soils that are accessible by the public. For example, the HIL Level A criterion also includes children's day-care centres, kindergartens, pre-schools, and primary schools. Of the 75 garden soil samples collected from 67 houses in the city's residential area, 18 houses exceeded the HIL Level A for metals and the metalloid to various levels as shown in Table 130. Therefore, these samples indicate potential health risks. Within this sub-set of 17 samples, exceedances also occurred for cadmium in one sample, copper in seven samples, and manganese in one sample. A summary of the houses where metal and metalloid total concentrations exceed HIL Level A values is shown in

⁴⁹ NEPC(2013) National Environment Protection (Assessment of site contamination) Measure guideline on investigation levels for soil and groundwater. Amendment of the NEPM 1999. National Environmental Protection Council. Canberra, Australia.

Table 131. The bioaccessibility-adjusted concentrations for cadmium, copper, lead, and manganese in the garden soil were also compared against the HIL Level A criteria. All samples were below the respective criteria. Because the HIL Level A criteria does not include any specific adjustment for the bioavailability of garden soils (enHealth, 2001, NEPC, 1999d), the bioaccessibility-adjusted concentrations more accurately provide a site-specific risk assessment for soil in Mount Isa City.

Table 130 Summary statistics for total concentrations (mg/kg) in garden soil (< 250 μm fraction) exceeding Health Investigation Level A (HIL level A) for cadmium (n = 1), copper (n = 7), lead (n = 18), and manganese (n = 1)

Element	n	Mean (SD)	Minimum	Median	75th percentile	Maximum	HIL Level A
Arsenic	18	22 (11)	6	18	27	50	100
Cadmium	18	9 (12)	3	5	7	51	20
Cobalt	18	17 (4)	11	15	19	27	100
Copper	18	993 (610)	108	723	1318	2680	1000
Lead	18	536 (222)	302	429	708	1070	300
Manganese	18	467 (328)	296	384	444	1747	1500
Nickel	18	19 (6)	12	18	21	36	600
Zinc	18	1030 (442)	245	1090	1449	1605	7000

Note: SD: Standard deviation; n: Number of samples

Table 131 Bioaccessibility-adjusted concentrations of copper, lead, and manganese in garden soil (< 250 µm fraction) for houses exceeding Health Investigation Level A (HIL Level A) for cadmium, copper, lead, and manganese

House ID	Fraction	Cadmium	Copper ⁵⁰	Lead	Manganese ⁵¹
	HIL Level A (mg/kg)	20	1000	300	1500
	BAc (%)			22	
3	BAc adjusted (mg/kg)			72	
	Total (mg/kg)			331	
	BAc (%)		14	22	
10	BAc adjusted (mg/kg)		249	71	
	Total (mg/kg)		1829	328	
	BAc (%)		20	29	
12	BAc adjusted (mg/kg)		273	125	
	Total (mg/kg)		1380	427	
	BAc (%)			20	
15	BAc adjusted (mg/kg)			120	
	Total (mg/kg)			597	
	BAc (%)			20	16
23	BAc adjusted (mg/kg)			105	288
	Total (mg/kg)			514	1747
	BAc%		4	19	
37	BAc adjusted (mg/kg)		49	60	
	Total (mg/kg)		1320	315	
	BAc%			18	
38	BAc adjusted (mg/kg)			76	
	Total (mg/kg)			430	
	BAc%			12	
39	BAc adjusted (mg/kg)			48	
	Total (mg/kg)			409	
	BAc%		21	31	
41	BAc adjusted (mg/kg)		562	228	
	Total (mg/kg)		2680	745	
	BAc%			26	
51	BAc adjusted (mg/kg)			135	
	Total (mg/kg)			522	
	BAc%			20	
53	BAc adjusted (mg/kg)			157	

 $^{^{50}\}mathrm{The}$ revised (NEPC, 2013) HIL A for copper 7000 mg/kg.

 $^{^{51}\}mathrm{The}$ revised (NEPC, 2013) HIL A for manganese 3000 mg/kg.

House ID	Fraction	Cadmium	Copper ⁵⁰	Lead	Manganese ⁵¹
	HIL Level A (mg/kg)	20	1000	300	1500
	Total (mg/kg)			778	
	BAc%			23	
55	BAc adjusted (mg/kg)			94	
	Total (mg/kg)			416	
	BAc%			38	
58	BAc adjusted (mg/kg)			158	
	Total (mg/kg)			418	
	BAc%	35	26	34	
60	BAc adjusted (mg/kg)	18	331	103	
	Total (mg/kg)	51	1280	302	
	BAc%			22	
61A	BAc adjusted (mg/kg)			182	
	Total (mg/kg)			840	
	BAc%			19	
61B	BAc adjusted (mg/kg)			206	
	Total (mg/kg)			1070	
	BAc%		13	51	
68	BAc adjusted (mg/kg)		200	200	
	Total (mg/kg)		1500	390	
	BAc%		23	36	
74	BAc adjusted (mg/kg)		300	292	
	Total (mg/kg)		1310	815	

Note: 61A and	161B are from	the same house
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4.2.1.1.2 US EPA clearance standards

Dust samples collected from Mount Isa City's residential area were compared with the US EPA's clearance standard (U.S. EPA, 2001) for houses (Table 132). Dust from floor, window sill, and window trough samples were collected (Section 2.3.6.2, page 129) and each category of sample shows various exceedance levels for lead. Sixteen out of 67 houses show exceedances for lead in floor wipes and window-sill wipes. Fifty-eight houses show exceedances for lead in window-trough wipes. This high level of exceedance may be explained by that fact the residents clean window troughs less frequently than floors and window sills. Therefore, window troughs capture and store historical particles, as well as present ones and may also include lead-based paint residues.

	Floor wipe	Window- sill wipe	Window- trough wipe
US EPA clearance standard	431	2691	4306
Number of exceeding houses	16	16	58
Houses exceeding guideline (67 houses in total)	24%	24%	87%
Number of exceeding samples	21	18	110
Samples exceeding guideline	12%	14%	82%
Minimum	433	3048	4370
25th percentile	523	3779	15,716
Median	1089	4541	30,197
75th percentile	1889	12,417	69,806
Maximum	23,333	81,833	251,282

Table 132 Comparison of Mount Isa city lead level (μ g/m²) in house dust samples with US EPA clearance standards

4.2.1.1.3 Air particulates

Lead levels in outdoor air PM_{10} samples collected from the city's residential area are summarised in Table 38 (page 188), Table 39 (page 188), Table 40 (page 189), and Figure 27 (page 191). The maximum lead level measured in those samples was 0.25 µg/m³. This level is lower than the NEPC guideline (oneyear mean lead level of 0.5 µg/m³) of lead in air-PM¹⁰ (NEPC, 2002, EPP, 2008) (Section 1.7.2, page 91).

High volume air (HVA) samples (Figure 13b [page 126] and Figure 17b [page 125]) were collected from five routine monitoring stations in Mount Isa City (Section 2.3.6.1, page 126) over 24-h periods on a six-day cycle to collect air particulates. The monitoring data for lead concentrations from total suspended particulates ('TSP') at those five routine HVA monitoring sites (Figure 13b) are summarised in Table 124 (page 302) and have a median value of 0.07 μ g/m³ during 2005–2010, not exceeding the EPP (2008) guideline.

The air PM_{10} samples collected using SKC cyclones in this study (Figure 16, page 128) are indications of the atmospheric levels at the mine site and the community residential area and the lead levels cannot be compared with the EPP guideline in Table 5 (page 92), because this guideline specifies TSP. These outdoor PM_{10} samples were collected for the sole purpose of comparison with indoor PM_{10} samples.

4.2.1.2 Lead sources via the air–dust pathway

4.2.1.2.1 Potential emission source

The lead isotope technique of a two-component mixture is demonstrated in Section 2.2.2 (page 98), following the approach by Faure (1986). Applying the mixture formula of lead isotope ratios (e.g.²⁰⁸Pb/²⁰⁴Pb) and 1/Pb (ppm⁻¹) to geological samples (Equation 1, page 99) enabled a straight line to be fitted to the data points (Figure 75).) Lead ore, haul road dust, and tailings dam samples clearly show no mixing features because the lead isotope ratio is constant across samples. There was evidence of mixing of lead in the copper smelter dust and mine site fallout samples (see Section 3.2 [page 202] and, specifically, Figure 30 [page 213]). The lead isotope ratios (²⁰⁸Pb/²⁰⁴Pb and others) for roof gutter dust and city fallout dust do not show significant changes with different lead concentrations, with r² < 5 per cent for both groups (Figure 76). Soil PM₁₀ fraction ('PM₁₀S') and carpet dust ('CD') samples are scattered. The r² values for the linear curve fitting are 67 per cent for soils and 55 per cent for carpet dust, indicating that these two groups of samples are likely to follow the two-component mixing system.

The plot of lead isotope ratios against the reciprocals of the lead concentrations for garden soil ('CS') (Figure 76) is very scattered, which is an indication of a mixing of lead from the Urquhart Shale with lead from some other geological background source, with the non-Urquhart Shale component becoming more important as the lead concentration decreases.

The upper plot in Figure 76 also shows a line of zero slope for many of the samples obtained from the mine site. This indicates that the ore is from a single source, without evidence of mixing. The FMM samples are the exception, indicating mixing from the second source as the total lead concentration decreases.



Figure 75 Plot of lead isotope ratios and the reciprocal lead concentrations in samples from the mine site and Mount Isa City

As described in Section 3.2 (page 202), the plots of lead isotope ratios $(^{208}Pb/^{204}Pb \text{ and } ^{206}Pb/^{204}Pb)$ indicate that the isotopic characterisations of city fallout and roof gutter dust are similar to lead ore materials, and that there are differences between carpet dust and soil PM₁₀ fraction compared to garden soil samples (Figure 30, page 213).



Figure 76 Plot of lead isotope ratios and the reciprocal lead concentrations in samples from Mount Isa City



Figure 76 Plot of lead isotope ratios and the reciprocal lead concentrations in samples from Mount Isa City (continued)

Principal component analysis (Section 2.6, page 157) was conducted on the lead isotope ratio data for samples (Figure 77). The principal component analysis eigenvalue scree plot of lead isotope ratios (²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁷Pb) for all samples from the mine site and city residential area showed that the first component 'PC1' comprised 92% of the total variance and dominated the isotope ratio data input for all the samples. PC1 was the only significant component of all samples and confirms the similarity between lead ore materials and natural mineralisation from Urquhart Shale (Figure 77). The second most important component, termed 'PC2', contributed the remaining small per cent of total variance (6.8%).

Based on the features of the lead isotope ratios and their association with total lead concentrations (Figure 30, page 213), it is appropriate to conclude that the lead in the city fallout dust, roof gutter dust, carpet dust, and soil PM_{10} fraction

samples all have the natural mineralisation from Urquhart Shale pattern of lead isotope ratios, indicating a common lead origin.

The presence of lead sulfide in the fallout dust collected in the City of Mount Isa (median value of 33 per cent) indicates that the material is, at least in part, likely to have orginated from lead mining and mineral processing, rather than the smelting, activities at Mount Isa City (Table 79, page 253). Lead sulfide is present in mine site fallout, with a median value of 52 per cent (Table 75, page 249), but was measured in the lead smelter thimble at less than 20 per cent. No known process would concentrate lead sulfide to the higher values in the city fallout samples. The association of fallout with dust from the mine site to the city's residential area was also inferred by the similarity of mine site lead isotopes from the high contribution of PC1 in the principal component analysis plot (Figure 77).



Score plot of principle components for lead isotope

Figure 77 Score plot of principal components for lead isotope ratios for natural mineralisation (Urquhart Shale) outcrops (NMU), lead ore materials from mine site (PO), fallout dust from city (FMT), roof gutter dust (RGD), carpet dust (CD), and garden soil < 250 μ m fraction (CS)

There has been no national-level blood lead survey conducted in Australia since 1995 (Donovan, 1996). Over the decade 1990–2000, the 206 Pb/ 204 Pb ratio in air particulates and blood collected from Australian adults and children increased (indicating a smaller contribution of leaded petrol to blood lead concentration after unleaded petrol was introduced), associated with decreasing blood lead level for the same group of people (4.7 to 2.3 µg/dL) in the urban environments (Gulson, 2008, Gulson et al., 2006). Previous studies with lead isotope ratios also

indicated significant decreases in lead contribution from leaded petrol in environmental samples (Zheng, 2010, Chiaradia et al., 1997b, Gulson et al., 2006). In urban situations, leaded petrol and the weathering of lead paints were identified as significant contributors to people's blood lead in earlier studies and for this reason unleaded petrol and paint were introduced to the market (Rabinowitz, 1987, Delves and Campbell, 1993, Gulson et al., 1995a). Historical lead paint makes the lead source allocation rather complicated, especially when the lead isotope ratios for different batches of paint used in the community varied over the time (Gulson et al., 1995a, Gulson, 2012). The relatively low contribution from lead paint measured in Australian communities near lead smelters, however, indicated that lead operations activities have been more significant blood lead source (Gulson et al., 1994, Chiaradia et al., 1997a, Gulson et al., 2009), compared with leaded petrol or lead paint.

Based on details given by previous studies (Gulson et al., 1994, Chiaradia et al., 1997a, Gulson et al., 2009), this study focused on the lead source from the lead mining and mineral processing associated activities and the geological background and applied these two lead isotope ratios into the two-component mixing model (Equation 1). Paint and petrol lead were not considered in this study (Table 133). Though paint and petrol show some differences in Pb isotope ratios from each other, they are both different from Mount Isa lead (SS26; Table 52).

