Identification and measurement of contemporary sources and exposure risks from lead emissions and depositions in Australia



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Cover photo:

Ongoing emissions from the copper (left) and lead (right) smelter stacks in Mount Isa, Queensland.

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Declaration

I certify that the work in this thesis has not been submitted previously, in whole or in part, for a degree at this or any other university. Nor does it contain, to the best of my knowledge, any material published or written by another person, except where acknowledged. This thesis is comprised solely of my own work.

Louise Jane Kristensen September 2015

ABSTRACT

Lead emissions in Australia have been occurring for almost two centuries. In that time, environmental quality and human health have been greatly affected. As a result, lead contaminated soils are widespread in Australian urban and industrial locations and lead emissions are ongoing in lead industrial locations. The removal of primary sources, leaded petrol and paint, as well as the decline in blood lead levels in mining and smelting communities has led to complacency that much of the problem has been resolved. However, elevated childhood blood lead levels are still being measured in lead towns.

Despite the global abundance of studies on environmental lead sources, emissions and human health consequences, relatively little research has been undertaken in Australia following the removal of lead from petrol in 2002. In light of this knowledge gap, this thesis includes twelve papers that present research into the current state of lead emissions in