Sample	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	Sourc e
Paint 1, wall	2.1994	0.9366	16.54	15.49	*
Paint 2, wall	2.1654	0.9140	16.94	15.49	*
Paint, front house	2.2102	0.9453	16.35	15.39	*
Paint, outer shed	2.2196	0.9557	16.10	15.47	*
Petrol August 1996	2.1769	0.9243	16.767	15.497	#
Petrol October 1996	2.1764	0.9232	16.782	15.492	#
Lead concentrator dust SS26 Mean±2σ	2.2029± 3.54E-05	0.9508± 7.39E-06	16.2660± 0.0010	15.4659± 0.0010	Table 52

Table 133 Isotopic lead data for samples from paint and petrol in Australia

Note:* Gulson et al., 2004; # Gulson et al., 1997a

4.2.1.2.2 Source of lead in carpet dust

Previous studies showed the role of indoor dust as an important lead exposure pathway (Paustenbach et al., 1997, Layton and Beamer, 2009, Thatcher and Layton, 1995). It is therefore important to understand the sources of lead in carpet dust in Mount Isa.

The HIL Level A for lead in soils (only) from a residential setting is 300 mg/kg (NEPC, 1999d⁵²). The spatial distributions of lead concentrations in garden soil and carpet dust at Mount Isa City is displayed in Figure 78. Most of soils that exceeded the HIL Level A for lead are located in, or near the, Urguhart Shale sequence of natural mineralisation (Figure 78), which is enriched with lead mineralisation. While lead concentrations in indoor dust indicate different spatial patterns from the soils (Figure 78), both data types show highest concentrations on the west side of the city. In addition to the high lead concentration in the dust from the western part of Mount Isa City (at or near the Urguhart Shale sequence), carpet dust samples from the northern part of the city also have high concentrations and quantities of lead compared with the samples from the southeast of the city. There could be three reasons for these observations: (i) the annual prevailing wind direction is much more frequent from SE than other directions; (ii) the houses in the SE corner of the city are newer than the remaining part of the city and don't have legacy dust build-up; and (iii) there are geological outcrops in the north part of the city that are accessible via backyard soil to those members of the community who live there.

⁵²The revised (NEPC, 2013) HIL A for lead 300 mg/kg.



Figure 78 Spatial distribution of lead (mg/kg) in garden soil < 250 µm fraction and carpet dust (CD)

Lead levels in garden soils and carpet dust are the key parameters to consider in the IEUBK model for assessing lead absorption via ingestion for young children undertaking both indoor and outdoor activities (Section 3.9). A previous study reported a strong correlation ($r^2 = 0.90$) between the isotopic composition of lead in human blood and dust samples collected from Broken Hill (Gulson et al., 1995b). The key issue for this study was to identify the possible lead-dispersion pathway associated with carpet dust and its source.



Dust/Soil Ratio for residential houses

Figure 79 Plot of ratios (carpet dust/garden soil) for elements of geogenic and anthropogenic sources

An exploratory tool used to find possible sources contributing to carpet dust in the Mount Isa City residential area was to plot the ratio of carpet dust to soil metal or metalloid concentration, against its cumulative percentage (Zota et al., 2011). If the assumption is that all materials in the carpet dust come from the garden soils at the same house, then the ratios for all the metals and the metalloid should be close to the vertical line at 1. Note that this is a logarithmic scale. However, Figure 79 indicates that the total concentrations of arsenic, cadmium, chromium, cobalt, copper, nickel, lead, and zinc in the carpet dust samples are up to 87 times more enriched than the soil samples, with zinc showing the highest enrichment in dust relative to soil. The patterns for iron and manganese were close to the vertical line at 1, meaning that they are likely to have originated from the garden soils. The ratios for cobalt, chromium, and nickel were lower than other metals and the metalloid. Therefore, different accumulation processes for metals and the metalloid in carpet dust were proposed to explain the differences compared with the soil samples. In other words, carpet dust samples have potential sources that are enriched in arsenic, cadmium, copper, lead, and zinc, and to a lesser extent in cobalt, chromium and nickel.

Spearman's Rank Test was used to compare elemental concentrations in the soil and carpet dust. The results indicate that arsenic, cadmium, copper, and lead in carpet dust are highly correlated (correlation between 0.64 and 0.87), followed by zinc (Section 3.1.8, page 194). The correlation between iron and manganese in the carpet dust was 0.85 (Table 50, page 201). The correlations of iron and manganese with heavy metals and the metalloid in carpet dust were much lower than 0.85 (Table 50).

Principal component analysis (Section 2.6, page 157) was conducted for the particle size range and total metals (including iron and manganese) and the metalloid concentrations for soil and dust materials collected from the city's residential area (Figure 80 and Figure 81). The eigenvalue scree plot of principle components conducted for total concentration and particle size analysis for city dust and soil samples for fallout dust from the city (FMT), roof gutter dust (RGD), carpet dust (CD), and soil < 250 µm fraction (CS), shows that the contributions to total variance were 50 per cent from 'PC1', 13 per cent from 'PC2' and 10 per cent from 'PC3'. Although 'PC1" was the major contributor to the total variance, in this case it was observed that plotting 'PC2' against 'PC3' gave a better visual separation of sample type (Figure 80). In particular, CS was clearly separated from CD. Indoor carpet dust samples clearly had compositional differences for particle size range, total metal and metalloid concentrations from nearly all garden soils and lead isotope data, but carpet dusts were very similar to outdoor deposited dust samples (fallout dust and roof gutter dust).



Figure 80 Score plot of principal component analysis scores of total concentrations and particle size analysis for city dust and soil samples for fallout dust from the city (FMT), roof gutter dust (RGD), carpet dust (CD), and soil < 250 µm fraction (CS)



Figure 81 Eigenvalue scree plot of principle components conducted for total concentrations and particle size analysis for city dust and soil samples for fallout dust from the city (FMT), roof gutter dust (RGD), carpet dust (CD), and soil < 250 μ m fraction (CS)

Mineralogical evaluation (Table 119) and SEM-EDS images of high volume air PM_{10} particles (Figure 58) from the five monitoring sites in Mount Isa City showed that the major matrix materials were quartz and silicates, which is similar to the composition of garden soils. The findings on metals and the metalloid concentration data, mineralogy, and lead isotopic features for carpet dust demonstrated that:

- i. the major contribution of the matrix in carpet dust (i.e. most of the material in the carpet dust) is garden soil or of similar geological origin to the garden soil
- ii. arsenic, cadmium, copper, lead, and zinc in carpet dust are likely to have contributions from sources that are enriched in these heavy metals and arsenic and associated with lower ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios, with features very similar to those of Urquhart Shalederived mine site dust.

4.2.1.2.3 Significance of location

The proximity of the houses sampled to the mining and processing operations was identified as being potentially important. The house wipes collected from three houses were analysed for lead isotope ratios using MC-ICP-MS (Table 134

and 2009 wipes in Figure 13 (page 125) and Section 2.3.6.2 (page 129) to evaluate the potential of lead exposure to children of the houses from mining operations when the sampling sites were located at different parts of Mount Isa. The three sample sets summarised in Table 134were sampled intensively and included measurements like XANES lead composition fitting (Table 82) not undertaken on all of the larger set of 67 houses.

I	D	Sampling site details	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb	House details	
	HW1F1	Hard floor wipe	35.9578	16.2421		
	HW1F2	Hard floor wipe	35.9093	16.1975	North of main city	
House	HW1S1	Interior window sill	35.9255	16.2144	residential area,	
1	HW1T1	Window trough	35.9063	16.1923	of mine site	
	HW1V1	Kids playground platform	35.9006	16.1917		
	HW2F1	Hard floor wipe 1	35.8507	16.1454		
	HW2F2	Hard floor wipe 2	35.9235	16.2086	West of main city	
House	HW2S1	Interior window sill	35.9220	16.2075	residential area,	
2	HW2T1	Window trough	35.8334	16.1258	south east of mine	
	HW2V1	Outdoor table	35.9534	16.2329	site	
	WCS2	Soil	36.0088	16.2823	†	
	HW3F1	New timber floor wipe	35.9951	16.2756	Southeast corner	
House	HW3S1	Interior window sill	35.9154	16.2051	residential area,	
3	HW3T1	Window trough	35.9071	16.1973	about 3.5 km	
	HW3V1	Veranda	36.0213	16.3026	south east of mine site	
	WCS3	Soil	36.7627	16.8572		

Table 134 Summary of wipe samples in city residential houses

House 2 is generally more exposed to the mining activities, compared with the other two houses, based on its geographical location and the metal and metalloid compositions in its samples (Figure 82). The lead isotope ratios for dust samples captured by the window-sill wipes (HWS in Figure 82) from all three houses are clustered in a very narrow range. However, the dust samples from the window-trough in House 2 indicate that the lead isotopic feature is identical to that of the mine site dust. Floor dust samples from House 2 also showed lead isotope ratios that are similar to the mine site dust range, but are different to House 1 and House 3. These patterns indicate possible lead dispersion from mine site to the city residential area in the case of House 2. However, there was not as clear an association with the other two houses. It is also noted that the time of dust collection in the carpet within the timeframe of the house since construction is not known.

The lead isotopic ratios for samples from House 1 and House 3 are considered to be less associated with mining activities, due to their geographical location within



Note: The ellipse covers the range of lead isotope for wipe samples collected from three houses (HW1: House 1; HW2: House 2; HW3: House 3; HWF: floor wipes; HWS: window-sill wipes: HWT: window-trough wipes; HWV: wipes from veranda or other sites). Note that the lower two graphs plot the house data on a slightly expanded axis to highlight some of the differences.

Figure 82 Lead isotope ratios for bulk dust collected from three residential houses.

a different geological (non-mineralised) sequence and the overall annual wind direction. No lead isotope data are available for soil from House 1, but the lead isotopic ratios for soil from a nearby house (160 m away) were 36.7694 for ²⁰⁸Pb/²⁰⁴Pb and 16.9783 for ²⁰⁶Pb/²⁰⁴Pb. The lead isotopic ratios for soil from House 3 are 36.7626 for ²⁰⁸Pb/²⁰⁴Pb and 16.8572 for ²⁰⁶Pb/²⁰⁴Pb (Table 134). Compared with the similar lead isotopic ratios for wipe dust samples and Urquhart Shale type lead, these two soil samples indicate that lead in soils in House 1 and House 3 are not the dominant source for dust materials collected from inside and outside of the houses 1 and House 3 are from a mixture of sources.

Some differences in lead isotope features for the samples from houses located in different parts of the city are also confirmed by the characterisation of the lead species by the XANES technique (Table 82 [page 253] and Figure 83). The lead isotope ratios of haul road dust (HR), surface tailings (TD), and natural mineralisation (Urguhart Shale) outcrops (NMU) are identical to other mine site samples (ATP, ATC, FMM) (Figure 30, page 213). However, there is no lead sulfide present in HR, TD, and NMU samples (Table 68 [page 240], Table 73 [page 248], and Table 74 [page 249]) as shown in Section 3.3.6. Therefore, lead sulfide found in the samples collected from the city's residential area (Table 134) is more likely to have originated from the lead mine and processing plants (Table 69 [page 244], Table 72 [page 248], and Table 75 [page 249]) rather than from natural mineralisation, surface tailings, or haul road dust. With these data, it is easier to understand the potential lead exposure pathway from the mining operation over a short period of time for House 1, House 2, and House 3. Samples from House 2 have higher portions of lead sulfide (19-45 per cent) in the floor wipe than those in House 1 and House 3 (Figure 82), indicating that House 2 might be more exposed to lead dispersion or vector transport from the lead mine, lead-zinc concentrator or the concentrate handling processes in the lead smelter.

This finding further highlights the significance of house location for potential transfer of lead-bearing materials from mining and mineral processing activities in Mount Isa. Another finding from this kind of comparison is the natural alteration by chemical reaction of lead species from the original mineral form of galena (PbS) to secondary minerals like lead-goethite or magnetoplumbite, which is chemically similar to lead-goethite, after deposition in the community over multiple years. The comparison of lead species from XANES fittings (Table 82) in House 2 trough wipe (90% historical accumulation of lead-goethite-) with veranda wipe (61% lead sulfide-recent deposition) suggests that oxidation of lead sulfide directly exposed to sunlight at high ambient temperature may occur (Polyanskiy, 1986). Heating of lead sulfide in the presence of air gives decomposition to give lead monoxide and lead sulfate (Polyanskiy, 1986) that may simply combine with readily-available iron in fallout dust in the presence of rainwater to give the commonly-found form of lead-goethite. However, the minimum temperature for oxidation of lead sulfide is not stated excepting that lead sulfate forms at low temperature in preference to lead oxide and that the minimum temperature is reported to be less than the lowest temperature reported

of 450 °C (Merrick, 1957). Another study of the reaction of lead sulfide with oxygen noted that the reaction proceeded at room temperature but the actual reaction rates were measured only above 100⁰C (Hillenbrand, 1964). In addition, iron sulfide minerals can also be involved in recombination reactions by providing a source of iron (Steger and Desjardins, 1980). Any lead sulfide in fallout that becomes roof gutter dust in Mount Isa City will be exposed to high ambient temperatures above 50°C, taking into account radiated heat from metal roofs and the metallic roof gutters exposure to direct sun. Therefore, in situ oxidation to lead sulfate and reaction with iron oxide, including in the presence of rain water, to give lead–goethite may be plausible if the loss of sulfur can be demonstrated⁵³. Moreover, aerobic chemolithotrophic sulfide oxidation rates are demonstrated to be three or more orders of magnitude higher than abiotic rates at room temperature (Luther III et al., 2011), suggesting that bacteria may also play a role in the conversion of lead sulfide to lead-goethite in roof gutter dust at Mount Isa. This further highlights that the actual time of such reactions occurring is not known.





Figure 83 XANES LCF-fitted results for house wipe samples

⁵³ Experimental worked is needed to confirm the mechanism for loss of sulfur, including the role of bacteria.

4.2.1.2.4 Dust from the lead smelter area

A comparison of arsenic, cadmium, copper, iron, lead, and zinc concentration data for outdoor air PM_{10} samples from three sampling episodes (November 2009, November–December 2010, and May–June 2011) in the city's residential area was undertaken using the Mann-Whitney U Test (Table 41, page 192). Comparison of the p values indicate that the outdoor air PM_{10} samples collected in 2009 and 2011 are not statistically different in terms of metal and metalloid concentrations. In particular, there is no statistically significant difference between total concentrations of copper, lead, and zinc for all three sampling periods (Table 41, page 192).

The lead smelter area at Mount Isa was undergoing maintenance during the 2010 sampling, and the sinter plant and blast furnace were not operating when the samples were taken (Section 2.3.6.1.1, page 127). The total concentrations of heavy metals and the metalloid in air PM₁₀ from the city residential area indicates no significant differences from other sampling trips (Table 41, page 192and Figure 27 [page 191]). However, the wind rose for each sampling episode indicates different wind speeds and directions (Figure 15, page 127).). This means that the dusts dispersed from the lead sinter plant and blast furnace when not operational are not the major lead source for the air particulates sampled from city residential area. This also implies that re-entrainment of surface dust may be the source of dispersed particles. The morphology of lead-containing particles captured during PM₁₀ sampling confirm that lead-containing particulates from the sinter plant and blast furnace site have smooth surfaces (Figure 60, page 293), which is different from the particles from the city's residential area such as

soil, carpet dust, and air particulates (Figure 58 [page 284] and









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Figure 59 [page 291]), as demonstrated in Section 3.7 (page 280). This finding does not rule out the contribution of lead particles re-entrained from dusts on the surface of the mine site, including tailings, roads, structures and stockpiles, or elsewhere (Figure 60).

4.2.1.2.5 Lead source allocation for city dust material

To examine the contribution of major lead dispersion sources to the city's residential area, a fundamental step was to understand the key lead source materials, of which the mine site and garden soils are potentially dominant, with the 1990s replacement of leaded petrol and lead-based paint (Australian Government, 2009, Australian Government, 2012). In particular, the contribution of lead from the mining and mineral processing activities to lead found in garden soils and other sources in the residential area of the study site needed to be better understood.

The outcrop samples ('BGR') were collected from different geological units across Mount Isa City (Section 2.3.6.2.10, page 134). The lead isotope results for

the outcrop samples were distributed over a wide range compared with samples from the mine site and city's residential area (Figure 30 [page 213] and Figure 84).

The lead isotopic characteristics of bedrocks from different geological units indicate that each unit had its own unique lead isotope signature. Application of the Kruskal-Wallis ANOVA test on the bedrocks showed that they were statistically different (p = 0.30 in Table 135). Soils within the relevant geological unit (CM, MS, BS, NBS, and US in Table 135) had some variations in lead isotope ratios and sometimes the lead isotope ratios of soils from neighbouring geological units overlapped, e.g. MS and BS in Table 135. The lead isotopic signature, however, indicated that the bedrocks and relevant soils collected from one geological unit were statistically different from the other units (p = 0.05 in Table 135). In principle, the observed difference in behaviour of lead isotopic ratios in soil-bedrock pairs can be explained by the demonstration that soils followed а two-component mixing feature (Figure 75[page 331] and Section 4.2.1.2 [page 330]) and were likely to contain lead mixed with the relevant bedrock and other sources, including soil brought to Mount Isa for gardens, at either lower or higher lead isotope ratios (²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb) compared with the relevant bedrock. For example, soils from the US (Urguhart) unit were mixed with other lead sources that had higher lead isotope ratios (²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb). The resulting lead isotope ratios for soils from the US unit, from which lead ore was mined, indicated relatively higher ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios than the underlying bedrock from US (US-B) in Table 135. These observed differences for lead isotope ratios between surface soils and outcrops may arise from the homogenising effect of biological activities (Reimann et al., 2008). However, the organic matter concentration is very low in Mount Isa soils (You, 2012, Noller et al., 2012) and is less likely to explain why lead is retained in the soil, most likely through retention as lead-goethite. The data shown in Figure 84 suggest that, apart from the Urquhart Shale, the Cromwell sequence could be the other member of the two-component mixing found in Mount Isa soils, and it has deposited soil across Mount Isa through flooding of its catchment drainage flows. The other bedrock sequences appear to be less important as they do not fall on the two-component mixing line.

Table 135 Kruskal-Wallis ANOVA by Ranks for lead isotope ratio (²⁰⁶ Pb/ ²⁰⁴ Pb) in
bedrocks and relevant soils from Mount Isa

Sample	Valid N	Sum of Ranks	Mean Rank	Sample	Valid N	Sum of Ranks	Mean Rank	
Bedrocks (p = 0.30)				Bedrocks and relevant soils (p = 0.05)				
CM-B	1	6	6	CM	2	65	32.5	
MS-B	1	2	2	MS	10	198	2	
BS-B	1	5	5	BS	7	112	16	
NBS-B	2	7	3	NBS	9	141	15.6	
US-B	1	1	1	US	5	45	9	

Note: CM: Cromwell member of ECV soil, MS: Moondarra siltstone soil, BS: Breakaway shale soil, NBS: Native bee siltstone soil, US: Urquhart Shale soil. X-B in plot (b) means outcrops collected from X unit.



Note: (a) natural outcrops (BGR), lead ore from Urquhart Shale, and garden soils. (b) Comparison of soil and outcrops from the same geological unit from the Cromwell member of ECV soil (CM), Moondarra siltstone soil (MS), Breakaway Shale soil (BS), Native bee siltstone soil (NBS) Urquhart Shale soil (US), -B in plot (b) means outcrops collected from the unit.

Figure 84 Lead isotope ratios for samples from Mount Isa

The delineation of lead source used in this study followed the isotope technique of two-component mixture model described in Section 2.2.2 (page 98). The first component was the Urquhart Shale characteristic lead isotope ratio. There are four possible categories for the other component, as follows:

i. the lead isotope ratio for the Cromwell sequence from the most easterly site — Breakaway Drive, 6 kilometres east of the mine site, as shown in Figure 13 (page 125)

- ii. the lead isotope ratio for the garden soil sample obtained from a property on the Breakaway Estate, 6 km east of the mine site (Figure 13, page 125)
- iii. the mean lead isotope ratios for all soils from the Mount Isa residential area considering the influence of lead isotope ratios in surface soil from the historical mining activities and physical disturbance, it is a conservative approach for estimating the contribution of lead from soil samples
- iv. the lead isotope ratio for the minimum level (Figure 30, page 213) of all garden soils is the end point case for the calculation for houses that are most likely to be located in Urguhart Shale.

The calculation of the contribution from Urquhart Shale-featured lead using the two-component mixture model for each of these scenarios is given by Equation 1 (page 99) and displayed in Figure 85. In Figure 85, 'Cromwell rock' refers to the isotopic ratio measured in samples of backround rock from the Cromwell sequence, 'Upwind site' refers to the isotopic ratio at Breakaway Drive, 'Average site' refers to the mean lead isotope ratio for all soils, and 'Min CS' refers to the minimum isotope ratio measured for the soils.

Comparing the categories of carpet dust ('CD') roof gutter dust ('RGD'), and air PM_{10} ('AH') in the city indicates that over 72 per cent of lead in these samples may come from the Urquhart Shale (Figure 85). The mean lead isotope ratios indicate that roof gutter dust samples are comprised of 74 per cent lead from the Urquhart Shale lead source. This indicated the dominant role of lead released from the Urquhart Shale type of lead and mixing in the relevant soil sequence in the residential area of the study site. This kind of mixing phenomena has been observed in previous studies at other sites (Gulson et al., 2004, Gulson et al., 2009, Soto-Jiménez and Flegal, 2011, Gulson et al., 2012).



Figure 85 Summary of lead source contribution from Urquhart Shale-featured lead based on ²⁰⁸Pb/²⁰⁴Pb ratio for carpet dust (CD), roof gutter dust (RGD), and air PM₁₀ (AH) in Mount Isa City

4.3 Understanding lead bioaccessibility via ingestion

4.3.1 Total and bioaccessible-adjusted lead concentration

The total concentrations of lead in samples from the mine site and city residential area covered a wide range of median values (Figure 86, Figure 22 [page 171], and Figure 23 [page 177]). The bioaccessibility-adjusted concentrations and bioaccessibility of samples from natural outcrops, mine site samples, and Mount Isa City are given in Section 3.4 (page 255).



Note: CS: soil < 250 μ m fraction for carpet dust (CD), fallout dust (FMT), and roof gutter dust (RGD) at Mount Isa City and the mine site overall (average of all mine samples as one set).

Figure 86 Summary of lead (median bioaccessibility-adjusted level, mg/kg) in different matrices from Mount Isa.

4.3.2 Relationship of lead bioaccessibility, lead speciation, and particle size

A key step in this study was to identify which parameters were influencing the bioaccessibility of samples and to better understand the differences in bioaccessibility, to allow bioaccessibility to be used to predict bioavailability, which is adopted as a practical measure by the health risk assessment process (Ng et al., 2010). The conceptual model in Figure 88 summarises the possible relationship between bioaccessible lead concentrations and key parameters, such as lead speciation, particle size distribution, organic matter, pH, the transit time of materials through the gastrointestinal ('GI') tract, and other physiological processes that may affect bioaccessibility. In this section, the relationship between lead bioaccessibility and two variables (lead speciation and the particle size distribution of samples) and the interaction between them in samples from Mount Isa City is examined.



Figure 87 Factors influencing bioavailability and bioaccessibility estimations of lead in environmental samples

Lead may occur as lead minerals or in processed forms, precipitated or absorbed to the surface of other non-lead materials in weathered soil, such as iron-manganese-aluminium oxides, iron sulfates, phosphate minerals, clay minerals, and soil organic matter (Ruby et al., 1999). The complex bonds between lead and host materials result in a variety of bioaccessible lead forms in environmental samples. The general trend of lead bioaccessibility in different matrices (for constant particle size distribution) is demonstrated in Figure 88. The bioaccessibility of lead in phosphate forms tends to have a wide range. Lead sulfide, lead metal (Pb^o), and pyromorphite (Pb₅(PO₄)₃Cl) are the lead species have the lowest bioavailability when other variables are constant for the samples (Ruby et al., 1999). The bioaccessibilities of lead bound to manganese minerals, and free lead ionic species are higher (Figure 88).



Figure 88 Schematic of how different lead species affect lead bioavailability with constant particle size (modified from Ruby et al. (1999)

4.3.2.1 Bioaccessibility and lead speciation

Principal component analysis was conducted with the XANES data analysis set to extract significant information relating to kind of sample from the spectra (Figure 89). The plot of cumulative percentage of total variance for principal components indicates that 'PC1' (49 per cent of the total variance) was significant, followed by 'PC2' (21 per cent). The remaining components are not significant. The first two principal components (PC1 and PC2) explained 70 per cent of the total variance in the XANES spectra dataset.



Figure 89 Cumulative percentage of total variance for principal components of XANES spectra

Based on the information from the principal component analysis on the XANES spectra (70 per cent), a further step was undertaken to extract information from the comparison of lead speciation and other measurements. From the XANES least-squares linear combination fitting (LCF) results for each type of sample from the mine site and the city, fittings of lead species containing over 70 per cent of compounds present (displayed as median percent lead sulfide + lead sulfate and lead–goethite in each class of sample type from Table 68, Table 69, Table 71, Table 72, Table 74, Table 75, Table 77, Table 78, Table 79, Table 80 and Table 81) are resummarised in Figure 90.

As shown in Figure 90, lead in fallout dust from the mine site and smelting facilities is characterised by lead sulfide or lead sulfate, depending on whether the activities being undertaken are associated with either lead or copper. However, haul road dust and surface tailings show totally different lead species features from the smelter area dust. The XANES LCF results for haul road dust and surface tailings indicate a combination of lead-goethite and lead sulfate. Lead-goethite comprised over 40 per cent of lead species for those two types of materials (Figure 90). Samples from the city's residential area show a much higher portion of lead-goethite (50 per cent in fallout dust from the city to 99 per cent in roof gutter dust), but less or less than detectable lead sulfide + lead sulfate (Figure 90). The roof gutter dust composition (Section 2.3.6.2.3 [page 130] and Table 80 [page 253]) appears to show chemical modification of lead sulfide giving lead-goethite by weathering effects and exposure to UV light as discussed in Section 4.2.1.2.3 (page 341). Application of the Kruskal-Wallis ANOVA test on three sample groups indicated statistically significant differences (p = 0.09 in Table 136). The Haul road dust and surface tailings in Figure 90 and Table 136 had the highest bioaccessibilities.

A comparison between lead bioaccessibility and lead speciation was also included (Figure 90). As demonstrated in Section 4.4 (page 362), the median lead bioaccessibility for mine samples is 29 percent, which is slightly higher than in samples from the city's residential area (21 per cent). However, the median bioaccessibility of lead is much higher for haul road dust (42 per cent) and surface tailings (31 per cent) from mine site the (Figure 90). The bioaccessibility of lead for other mine site samples, characterised as lead sulfide + lead sulfate, is lower than that of haul road dust and surface tailings.

A comparison of data for lead species and bioaccessibility between the sample sets in Figure 90 shows that there are two apparent groups. These are: (i) mine site dusts showing lead sulfide with lead sulfate; and (ii) haul road dust and surface tailings from the mine site and residential samples (CS, CD, PM₁₀S, RGD, FMT, Footpath and NMU) showing lead sulfide with lead sulfate and lead–goethite. The dominant parameter that influences lead bioaccessibility is the lead speciation for these two categories. Lead–goethite is less bioaccessible than lead sulfate but more than lead sulfide form (Figure 88). Figure 90 therefore shows that the mine samples are in two separate groups with respect to lead species.



Note: The red line indicates the median level of bioaccessibility for the group of samples. PbS+PbSO₄ refers to a mixture of lead sulfide and lead sulfate unless there is only one present in the linear combination fit (lead–goethite). X-axis labels are: thimbles from the lead smelter area (ATP); thimbles from the copper smelter area (ATC); general mine site source (SS); fallout dust from mine site (FMM); haul dust (HR); surface tailings material (TD); soil < 250 μ m fraction (CS); carpet dust (CD); PM₁₀ fraction from garden soil (PM₁₀S); roof gutter dust (RGD); fallout dust form city (FMT); footpath samples (FP); and natural mineralisation (NMU)

Figure 90 Lead species and bioaccessibility of soil and dust from Mount Isa.

Table 136 Kruskal-Wallis ANOVA by Ranks for lead concentration in samples from Mount Isa (p = 0.09)

Sample type	Valid N	Sum of Ranks	Mean Rank
Mine site dusts (ATP, ATC, SS, FMM)	4	22	5.4
Haul road dust and surface tailings (HR, TD)	2	25	12.5
City (CS, CD, PM10S, RGD, FMT, Footpath, NMU)	7	45	6.4

4.3.2.2 Bioaccessibility and particle size

Principal component analysis was conducted on the median particle size distribution data for all samples to understand the relationships between different sample groups and identify their principal components. The plot of 'PC1' (46 per cent of the total variance) versus 'PC2' (26 per cent) in Figure 91 shows four groups of samples: (i) circled (CS < 2 mm, CS < 250 μ m and CD); (ii) circled (RGD and FMT); (iii) PM₁₀S, FMM, SD, SS and HR; and (iv) TD. When the PCA plot (Figure 91) and the cumulative particle size plot (Figure 62, page 296) are compared visually, TD has a tri-modal distribution curve that includes ultrafine

particles which are finer than found in all other sample groups. Samples from the city's residential area are coarser than mine site samples. This feature agrees with the highest positive PC1 score value of surface tailings, while coarser samples from the city's residential area have negative PC1 score values. Although the particle size range for $PM_{10}S$ samples is close to mine dust samples, these samples were artifically extracted from soil of the < 250 µm fraction. The discussion of particle size analysis in this section does not cover $PM_{10}S$, except as noted.

Particle size is a dominant feature of the sample groups and may be the reason for the observed differences in lead bioaccessibility for garden soil of the < 250 µm size fraction (22%) and soil PM_{10} fraction (28%), which was extracted from garden soils (Figure 90). Samples with a finer particle size have larger surface areas and result from mineral processing or chemical reactions. Comparing (i) haul road dust and surface tailings and (ii) samples from the city's residential area in Figure 90 indicates that the majority of lead composition from XANES-fitting is lead–goethite, but the particle size ranges were different (Figure 62 and Figure 91). It is likely that the major parameter that influences lead bioaccessibility for these two categories is particle size, but the contribution from other variables, such as pH and percentage of organic matter cannot be ruled out. Sediments and surface soils from Mount Isa show low levels of organic matter (< 1.8 per cent of organic carbon in river sediment and < 4 per cent in plant-covered soil) (Noller et al., 2012, You, 2012).



Note: garden soil (CS < 2 mm) garden soil < 250 μ m fraction (CS < 250 μ m); carpet dust (CD); fallout dust from the city (FMT); roof gutter dust (RGD); PM₁₀ fraction from garden soil (PM₁₀S); fallout dust from the mine site (FMM); copper and lead smelter area dusts (SD); general mine site source (SS); haul dust (HR); and surface tailings material (TD)

Figure 91 Plot of principal components for particle size (median level of each group) for soil and dust samples from Mount Isa

4.3.2.3 Overall relationship of variables

Figure 92 shows a three-dimensional summary plot of lead bioaccessibility, lead compound composition from XANES fitting (Section 3.3.6, page 240 and Figure 90, page 358), and particle size distribution of the samples from the mine site ('SS', 'FMM', 'HR', and 'TD') and city's residential area (CD, CS, FMT, RGD, and $PM_{10}S$) shown in Figure 91 (Section 3.8.2, page 295). According to the discussion in Section 4.3.2.1 (page 356) and Section 4.3.2.2 (page 358), three groups of bioaccessibility data were identified:

- i. general source samples (SS) and fallout from the mine site (FMM)
- ii. haul road dust (HR) and surface tailings (TD)
- iii. carpet dust (CD), garden soil < 250 μm (CS), fallout from the city (FMT) and roof gutter dust (RGD).

Samples from group (i) are dust from the mine site, which has lower lead bioaccessibility and the dominant lead species is lead sulfide plus lead sulfate. Samples from (ii) are mine site dust characterised by high lead bioaccessibility
and the dominant lead species is lead–goethite. Group (iii) includes soil and dust samples from the city's residential area. These city samples, except for $PM_{10}S$ fraction, are characterised by low lead bioaccessibility, higher particle size range, and the presence of lead–goethite (Section 2.4.3.1, page 138). $PM_{10}S$ fraction samples, which were mechanically extracted from soil < 250 µm fraction (Section 2.3.6.1.2), have a similar particle size range to mine dust samples. $PM_{10}S$ fraction is not representative of soil samples that occur naturally, but could be used to estimate the potential risk of exposure to lead in finer soil samples via inhalation and in particular ingestion routes.



Note: XANES ratios were calibrated according to the fitted portion (> 70% of total variance explained based on principal component analysis) and the possibility of lead chemical compounds fitted for each group. In this group, positive ratio means lead sulfide + lead sulfate fitting; negative ratio means lead absorbed on goethite fitting. For example, -86% for PM₁₀S group means 86% of lead in PM₁₀S samples existed as lead absorbed on goethite. The categories are: garden soil < 250 μ m fraction (CS); PM₁₀ fraction from garden soil (PM₁₀S); carpet dust (CD); fallout dust from the city (FMT); roof gutter dust (RGD); fallout dust from the mine site (FMM); general mine site source (SS); haul dust (HR); and surface tailings material (TD)

Figure 92 Three-dimension plot of XANES, particle size, and lead bioaccessibility (BAc %)

Thus, the variables (median bioaccessibility, XANES fitting and particle size) in Figure 92 can be grouped into the three categories given in the note and show that there is a relationship between lead bioaccessibility, lead speciation by XANES and particle size. Samples having smaller median particle size with more soluble lead speciation are shown to have a higher median lead bioaccessibility.

4.4 Exposure assessment

Exposure assessment (Figure 1) involves understanding the target substance (lead in this study) and its concentrations and distribution in the exposed populations. Exposure assessment requires understanding the fate of the lead either by direct measurement of biological matrices or by indirect methods, such as using the IEUBK model for predicting children's blood lead levels. Good correlations have been found between measured blood lead test and IEUBK predicted blood lead for children living in different sites, such as in the USA (Hogan et al., 1998), Mexico (Carrizales et al., 2006), and Europe (Glorennec and Declercq, 2007, Tristan et al., 2000), when sufficient data about lead exposure were given. It should also be noted that the IEUBK model is expected to yield more accurate prediction on a population level than for single individuals (Lewandowski, 2009).

In this study, the IEUBK model was used with site-specific data. The results are discussed in the context of previous child blood lead level surveys in Mount Isa City conducted by Queensland Health and compared against the NHMRC blood lead level guideline value of 10 μ g/dL⁵⁴ (NHMRC, 2009). In the following sections, factors associated with understanding IEUBK model's predicted results are discussed.

4.4.1 Lead source allocation

The IEUBK model was used to predict blood lead levels for children 6–84 months old living in 67 houses in Mount Isa City's residential area, as described in Table 128 (page 314),





Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 μ g/dL.

⁵⁴ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Note: The red line indicates the NHMRC (2016) recommended maximum level of 5 µg/dL.

Figure 72 (page 313). The comparison between predicted results and the 10 µg/dL blood lead guideline (NHMRC, 2009) for Australian children indicated that 1 out of 67 houses exceeds 10 µg/dL with a predicted blood Pb of 10.2 µg/dL or for the 5 µg/dL guideline (NHMRC, 2016) for Australian children indicated that 1 out of 67 houses exceeds 5 µg/dL with a predicted blood Pb of 11.2 µg/dL, respectively, when bioaccessibility-adjusted data are used, including the geometric mean of different age groups. When data for bioavailability-adjusted lead concentrations in soil and dust matrices were used as the input to the IEUBK model, the blood lead levels did not exceed 3.5 µg/dL for the 10 µg/dL blood lead guideline (NHMRC, 2016) (Table 129). This occurred in the age group range believed to be the most vulnerable, children aged 12–24 months at the time of testing for both the 5 µg/dL and 10 µg/dL blood lead guidelines, as found in previous epidemiology studies (Lyle et al., 2006).

The potential sources contributing to the blood lead for young children were investigated. As described in Section 3.9, the input sources of lead into the IEUBK model included diet, water, air, soil, and dust. The contributions from these five input sources were assessed by conducting a site-specific risk assessment at Mount Isa City, summarised in Table 137 and Figure 93. The significant contribution of soil and surface dust to the total lead intake stands out, with median contributions of 19 per cent and 51 per cent respectively. Alternatively, lead from water and air (airborne dust) only showed median contributions of 1 per cent respectively. The contribution of diet was significant and comparable to the contribution of soil and dust, with a median level of 22 per cent.

The IEUBK model's predicted geometric mean for blood lead levels was compared with the contributions from allocated lead sources of diet, water, air, soil, and dust in 67 houses (Figure 94). As demonstrated in Figure 93, the contributions from airborne dust and water were insignificant compared to soil, surface dust, and food. The role of diet as a lead source is very significant for the houses with relatively low contributions from soil and dust. The dietary source of lead is less significant when there is heavy dust and soil loading of lead in the house, which normally indicates higher blood lead levels in children.

	Diet (%)	Water (%)	Airborne dust (%)	Soil (%)	Surface dust (%)
n	67	67	67	67	67
Mean	24	1.1	0.9	23	51
SD	11	0.5	0.4	16	17
Minimum	6	0.3	0.2	0.3	21
25th percentile	16	0.7	0.6	10	38
Median	22	1.0	0.8	19	51
75th percentile	30	1.4	1.1	32	62
Maximum	57	2.8	2.1	58	84

Table 137 Summary of lead source allocation into the IEUBK model for 67 houses

Note: Only the sets of values for mean levels add up to 100% in the table because the specific values given for each percentile contribution do not correspond to individual houses



Note: solid line = median, boxes = lower and upper quartiles, and whiskers = maximum and minimum values.

Figure 93 Lead source allocation of the IEUBK model for 67 houses



Predicted blood lead (μg/dL) Lead source allocation (%) Houses Mean BLL ▲ Diet (%) × Water (%) Air (%) • Soil (%) • Dust (%)

A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 $\mu\text{g/dL}$

B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 94 Relationship of the IEUBK model's predicted geometric mean of blood lead (mean BLL) and allocated sources

4.4.2 Importance of ingestion and inhalation

The two major routes of lead absorption by the human body are through the ingestion and inhalation pathways (Figure 8, page 72), whereas dermal absorption is considered to be insignificant (IPCS, 1995). As described in Section 4.4.1 (page 362), the contributions of lead from air sources via inhalation pathways ranges from 0.2–2.1 per cent. In comparison, the sum contribution from dust and soil via ingestion varies from 37–93 per cent, with a median of 74 per cent (note: these values are related to the whole population rather than individual houses). This result highlights the dominant role of the ingestion pathway over inhalation pathway in Mount Isa. Only a few publications have previously described urban scenarios where less than 6 per cent of the lead contribution was from the inhalation route (Davies et al., 1990, Dong and Hu, 2012). The higher contributions previously reported for the inhalation route is likely to be due to an additional contribution from leaded petrol exhaust. This finding in Mount Isa City further highlights the important role of personal hygiene and the home environment, particularly for surface dust in all the residences in Mount Isa Citv. especially for houses where children live. Queensland Health found associations in Mount Isa between children's blood lead and factors, such as owning pets, chewing non-food items, and bare soil in the backyard (Queensland Health, 2008, Queensland Health, 2011).

4.4.3 Relationship of the IEUBK model's predicted blood lead concentrations to garden soil and house dust

A comparison was made of the IEUBK model's predicted blood lead concentrations and garden soil bioaccessibility-adjusted lead concentrations that



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 95 and Table 130). The predicted geometric means for blood lead levels for young children aged 0.5–7 years range from 2.8 μ g/dL to 10.2 μ g/dL. For the most vulnerable age group, 1–2 years, the maximum predicted value was 11.9 μ g/dL. The house with the highest total lead concentration in soil did not have the highest predicted blood lead level did after an adjustment was made for bioaccessibility giving the prediction of bioavailability.

A more accurate demonstration of understanding the prediction of blood lead results is shown in. B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 μ g/dL

Figure 96 for the relationship between the bioaccessibility-adjusted lead concentration in the soil and dust matrices and the predicted blood lead concentrations from the IEUBK model. The IEUBK model predicts that blood lead concentrations for young children in Mount Isa are significantly correlated with bioaccessibility-adjusted lead in carpet dust ($r^2 = 0.8$), while r^2 is only 0.35 for garden soil (B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 96). This finding confirms the significant contribution of lead in carpet dust as described in Table 137 (page 365) and Figure 93 (page 365).

⁵⁵ The revised (NEPC, 2013) HIL A for lead 300 mg/kg.



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 µg/dL



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 μ g/dL

Figure 95 Blood lead level for houses exceeding HIL Level A. The plot is in ascending order of lead level in the soil.



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 $\mu\text{g/dL}$



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 96 Relationship of the IEUBK model's predicted blood lead levels and bioaccessibility-adjusted lead from (a) soil and (b) carpet dust (including hard-floor dust) in Mount Isa City's residential area

4.4.4 Refinement using bioavailability data

Based on the linear regression of bioaccessibility (BAc) and bioavailability (ABA) (Section 3.5, page 3.5), the uptake parameters for soil and dust lead concentrations were adjusted in the IEUBK model. In most circumstances, the more accurate prediction of blood lead results is obtained when the bioavailability-adjusted lead concentration data are used for input values to the IEUBK model (Section 3.9.3, page 315).

In this study, when bioavailability-adjusted soil and dust lead concentrations were used, there was no sampled house in which the blood lead level predicted by the IEUBK model exceeded the NHMRC's recommended level I (Section 3.9.3). Possible reasons to explain the differences between the 2010 blood lead survey (4.8 per cent of children exceeding 10 μ g/dL⁵⁶ in Section 1.5.3, page 75) and the IEUBK blood lead prediction with bioavailability-adjusted approach are:

- a. the same houses were not sampled in both studies, which means that there might have been differences in the environment to which the children were exposed between the Queensland Health study and this lead pathway study
- b. children with high blood lead levels may be exposed to more dust or soil compared to the default ingestion rate of 100 mg/day
- c. the dietary intake of lead by children in Mount Isa might be higher than the assumed FSANZ national diet evaluation (a national average that might be underestimate the dietary intake of a population who live in a mineral rich or smelting area).

Because lead bioavailability values for both dust and soil are lower than the bioaccessibility-adjusted data, diet (60 per cent) becomes the most significant contribution to lead exposure (Figure 98). Figure 98 and Figure 99 show the relationship between bioavailability-adjusted lead concentrations in soil and dust matrices and the accompanying predicted blood lead concentrations from the IEUBK model. It is also clear that the IEUBK model's predicted blood lead concentrations for young children in Mount Isa shows a significant correlation with bioavailability-adjusted lead concentrations in carpet dust ($r^2 = 0.8$) (IEUBK 0.5-7 years of age and NHMRC (2009) 10 µg/dL

⁵⁶The NH&MRC blood lead level for investigation is currently 5 μg/dL NHMRC (2016) 'Managing individual exposure to lead in Australia – a guide for health practitioners'. National Health and Medical Research Council, Commonwealth of Australia. Canberra. April 2016.



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 μ g/dL

Figure 100), while r^2 is only 0.34 for garden soil (A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 µg/dL



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 101).



Note: solid line = median, boxes = lower and upper quartile, and whiskers = maximum and minimum values.

Figure 97 Lead source allocation of the IEUBK model with bioavailability-adjusted concentration for 67 houses



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 98 Relationship of bioavailability-adjusted concentration from the IEUBK model's predicted blood lead levels for children of different age groups and bioavailabilityadjusted lead in soil



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 µg/dL





Figure 99 Relationship of bioavailability approach and the IEUBK model's predicted blood lead levels for children of different age groups and bioavailability-adjusted lead concentrations in carpet dust



A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 $\mu\text{g/dL}$



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 $\mu\text{g/dL}$

Figure 100 Relationship between the bioavailability approach and predicted blood lead and bioavailability-adjusted lead concentrations in carpet dus



B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 µg/dL

Figure 101 Relationship between the bioavailability approach and predicted lead and bioavailability-adjusted lead concentrations in soil

4.5 Risk characterisation

Risk characterisation (Figure 1, page 61) is the final step of the risk assessment process, integrating the information from hazard assessment and exposure assessment (enHealth, 2012). In this section, the outcomes of this project are integrated and summarised following the process of hazard assessment and exposure assessment to give a risk characterisation.

The key findings of the hazard assessment in this study are:

- 1. The Q-Q plots and Shapiro-Wilk Test (Section 3.1.1) indicate non-normal distribution of elements in most samples taken from various locations around Mount Isa City. Kruskal-Wallis ANOVA tests show statistically significant differences in total lead concentrations in samples from the mine site (Section 3.1.4) as well as soil and dust samples from the city's residential area (Section 3.1.5 and Section 3.1.6). The Mann-Whitney U Test indicated that the total concentrations for Pb are not statistically different between indoor and outdoor air PM₁₀ samples, and outdoor air PM₁₀ samples between each individual sampling trip (Table 41, page 192).
- 2. Soil samples from 18 houses exceed the HIL Level A criteria for metals and the metalloid to varying levels and pose potential health risks (Section 4.2.1.1). The HIL Level A criterion for cadmium is also exceeded in one sample, for copper in seven samples, and for manganese in one sample. The bioaccessibility-adjusted concentrations for cadmium, copper, lead, and manganese in garden soils are all below the HIL Level A criteria values for garden soils in Mount Isa City (Section 4.2.1.1). Sixteen houses out of 67 exceed the HIL Level A criterion for lead in floor wipes and window-sill wipes and 58 houses exceed the criterion for lead in window-trough wipes (Section 4.2.1.1).
- 3. The lead in fallout dust from the city, roof gutter dust, carpet dust, and soil PM₁₀ samples all have the Urquhart Shale pattern of lead isotope ratios and are likely to be associated with dusts from lead mining activities and mineral processing (Section 3.2 and Section 4.2.1.2), but not recent lead smelting.
- 4. The spatial distributions of lead concentrations in garden soil and carpet dust in Mount Isa City show different patterns. Most soils that exceed the HIL Level A criterion for lead are located in, or near, the Urquhart Shale sequence (Figure 78) in the western suburbs of the city's residential area. In addition to high lead concentrations in the dust from the western part of Mount Isa City, carpet dust samples from the northern part of the city also have high lead concentrations compared with samples from the south-east (Section 4.2.1.2). However, no firm explanation was determined for this.
- 5. The major contribution to carpet dust was garden soil. However, the arsenic, cadmium, copper, lead, and zinc in carpet dust are likely to have

contributions from sources similar to the mine site dust and the Urquhart Shale outcrops in the residential areas, which are largely enriched in these heavy metals and the metalloid and associated with lower ²⁰⁸Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios (Section 4.2.1.2).

- 6. Chemical concentrations, lead isotope features, and lead species data indicate that houses closer to the mining operation (< 1 kilometre) have higher potential exposure to dusts generated by the mining activities at Mount Isa (Section 4.2.1.2).
- 7. There is no statistically significant difference between total concentrations of copper, lead, and zinc for all three outdoor air–particulate sampling periods (2009, 2010 and 2011) (Section 3.1.6 and Section 4.2.1.2). The air PM_{10} concentrations, reported in units of $\mu g/m^3$, are higher in outdoor samples, but the total concentrations of arsenic, cadmium, cobalt, lead, and zinc in the dusts collected indoors and outdoors are not statistically different (Section 3.1.6).

Most of the materials collected (i.e. the major matrices) are silicate in air particulates, soil, dust samples, and some mine site samples. These silicates are geogenic materials and generally derived from soils. Spatial differences among five high-volume air sites and air PM₁₀ filters from the city's residential area are identified (Section 3.7.1, page 282). Particles from the lead ore open pit are irregular, but the surface of samples from the smelting process and post-smelting procedures show smooth and aggregated features. The lead-containing particles captured on air PM₁₀ filters are lead–iron–sulfur

and lead-sulfur



Site B54

Site B50



Site B54-01-002

(

Site B50-01-002

- 8. Figure 59d) with clear isometric crystal structures of galena (Section 3.6 and Section 3.7).
- 9. XANES linear combination fitting results for samples from the mine site and the city's residential area indicate that lead species alter from the original mineral form of galena (PbS) to lead–goethite or magnetoplumbite after deposition in the community over a period of time greater than that used to collect fallout dust samples. The lead sulfide particles found in the city fallout and carpet dust samples are most likely from mining operations, showing a higher percentage of sulfide content than samples collected in the lead smelter (Table 69, page 244). The composition of HVAP from XANES fitting (Table 76)⁵⁷ is 27% lead-goethite and 72% molydophyllite

⁵⁷ Table 76 also indicates that HVA1 (Station Street-MIM TEOM) and HVA2 (K-Oval) show the presence of lead sulfide and are closer to the lead smelter facility. HVAP slurry composite used as a sample to dose rats for bioavailability measurement did not contain lead sulfide.

and therefore similar to soil, including for % BAc (Table 114). The XANES analysis of PM₁₀ air particulates exiting from the Mount Isa lead smelter stack contained negligible lead sulfide whereas near surface samples of dust and fallout from the lead smelter/ sinter plant area collected at the surface or at 2-3m above ground usually contained lead sulfide. Some HVAs, namely HVA1 (Station Street-MIM TEOM) and HVA2 (K-Oval), show the presence of lead sulfide (Table 76) and are closer to the lead smelter facility. Roof gutter dust samples show no lead sulfide and only lead–goethite indicating that photochemical oxidation of lead sulfide has probably occurred associated with exposure over a longer time frame than fallout collected in deposition bottles for a period of weeks to a few months. Lead isotope ratios can show origin of lead regardless of chemical or mineral form while XANES analysis gives the chemical form. XANES analysis may show differences even when lead isotope ratios are shown to be the same.

- 10. The dusts dispersed from the lead sinter plant and blast furnace are not the most important lead source for the air particulates sampled from the city's residential area, based on the elemental concentrations and the morphology of lead-containing particles (Section 3.1.6, Section 3.7, and Section 4.2.1.2). The contribution of lead particles dispersed from mine dusts associated with transport activities for the lead mineral processing cannot be ruled out (Section 4.2.1.2).
- 11.Based on lead isotope ratios and a two-component mixing model, it appears that over 70 per cent of lead in city dust samples may be derived from Urquhart Shale lead (Section 4.2.1.2, Figure 85, page 353).
- 12. The median bioaccessibility for samples from the mine site and the city's residential area also show differences, namely, an overall bioaccessibility of 29 per cent for mine site dust compared with 21 per cent for city soil and dust samples (Section 3.4). Outcrop samples have low metals and metalloid concentrations except for natural mineralisation (Urquhart Shale) samples (Section 3.1.2 [page 167] and Section 3.1.3 [page 168]). The mean bioaccessibility of lead for mineralised outcrop samples, including those from Urquhart Shale, is 2 per cent compared with 24 per cent in garden soil samples (Section 3.4). The actual individual % BAc value obtained from each house specific dust sampling program was used in the IEUBK modelling of blood lead level.
- 13. The relationship between lead bioaccessibility and two variables (lead speciation and the particle size distribution of samples) and the interaction among these factors in samples from Mount Isa City were examined (Section 4.3.2, page 354). Three groups were identified: (i) general mine site source samples and mine site fallout dust; (ii) haul road dust and surface tailings from the mine site; and (iii) carpet dust garden soil < 250 µm fraction, fallout from the city and roof gutter dust from the city's residential area samples (Section 4.3.2, page 354). These three groups (Figure 92) indicated that samples having smaller median particle size with</p>

more soluble lead speciation have a higher median lead bioaccessibility (Section 4.3.2.3, page 360).

- 14. Comparison of total concentrations and bioaccessibility-adjusted concentrations of metals and the metalloid between haul road dust and surface tailings show that these two types of mine site samples have similar levels of lead and other heavy metals, but the bioaccessibility-adjusted lead concentrations in surface tailings are more than three times that in haul road dust (Section 4.3.2, page 354).
- 15. Mine site dust materials are finer than dust and soil collected from the city's residential area (Figure 62). The sizes range from fine to coarse listed in the following order: mine dust (surface tailings, fallout mine, general mine source dust, smelter area dust, and haul road dust), and city dust and soil samples (roof gutter dust, fallout city, carpet dust, soil < 250 μm fraction, and soil < 2 mm). The particles that were less than 250 μm represented over 90 per cent, by volume, of all particles in samples (Section 3.8). Tailings dam materials have a tri-modal distribution curve that includes ultrafine particles that are finer than found in all other sample groups.</p>
- 16. The blood lead concentrations for children living in 67 houses in Mount Isa City's residential area, as predicted using the US EPA's IEUBK model are summarised in Section 3.9. The blood lead results predicted for children based on exposure, using bioaccessibility-adjusted lead input data from the statistically representative set of houses in Mount Isa City, indicate that only children living with the lead exposures at one house were likely to have blood lead levels that exceed the Australian NHMRC recommended blood lead level of 10 μg/dL⁵⁸.
- 17. The absolute bioavailability of lead measured by rat uptake experiments on 10 classes of sample from Mount Isa give a median of 1.05 per cent (Section 3.5, page 272). Comparison of the median bioaccessibility of 14.9 per cent (see Table 117, page 276) for the same set of samples shows that the ratio of bioaccessibility to bioavailability is 8.37 and confirms that bioaccessibility is an overly conservative prediction of bioavailability of lead in Mount Isa environmental samples. When the line of best fit is obtained from the bioaccessibility and bioavailability data, Equation 11 (page 277) is derived. It has a slope of 0.17, and thus the ratio of bioaccessibility to bioavailability is 5.9. Equation 11 was used to calculate the bioavailability of samples of all mine site and soil from the residential area. The most accurate prediction of blood lead results should occur when bioavailability-adjusted lead concentration data are used (Section 3.9.3). The relationship between bioavailability-adjusted lead concentrations in soil and dust matrices (defined by Equation 11) and the

 $^{^{58}}$ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

accompanying predicted blood lead concentrations from the IEUBK model is clear. The absolute bioavailability measures the actual quantity of lead that can be absorbed by the human body. Comparison of the blood values showed that bioavailability-adjusted blood lead concentrations using the IEUBK model was 1.46 μ g/dL (0.5-7 years) or 1.63 μ g/dL (1-4 years), which was lower than the measured blood lead show 4.97 and 4.27 μ g/dL, respectively for 2006-2007 and 2010 Queensland Health surveys at Mount Isa.

The key exposure assessment findings in this study are:

- Lead contained in soil and dust makes a significant contribution to blood lead levels, with median contributions of 19 per cent and 51 per cent, respectively, for bioaccessibility-adjusted data. On the other hand, water and air contribute only 1 per cent and 0.8 per cent, respectively, to predicted blood lead levels in children. The contribution of diet is comparable to soil and dust, with a median level of 22 per cent. The quantity of dietary sources of lead is a relative contribution, as compared with actual dose, to the total lead dose and may become a significant proportion of total dose for the houses with low levels of contributions from soil and dust. The dietary source of lead is less significant when there are higher loadings of lead in dust and soil in the house, which normally indicate higher blood lead levels in children (Section 4.4.1, page 362). When data for bioavailability-adjusted lead concentration in soil and dust matrices are used as an input to the IEUBK model, the accompanying predicted blood lead concentrations from the IEUBK model (for the house showing the highest predicted blood lead maximum of 2.8 µg/dL) show that no value exceeds a blood lead of 3.5 µg/dL (Table 129). Possible reasons to explain the differences between the 2010 blood lead survey (4.8 per cent of children exceeding 10 μ g/dL59 in Section 1.5.3, page 75) and the IEUBK blood lead prediction with bioavailability-adjusted approach are given in Section 4.4.4 (page 372). The contribution to diet increased to 60 per cent and showed that soil and dust contributions are most important when the bioavailability of lead is sufficiently high to give a blood lead concentration above 5 or 10 µg/dL.
- 2. The contribution from air sources of lead via the inhalation pathway ranges from 0.2–2.1 per cent. In comparison, the sum of the contributions from dust and soil via the ingestion route varied from 37–93 per cent, with a median of 74 per cent. These results highlight the dominant role of the ingestion pathway over the inhalation pathway in Mount Isa (Section 4.4.2). This finding further highlights the important role of personal hygiene and the home environment, particularly surface dust, for all the residences in Mount Isa City, particularly those with children.

 $^{^{59}}$ This compares with 50.8% exceeding 5 µg/dL in 2008 and 43.7% exceeding 5 µg/dL in 2011 given in Table 140.

- 3. The significant contribution of lead in carpet dust is confirmed by the high correlation ($r^2 = 0.8$) between the IEUBK model's predicted blood lead concentrations for young children 1-4 years of age in Mount Isa and the bioaccessibility-adjusted lead in carpet dust (Section 4.4.3). The IEUBK model using Mount Isa site-specific data predicts blood lead concentrations for young children in Mount Isa are significantly correlated with bioavailability-adjusted lead in carpet dust ($r^2 = 0.8$), while r^2 is only 0.35 for garden soil according to the IEUBK built-in functions and other default values (Table 12, page 154). This information confirms the significant contribution of lead in carpet dust as a source of lead, compared with garden soil (Section 4.4.1).
- 4. As discussed in Section 4.2.1.1, about 87 per cent of the houses exceed the US EPA's clearance standard for window-trough wipes and 16 out of 67 houses exceed the US EPA's clearance standard for window-sill wipes or floor wipes. Garden soil samples from 17 houses had total lead concentrations above HIL Level A criterion (300 mg/kg)⁶⁰ and bioaccessibility-adjusted lead concentrations are below the criterion. Of the seventeen houses exceeding HIL Level A criterion for lead concentration, eight are located on Urguhart Shale but none exceeded the criterion when bioaccessibility-adjusted lead concentrations were used (Table 138, page 387). Considering the potential for health concerns arising from the total lead concentration exceeding the HIL Level A criterion and the important role of lead absorption from garden soil via the ingestion route, a summary of houses that exceed the HIL Level A criterion for lead is given in Table 138. Using bioaccessibility data, the IEUBK model predicts blood lead concentrations ranging from 3 µg/dL for H37 to 10.2 μ g/dL for H41 for 0.5 – 7 years of age and from 3.3 μ g/dL for H37 to 11.2 μ g/dL for H41 for 1 – 4 years of age. The IEUBK model predicts blood lead levels for only one house (H41) that are at or exceed the NHMRC 2009 recommendation of 10 µg/dL but eleven houses (H10, H3, H68, H39, H58, H12, H23, H51, H41, H74 and H61) that are at or exceed the NHMRC 2016 recommendation of 5 µg/dL. H41 also has the highest contribution of lead from soil and dust (a total of 93 per cent). Table 138 indicates that the dominant lead sources are soil (mean of 40 per cent) and indoor carpet dust (mean of 43 per cent). Dietary intake of lead is significant, rising to an average of 76 per cent of the total lead sources when soil and dust lead concentrations are relatively low. Note that individual sets of source data add up to 100 percent but average and median percentages of sources do not. Lead sources from air and water are negligible, with less than 1.2 per cent for all houses in Table 138. Similar patterns were found by the IEUBK model's prediction with the absolute bioavailability approach (Table 139) and the contribution from diet is more significant compared with the bioaccessibility approach (Table 140) because of the greater contribution to total lead intake.

⁶⁰ The revised (NEPC, 2013) HIL A for lead 300 mg/kg.

- 5. Table 140 shows the comparison of blood lead concentrations predicted by the IEUBK model and blood lead screening surveys undertaken for young children living in Mount Isa City described in Section 1.5.3. The geometric mean blood lead concentrations of the tested children were 4.97 µg/dL and 4.27 µg/dL in 2006–2007 and 2010 blood lead screening programs respectively (Table 140). The IEUBK model predicted blood lead concentrations with a geometric mean of 3.48 µg/dL for 0.5-7-year-old children or 3.8 µg/dL for 1–4-year-old children living in 67 statistically representative houses in different parts of Mount Isa City's residential area. When data for bioavailability-adjusted lead concentrations in soil and dust matrices are used as inputs to the IEUBK model, blood lead levels do not exceed 2.8 µg/dL for 0.5–7-year-old children or 3.1 µg/dL for 1-4-year-old children, but are lower than the median level reported in the screening programs conducted by Queensland Health (Table 140). Using the bioaccessibility-adjusted approach, the IEUBK model predicts that 1.5 per cent of houses may have children aged 1-4 years with blood lead levels at or above the NHMRC 2009 10 µg/dL guideline, and that 25.37 per cent of houses may have children with blood lead levels at or above the NHMRC 2016 5 µg/dL guideline. The predicted percentages for children aged 1-4 years are lower than both the 4.8 per cent of blood lead levels for the 10 µg/dL guideline and the 43.7 per cent of blood lead levels for the 5 µg/dL guideline, found by the screening program conducted by Queensland Health in 2010 (Table 140). When the actual bioavailabilityadjusted soil and dust data are used, none of the blood lead levels predicted by the IEUBK model for the houses sampled exceed the NHMRC's recommended level (
- 6. Figure 97). Possible reasons for difference between the 2010 blood lead survey (Section 1.5.3, page 75) and IEUBK blood lead prediction with bioavailability-adjusted approach are:
 - a. the same houses were not sampled in both studies, and differences in the local environment (such as ground cover) or childhood behaviour might lead to different outcomes
 - b. children with high blood lead levels may be exposed to more dust or soil compared to the default ingestion rate of 100 mg/day
 - c. the dietary intake of lead by children in Mount Isa is higher than the assumed FSANZ national diet evaluation (a national average that might be underestimate the dietary intake of a population who live in a mineral-rich or smelting area).

Table 138 Houses exceeding HIL Level A criterion and the potential health risk (blood lead levels) for young children using the bioaccessibility approach

	Soil lead concentration		Carpet dust lead concentration		IEUBK mo bloc (0.5–84 ו	del predicted od lead nonths old)	Lead source allocation				
nouse iD	Total (mg/kg)	BAc- adjusted (mg/kg)	Total (mg/kg)	BAc- adjusted (mg/kg)	Geometric mean BLL (µg/dL)	Exceedance (%)	Air (%)	Diet (%)	Water (%)	Soil (%)	Dust (%)
H60	302	103	541	70	3.6	2%	0.7	21	0.9	46	31
H37	315	60	240	70	3	0.50%	0.9	26	1.2	33	39
H10	328	71	1300	164	4.5	4%	0.6	16	0.7	25	57
H3	331	72	490	188	4.8	6%	0.5	15	0.7	23	60
H68*	390	200	1690	130	5.8	12%	0.4	12	0.5	52	34
H39*	409	48	2860	516	9.2	43%	0.3	8	0.3	8	84
H55	416	94	735	62	3.4	1%	0.8	23	1	45	30
H58	418	158	1090	90	4.7	5%	0.6	16	0.7	53	30
H12*	427	125	640	139	4.9	6%	0.5	15	0.6	40	44
H38	430	76	309	84	3.4	1%	0.8	22	1	36	40
H23	514	105	1100	162	4.9	7%	0.5	15	0.6	33	51
H51*	522	135	885	124	4.8	6%	0.5	15	0.7	43	40
H15*	597	120	600	100	4.3	3%	0.6	17	0.8	44	37
H41*	745	228	1310	480	10.2	52%	0.2	6	0.3	30	63
H53	778	157	970	71	4.4	4%	0.6	17	0.7	56	25

A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 μ g/dL

H74*	815	292	1560	194	7.7	29%	0.3	9	0.4	54	36
H61*	1070	206	982	96	5.8	12%	0.5	13	0.6	58	27

Note: * means the house is located on Urquhart Shale

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B. Queensland Health survey 1-4 years of age and NHMRC (2016) 5 μ g/dL

House	Soil lead concentration		Carpet dust lead concentration		IEUBK pre blood lea	Lead source allocation					
ID	Total Con (mg/kg)	BAc adjusted (mg/kg)	Total (mg/kg)	BAc adjusted (mg/kg)	Geometric mean BLL (µg/dL)	Exceedance (%)	Air (%)	Diet (%)	Water (%)	Soil (%)	Dust (%)
H60	302	103	541	70	4.1	1.5%	0.7	20.9	0.9	46	31
H37	315	60	240	70	3.3	0.5%	0.9	25.9	1.2	33	39
H10	328	71	1300	164	5.0	4.4%	0.6	16.4	0.7	25	57
H3	331	72	490	188	5.4	6.0%	0.5	15.1	0.7	23	60
H68*	390	200	1690	130	6.5	12.5%	0.4	12.2	0.5	52	34
H39*	409	48	2860	516	9.5	42.6%	0.3	7.6	0.3	8	84
H55	416	94	735	62	3.8	1.0%	0.8	22.6	1.0	45	30
H58	418	158	1090	90	5.2	5.2%	0.6	15.7	0.7	53	30
H12*	427	125	640	139	5.4	6.3%	0.5	14.9	0.6	40	44
H38	430	76	309	84	3.8	1.1%	0.8	22.2	1.0	36	40
H23	514	105	1100	162	5.5	6.5%	0.5	14.8	0.6	33	51
H51*	522	135	885	124	5.3	6.0%	0.5	15.2	0.7	43	40
H15*	597	120	600	100	4.8	3.5%	0.6	17.4	0.8	44	37
H41*	745	228	1310	480	11.2	51.8%	0.2	6.2	0.3	30	63
H53	778	157	970	71	4.9	3.9%	0.6	16.8	0.7	56	25

H74*	815	292	1560	194	8.5	28.9%	0.3	8.7	0.4	54	36
H61*	1070	206	982	96	6.0	12.0%	0.5	13.3	0.6	58	27

Note: * means the house is located in Urquhart Shale

Table 139 Houses exceeding HIL level A criteria and the potential health risk (blood lead levels) for young children using the bioavailability approach

House ID	Soil concentr	lead ation	Carpet concentra	dust lead ation	IEUBK pr blood lead (0.5-84 mont	edicted model ths old)	Lead s	Lead source allocation					
nouse ib	Total (mg/kg)	ABA- adjusted (mg/kg)	Total (mg/kg)	ABA- adjusted (mg/kg)	Geometric mean BLL (µg/dL)	Exceedance (%)	Air (%)	Diet (%)	Water (%)	Soil (%)	Dust (%)		
H60	302	17.6	541	11.8	1.4	0.002%	2.2	58.1	2.8	21.7	14.6		
H37	315	10.2	240	11.9	1.3	0.001%	2.4	63.8	3.2	13.8	16.2		
H10	328	12.1	1300	27.8	1.6	0.005%	1.9	51.3	2.5	13.3	30.4		
H3	331	12.2	490	31.9	1.7	0.007%	1.8	49.1	2.3	12.7	33.3		
H68*	390	33.9	1690	22.1	1.9	0.017%	1.6	43.7	2.1	31.5	20.5		
H39*	409	8.1	2860	87.7	2.5	0.148%	1.1	31.9	1.5	5.5	59.5		
H55	416	16.0	735	10.5	1.4	0.001%	2.3	60.2	3.0	20.5	13.5		
H58	418	26.9	1090	15.3	1.6	0.006%	1.9	50.2	2.4	28.6	16.3		
H12*	427	21.3	640	23.6	1.7	0.008%	1.8	48.7	2.3	22.0	24.5		
H38	430	13.0	309	14.2	1.4	0.002%	2.3	59.7	2.9	16.4	18.0		
H23	514	17.8	1100	27.6	1.7	0.008%	1.8	48.5	2.3	18.3	28.5		
H51*	522	22.9	885	21.1	1.7	0.007%	1.8	49.2	2.4	23.9	22.0		
H15*	597	20.3	600	17.0	1.6	0.004%	2.0	52.9	2.6	22.9	19.1		
H41*	745	38.8	1310	81.6	2.8	0.372%	1.0	27.3	1.2	22.6	47.4		
H53	778	26.6	970	12.0	1.6	0.005%	1.9	52.1	2.5	29.5	13.3		
H74*	815	49.7	1560	33.0	2.3	0.081%	1.3	35.0	1.6	37.0	24.5		

A. IEUBK 0.5-7 years of age and NHMRC (2009) 10 μ g/dL

H61*	1070	35.0	982	16.4	1.8	0.013%	1.7	45.6	2.2	34.0	15.9

Note: * means the house is located in Urquhart Shale

D. Queensianu nealth suivev 1^{-4} veals of age and minimule (2010) $3 \mu u/u$	В.	Queensland Health survey	/ 1-4	vears of age	and NHMRC	(2016) 5 µa/d
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Soil lead concentration		Carpet dust lead concentration		IEUBK pred blood lea	Lead source allocation						
ID	Total Conc (mg/kg)	ABA adjusted (mg/kg)	Total (mg/kg)	ABA adjusted (mg/kg)	Geometric mean BLL (µg/dL)	Exceedance (%)	Air (%)	Diet (%)	Water (%)	Soil (%)	Dust (%)
H60	302	17.6	541	11.8	1.6	0.002%	2.2	58.1	2.8	21.7	14.6
H37	315	10.2	240	11.9	1.5	0.001%	2.4	63.8	3.2	13.8	16.2
H10	328	12.1	1300	27.8	1.8	0.005%	1.9	51.3	2.5	13.3	30.4
H3	331	12.2	490	31.9	1.8	0.007%	1.8	49.1	2.3	12.7	33.3
H68*	390	33.9	1690	22.1	2.0	0.017%	1.6	43.7	2.1	31.5	20.5
H39*	409	8.1	2860	87.7	2.8	0.148%	1.1	31.9	1.5	5.5	59.5
H55	416	16.0	735	10.5	1.5	0.001%	2.3	60.2	3.0	20.5	13.5
H58	418	26.9	1090	15.3	1.8	0.006%	1.9	50.2	2.4	28.6	16.3
H12*	427	21.3	640	23.6	1.8	0.008%	1.8	48.7	2.3	22.0	24.5
H38	430	13.0	309	14.2	1.5	0.002%	2.3	59.7	2.9	16.4	18.0
H23	514	17.8	1100	27.6	1.9	0.008%	1.8	48.5	2.3	18.3	28.5
H51*	522	22.9	885	21.1	1.8	0.007%	1.8	49.2	2.4	23.9	22.0
H15*	597	20.3	600	17.0	1.7	0.004%	2.0	52.9	2.6	22.9	19.1
H41*	745	38.8	1310	81.6	3.2	0.372%	1.0	27.3	1.2	22.6	47.4
H53	778	26.6	970	12.0	1.7	0.005%	1.9	52.1	2.5	29.5	13.3
H74*	815	49.7	1560	33.0	2.6	0.081%	1.3	35.0	1.6	37.0	24.5

H61*	1070	35.0	982	16.4	2.0	0.013%	1.7	45.6	2.2	34.0	15.9
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Note: * means the house is located in Urquhart Shale

Table 140 Comparison of blood lead concentrations between the IEUBK model's prediction and blood lead testing programs for children in Mount Isa

Location	Mount Isa	Mount Isa	Mount Isa	Mount Isa	Mount Isa	Mount Isa
Data source	Queensland Health (2008)	Queensland Health (2011)	IEUBK model prediction (BAc approach) in this study	IEUBK model prediction (ABA approach) in this study	IEUBK model prediction (BAc approach) in this study	IEUBK model prediction (ABA approach) in this study
Test time	2006-2007	2010	2008 and 2010	2008 and 2010	2008 and 2010	2008 and 2010
Age group	1-4 years	1-4 years	0.5-7 years	0.5-7 years	1-4 years	1-4 years
Test number	400	167	67	67	67	67
Maximum (µg/dL))	31.5	22.4	10.2	2.8	11.2	3.19
Minimum (µg/dL))	1.3	1.9	1.5	1.1	1.6	1.18
Number 10 µg/dL or over	45	8	1	0	1	0
Percentage 10 µg/dL or over	11.30%	4.80%	1.50%	0	1.50%	0
Geometric mean (µg/dL)	4.97	4.27	3.48	1.46	3.8	1.63
95% confidence interval	(4.69, 5.24)	(3.96, 4.61)	(3.05, 3.90)	(1.37, 1.54)	(3.35, 4.25)	(1.53, 1.72)
Number 5 µg/dL or over	203	73	9	0	17	0
Percentage 5 µg/dL or over	50.8	43.7	13.43%	0	25.37%	0

Note: Time for environmental samples (garden soil and dust) collection

Infants and young children are the groups most sensitive to lead exposure (JECFA, 2011). The inverse relationship of children's IQ points and blood lead concentrations has been demonstrated in previous studies (JECFA, 2011, Lanphear et al., 2005). Based on the dose-response analyses, the mean dietary exposure estimation for children aged 1-4 years children ranged between 0.03-9 µg/kg bodyweight ('bw') per day (JECFA, 2011). The lower end of this range (0.03 µg/kg bw per day) is below the 0.3 µg/kg bw per day associated with a 0.5 IQ point decrease (JECFA, 2011). Therefore, the lower end of the mean dietary exposure range is considered negligible. The higher end of the mean dietary exposure range is identified as a concern because it is higher than 1.9 µg/kg bw per day, which is associated with a 3 IQ points decrease (JECFA, 2011). Increases in blood lead from 2.4–10 µg/dL and 10–20 µg/dL were associated with the estimated IQ point decrements of 3.9 (95% CI, 2.4-5.3) and 1.9 (95% CI, 1.2–2.6) respectively for 1333 children aged 5–10 years in a multinational study (Lanphear et al., 2005). When the blood lead increased from 20 to 30 µg/dL, a further 1.1 (95% CI, 0.7–1.5) IQ point decrease was identified, although this was less significant than the lower blood lead increase range of 2.4 to 10 µg/dL (Lanphear et al., 2005). This reverse relationship between children's IQ points and blood lead concentrations indicated the possible effect of lead exposure when the children's blood lead levels were higher than 10 μ g/dL. This study also emphasises the importance of minimising the blood lead levels in children living in Mount Isa, whenever possible. It is clear from IEUBK model that the increasing blood lead is due to ingestion of soil and dust when bioavailability is high and the environmental concentration of lead is high. This result highlights the need for mitigation steps to minimise soil and dust ingestion by children in houses in Mount Isa.

4.6 Risk-based outcomes

Risk characterisation in this study identified that mine-derived dust at Mount Isa (historical or otherwise) is a key potential source of exposure to lead and other metals and the metalloid. The ingestion pathway is significant when the bioavailability of lead is high. In contrast, the inhalation pathway is insignificant. Although the bioaccessibility-adjusted input data produced a good prediction of the percentage of population likely to exceed the 10 μ g/dL⁶¹ blood lead reported in the 2010 Queensland Health blood lead survey, use of the bioavailability-adjusted data follows more closely the health risk assessment procedure for modelling the uptake of lead from geological material. Possible reasons for the difference are given in Section 4.4.4 (page 372).

A comparison of the lead isotope features for samples collected from the study area was made to distinguish the source of lead deposited in the houses.

⁶¹ 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

Comprehensive application of XANES and PBET, which were used to investigate lead species and bioaccessibilities for samples collected from the study area, enabled a site-specific human health risk assessment of lead exposure to children at Mount Isa to be performed. The exposure assessment using the IEUBK model as a predictive tool, was undertaken to evaluate the potential risks to the young children (0.5–7 years of age or 1-4 years of age) with the best accuracy using bioavailability-adjusted concentration data and reliable default inputs (see Table 12, page 154) from the pre-prescribed model protocol. These data and their assessment collectively give indications of key risk factors.

Three areas are suggested to minimise lead exposure for residents and to immobilise lead in the environment based on the risk assessment conducted in this study for Mount Isa City:

- (i) Industry operations: Maximise the effectiveness of reducing mine dust transfers from key lead sources at the mine site operations, such as haul road dust, surface tailings, crushed ore transfer, and surface accumulation of dust in plant areas of the lead smelter facility.
- (ii) Maintaining the home environment: Mine workers who are also parents of young children should continue to change their clothes and boots after work to minimise take-home lead dust. Bare patches in gardens should be covered with grasses. Carpets should be replaced with timber or other hard floor coverings, and cleaned with phosphatebased cleaning agents. Phosphate is known to immobilise lead and render its bioavailability upon ingestion. Houses should be cleaned frequently, by vacuuming and wiping away any accumulated dust (preferably with a damp cloth).
- (iii) Personal hygiene: Ensure children clean their hands frequently, particularly before meals. Try to reduce children's habits such as sucking on-food items. Keep children away from all potential sources of lead from both geogenic and anthropogenic origins.

These aspects all relate to the community having a clear understanding of the link between the sources of exposure and minimising their exposure and impact.

5 CONCLUSIONS

This project developed an integrated procedure to assess the human health risk of lead–zinc–copper mining and mineral processing activities on the surrounding community of Mount Isa. The procedure was based on the Australian Government's enHealth (enHealth, 2012) risk assessment framework. This framework consists of:

- issue identification
- hazard assessment
- exposure assessment
- risk characterisation.
The potential sources of the problem in the residential areas near the mine-site operations were firstly identified (the issue identification step). The hazards of exposure to minerals and metalloids via air-dust pathways from the mine site and natural outcrops to the community were then assessed. Total concentrations of samples were analysed and compared with Australian and international guidelines. The lead isotope signatures of samples from the study area were compared to distinguish the source of lead deposited in houses in the residential area, which are most likely to be ingested or inhaled by young children. The spatial distributions of the chemical and physical properties of lead-containing particles in the study area were also examined. XANES and PBET were used to investigate lead species and bioaccessibilities for samples from the study area, to enable site-specific human health risk assessments, a process that is both practical and reliable. The exposure assessment used the IEUBK model as a conclusive tool to evaluate the potential risks to young children with the most accurate and reliable knowledge from the pre-prescribed analysis. The characterisation of the human health risk in the study area was addressed as a final step.

Lead isotope ratios for potential mine dust emissions from the mine site were measured. Information from elemental concentrations, lead speciation and SEM-EDS (giving elemental and morphological information) supports the significance of house location in terms of potential risk from mining and mineral processing activities in Mount Isa (see Table 139, page 390). The total concentrations of heavy metals and a metalloid were analysed and the spatial distributions of lead concentrations in garden soil and carpet dust show different patterns. Samples from only 18 of the 67 houses show HIL Level A criteria values are exceeded at various levels for metals and the metalloid, but the bioaccessibility-adjusted concentrations of cadmium, copper, lead, and are all below HIL Level A criteria values for garden soils. Sixteen houses out of 67 houses exceed the criterion value for lead in floor wipes and window-sill wipes and 58 houses (87 per cent) exceed the criterion for lead in window-trough wipes. Although the lead isotope ratios indicate similar features for lead ore materials from the mine site and Urguhart Shale, the lead speciation and morphology information for these two groups of samples indicates that lead sulfide particulates found in the samples from the residential area came from the mining operation, rather than Urguhart Shale outcrops. The two-component lead isotope mixing model shows a high portion of lead contribution coming from Urguhart Shale type of lead.

Quantitative XANES analysis with LCF against model compounds indicated that lead species in samples from Mount Isa are generally dominated by lead sulfide, lead–goethite, lead sulfate, and other lead-containing minerals. Lead species for samples from the residential areas and outcrops are different from mine site samples. Lead species in the Urquhart Shale outcrop are mainly lead–goethite + plumbogummite. Galena and anglesite are common in surface dust from most of the lead smelter sites, which were mainly near the lead smelter sinter plant and lead concentrate feed handling system. Haul road dusts from the mine site primarily feature large portions of lead-goethite and small percentages of lead chloride and lead sulfate. The XANES fitting for surface tailings materials is very similar to haul road dust. Lead–goethite is the primary lead species in samples from the residential area, and some galena is also present in these samples.

Bioaccessibility data indicate that the median level of lead in all mine dust samples is 29 per cent and in soil samples from the community is 21 per cent. The absolute bioavailability of lead measured by rat uptake experiments on 10 classes of samples gives a median of 1.05. Comparison of the median bioaccessibility of 14.9 per cent (see Table 117, page 276) for the same set of samples shows that the ratio of bioaccessibility to bioavailability is 8.37 and confirms that bioaccessibility is an overly conservative prediction of bioavailability of lead in Mount Isa environmental samples. When the line of best fit is obtained from the bioaccessibility and bioavailability data, Equation 11 (page 277) is derived. It has a slope of 0.17, and thus the ratio of bioaccessibility to bioavailability is 5.9. The most accurate prediction of blood lead levels is achieved when bioavailability-adjusted lead concentration data is used. Using the relationship bioavailability-adjusted IEUBK model. the between lead concentration in soil and dust matrices and the predicted blood lead is clear.

Lead absorption via the ingestion route is identified as being more significant than that of inhalation route in Mount Isa City. The risk assessment procedure in this study estimated the health risk to young children living in Mount Isa by predicting the blood lead levels using the IEUBK model. The results for the predicted increase in blood lead levels of children, based on exposure from a statistically representative set of houses in Mount Isa City, shows that, based on bioaccessibility-adjusted result, children living in only one house sampled are likely to exceed the Australian NHMRC 2009 recommended blood lead level of 10 μ g/dL⁶², with a 52 per cent probability of exceedance (blood lead level > 5 or 10 µg/dL) for children who live in that particular house. Soil and dust make significant contributions to blood lead levels, with the median contributions of 19 per cent and 51 per cent to the total daily intake of lead, respectively. On the other hand, water and air only show 1 per cent and 0.8 per cent contributions to predicted blood lead levels in children. The contribution from air-based sources of lead, via inhalation pathway, range from 0.2 per cent to 2.1 per cent. These results highlight the dominant role of the ingestion pathway over the inhalation pathway in Mount Isa City. When data for bioavailability-adjusted lead concentrations in soil and dust matrices are used as an input to the IEUBK model, the predicted blood lead concentrations from the IEUBK model show that no value exceeds a blood lead concentration of 5 or 10 µg/dL. The contribution of diet to blood lead levels increases to 60 per cent, showing that soil and dust contributions are most important when the bioavailability of lead is sufficiently high and at high concentrations to give a blood lead concentration above 5 or 10 µg/dL. The findings for the residential area also indicate the importance of personal hygiene and a clean household environment, particularly for young children.

⁶² 5 µg/dL is the current NH&MRC (2016) blood lead level for investigation.

The study emphasised the importance of minimising the blood lead levels in children living in Mount Isa whenever possible, even though their blood lead concentrations are predicted to be lower than 5 or 10 μ g/dL. It is clear from IEUBK model that increased blood lead is due to ingestion of soil and dust and that diet has a significant contribution to lead exposure, highlighting the need for mitigation steps to minimise soil and dust ingestion of children in the houses in Mount Isa.

The blood lead concentrations predicted by the IEUBK model were compared with blood lead screening programs undertaken by Queensland Health in Mount Isa in 2006–2007 and 2010 for children aged 1–4 years. The geometric mean blood lead concentrations of the children tested by Queensland Health were 4.97 μ g/dL in 2006–2007 and 4.27 μ g/dL in 2010. The IEUBK model predicts a geometric mean blood lead concentrations of 3.48 μ g/dL (0.5-7 years of age) or 3.8 μ g/dL (1-4 years of age) The IEUBK model predicts that 1.5 per cent of children aged 1-4 years could exceed the NHMRC 2009 recommended blood lead level at or above 10 μ g/dL or 25.37 per cent of children could exceed the NHMRC 2016 recommended blood lead level at or above 5 μ g/dL which is lower than the 43.7 per cent identified in the 2010 Queensland Health screening program. When data for bioavailability-adjusted lead concentration in soil and dust matrices is used as an input to the IEUBK model, the blood lead predictions do not exceed 1.6 μ g/dL. The bioaccessibility-adjusted approach is considered to be suitable for screening and monitoring purposes.

Possible reasons for the results of the Queensland Health 2010 survey and IEUBK model's predictions using the bioavailability-adjusted approach are:

- a. the same houses were not sampled in both surveys and so the exposures of the children in these houses to lead in soil and carpet dust might have been lower in this Lead Pathway Study than in the Queensland Health surveys
- b. children who had high blood lead levels may have been exposed to more dust or soil than the model's default ingestion rate of 100 mg/day
- c. the dietary intake of lead by children in Mount Isa may be higher than the assumed FSANZ national diet evaluation used in the IEUBK model (a national average that might be underestimate the dietary intake of a population who live in a mineral rich or smelting area).
- d. lead intake from other potential sources, such as lead paint on toys, lead incorporated into plastic toys, lead solder used in making stained glass, lead in batteries being recycled at residences, lead in ceramic dishware or leaded crystal beverage containers.

Recommendations for future work

The recommendations of this report related to the community having a clear understanding of the link between the sources of exposure and how to minimise the impact of these sources. It is recommended that improvements in three areas are implemented to minimise lead exposure for residents and to immobilise lead in the environment:

- 1. Ensure that all Mount Isa residents, in particular young children, have their blood lead levels monitored. This is to ensure that health management actions are taken, any circumstances leading to elevated blood lead levels in children are identified early, and exposures to lead are minimised.
- 2. Promote the importance of a clean home environment for Mount Isa residents.
- 3. Promote personal hygiene, such as cleaning children's hands frequently and before meals and minimising specific habits of very young children such as sucking non-food items and keep away from nonessential uses of lead including historical paint and petrol residues.
- 4. Investigate the home for other sources of lead, such as lead paint on toys or lead incorporated into plastic toys, lead solder used in making stained glass, lead in batteries being recycled at residences, and lead in ceramic dishware or leaded crystal beverage containers.
- 5. Wash all home grown fruit and vegetables thoroughly before eating/cooking; peeling root crops will also reduce lead exposure. For those children who have high blood lead levels, an examination of the default 100 mg/day dust and soil ingestion rate is warranted, together with an examination of both the children's specific habits and their dietary intake of lead compared to the assumed FSANZ national diet evaluation. This investigation would help to establish more reliability between predicted and measured values for blood lead in children.

6 PROFESSIONAL BACKGROUND

6.1 Centre for Mined Land Rehabilitation

Formally established in 1993, the Centre for Mined Land Rehabilitation (CMLR) at The University of Queensland (UQ) consists of a collaborative and multidisciplinary grouping of research, teaching and support staff and postgraduate students dedicated to delivering excellence in environmental research and education to the Queensland, national and international minerals industry and associated government sectors.

The Centre is widely recognised as the source of quality research and postgraduate students at the cutting edge of issues in mining environmental management and sustainability. It has built a reputation for the provision of the scientific research that is necessary to support and underpin the decisions that need to be made to minimise the environmental risks by the mining and processing of the full spectrum of commodities including coal, gold, bauxite, alumina, base metals, heavy mineral sands and oil, both in Australia and overseas.

The Centre is one of six UQ research centres that make up the Sustainable Minerals Institute (SMI – <u>www.smi.uq.edu.au</u>). The SMI was established in 2001 as a joint initiative of the Queensland Government, UQ and the minerals industry, to provide an over-arching framework for progressing minerals industry research and education, with the purpose of providing 'knowledge-based solutions to meet the sustainability challenges in the global mining industry'.

6.2 Experience of consultants

Associate Professor Barry Noller

Associate Professor Noller has a PhD (1978) in Environmental Chemistry from the University of Tasmania. He worked as a Research Fellow at the Australian National University (1978-1980), Senior Research Scientist at the Alligator Rivers Region Research Institute, Jabiru, Northern Territory (1980-1990) and then as Principal Environmental Chemist for the Department of Mines and Energy, Darwin Northern Territory (1990-1998). During this period Professor Noller was involved with the environmental management and regulation of all mines in the Northern Territory and was technical manager of the Northern Territory study on Bird Usage Patterns on Mining Tailings and their Management to Reduce Mortalities completed in 1998. He was also a co-author and reviewer of the Best Practice Environmental Management in Mining Handbook on Cyanide Management. From 1998-2006 Professor Noller was Deputy Director of the National Research Centre for Environmental Toxicology (EnTox) – The University of Queensland, Coopers Plains, Qld. EnTox has a strong involvement with the utilisation of the risk assessment process to deal with toxicological hazards, including in environmental systems. Since November 2006, Professor Noller has been appointed as Honorary Research Consultant and Principal Research Fellow at the Centre of Mined Land Rehabilitation (CMLR) a centre at The University of Queensland's St Lucia campus and a part of the Sustainable Minerals Institute.

Associate Professor Noller has been working and publishing in the field of environmental chemistry and industrial toxicology for the past 40 years and has presented > 400 conference papers and published > 200 papers. His professional activities undertaken at 4 different centres have covered processes and fates of trace substances in the environment, particularly in tropical environmental systems with special reference to risk management associated with their application and studies of the bioavailability of toxic elements in mine wastes, including waters. He has undertaken a number of consulting activities in Queensland, Tasmania, New South Wales and the Northern Territory and was appointed in 2007 as Lead Author of the Australian Government Leading Practice Sustainable Development Program for the Mining Industry Handbook on Cyanide Management. He has been project leader of the Lead Pathways Study conducted for Mount Isa Mines since 2007. The Land Report was released in 2009 and the Water Report in September 2012.

Dr Jiajia Zheng

Dr Jiajia Zheng was a Research Officer at CMLR, the University of Queensland. Dr Zheng completed her PhD at CMLR in June 2013 and looked at the lead from mining and mineral processing activities to the community via the air-dust pathway. Dr Zheng has a Masters degree in Environmental Geochemistry from the School of Earth Science, the University of Queensland. Her Masters research project was on Peat Deposits of Moreton Bay: Natural Archives of Environmental Pollution. Prior to her study in Australia, Dr Zheng was studying at the China University of Geosciences (Wuhan), majoring in Economic Geology.

Dr Zheng's research interests are principally in environmental risk assessment and management in mining and mineral industry by combining chemical and physical properties of hazardous materials using various approaches such as Xray absorption spectroscopy and radiogenic isotope measurements as forensic tools. Dr Zheng is also interested in the fate and the interaction of heavy metals and metalloids in the air-soil-dust materials and their potential toxicological responses to human and ecology system.

Dr Trang Huynh

Dr Trang Huynh has a PhD degree in Environmental Science from the University of Melbourne (2008). Her PhD research project was on *Bioavailability of heavy metals in soil and biosolids during phytoextraction*. She completed her Master of Science Degree majoring in Soil Science at The University of Sydney (2001) with thesis on *Crystallographic and chemical properties of Copper and Cd substituted goethites using X-ray Synchrotron technique*. She worked as a researcher and lecturer on soil and environmental chemistry in Vietnam for 7 years. During this period, she was involved in several international funded projects in Vietnam as a project coordinator, researcher and project evaluator. Dr Trang Huynh is currently a Postdoctoral Research Fellow with the CMLR at The University of Queensland. Dr Trang Huynh research interests are principally in biogeochemistry, environmental and water/soil chemistry, plant-soil interaction and the behaviour of heavy metals and metalloids in the environment. She is also interested in understanding and applying advanced techniques such as Diffusion Gradient in Thin-film (DGT) and Synchrotron Technique to measure heavy metal/loid speciation in the environment especially at mining sites. One of her current research focus is on the impacts of contaminants from mining activities to human and ecological health.

Professor Jack Ng

Professor Jack Ng has a PhD in Environmental Toxicology and Chemistry from The University of Queensland. He is a certified toxicologist (Diplomate of the American Board of Toxicology). Jack is currently the Theme Leader of Environmental Health Risk Assessment at the Queensland Alliance for Environmental Health Sciences (QAEHS) (incorporating the former National Research Centre for Environmental Toxicology (Entox)), Faculty of Health and Behavioural Sciences of The University of Queensland. He is also the Program Leader for Minimising Uncertainty in Risk Assessment Program in the CRC-CARE (Contamination Assessment and Remediation of the Environment). He has extensive research experience in the fields of Environmental Toxicology and Chemistry, heavy metals and natural toxins. He focuses on the relevance of speciation and bioavailability as key parameters for risk assessment. Much of his research aims to generate data to fill gaps that are necessary for a risk-based approach under the risk assessment framework. Jack has a list of over 400 publications of which about 200 are peer reviewed articles, monographs, technical reports and book chapters. He has completed numerous technical reports related to risk assessment of contaminated sites for the industrial as well as government agencies.

At an international level, Jack's expertise in his field of environmental toxicology research and risk assessment has been recognised by World Health Organisation (WHO), International Agency for Research on Cancer (IARC), and WHO/FAO Joint Expert Committee on Food Additives (JECFA) as demonstrated by his contribution to a number of monographs and technical reports produced by these agencies. Jack is a Coordinating Editor of the Environmental Geochemistry and Health Journal, editorial board member of Journal of Toxicology, and reviewer of numerous international scientific journals, national and international granting agencies.

At national level, Jack served as a member of the National Health and Medical Research Council Health Investigation Levels (HIL) Working Committee who oversaw the setting of the current National Environmental Protection Measures (NEPM) HILs. He was also a member of the CRC CARE Project Advisory Group for the setting of Health Screening Levels (HSL) for petroleum hydrocarbons which have been adopted nationally by various jurisdictions and stakeholders. Jack is the lead author of the Bioavailability/Bioaccessibility Technical and Guidance documents, and the latter has been adopted into the current NEPM by the National Environmental Protection Council (NEPC) in 2013. Jack is an

assessor for Registrants and Fellows of Toxicologist and/or Risk Assessor of the Australasian College of Toxicology and Risk Assessment. Jack provides toxicology expert support to a number of environmental auditors in Australia.

Professor Hugh Harris

Professor Hugh Harris is an Australian Research Council Queen Elizabeth II Fellow in the School of Chemistry and Physics at the University of Adelaide. He has a PhD in Chemistry from the University of New South Wales (2000), and has worked as a postdoctoral fellow at Stanford University and the University of Sydney. His main research focus is on utilising synchrotron-based techniques, such as x-ray absorption spectroscopy and x-ray fluorescence imaging, to understand the roles that metals play in biological systems. This spans work on fundamental biochemical and structural studies of metalloproteins, deciphering modes of action of metal-based pharmaceuticals, and the relationship between intake of essential or toxic heavy elements and the development and progression of a range of diseases. He has demonstrated the advantages of x-ray techniques in the area by determining the chemical form of mercury in fish bound for human consumption, showing that mercury from dental amalgams can migrate through teeth to the bloodstream and by mapping intracellular targets for elements such as selenium and arsenic.

He is the author of nearly fifty journal publications, including papers in highly regarded journals such as *Science*, *Environmental Science and Technology* and *Chemical Research in Toxicology*. He has served on a number of committees for the Australian Synchrotron including as chair of the X-ray Fluorescence Microscopy Proposal Advisory Committee, the User Advisory Committee and the National Science Consultative Group.

Dr Violet Diacomanolis

Dr Violet Diacomanolis has completed her PhD in June 2013 with the National Research Centre for Environmental Toxicology, the University of Queensland, and undertaking the rat bioavailability study for the Lead Pathway Project at Mount Isa. Dr Diacomanolis has a Masters degree in Toxicology from the University of Tehran.

Dr Raijeli Taga

Dr Raijeli Taga has completed her PhD in 2016 with the CMLR, the University of Queensland, and undertook a variety of the studies for the Lead Pathway Project at Mount Isa. Dr Taga also has undertaken a Masters degree in Environmental Toxicology at the University of Queensland.

7 LIMITATIONS

CMLR has prepared this report for the use of Glencore Mount Isa Mines Limited. It has been prepared in accordance with the scope of work.

This report should be read in full. No responsibility is accepted for use of any part of this report in any other context or for any other purpose or by third parties. This report does not purport to give legal advice. Legal advice can only be given by qualified legal practitioners.

The methods adopted and sources of information used by CMLR are outlined in this report. Our conclusions are based on the analytical data presented in this report and on our experience. Opinions and recommendations presented herein apply to the information available at the time of our investigation and cannot necessarily apply to matters of which CMLR is not aware and has not had the opportunity to evaluate.

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9 APPENDICES

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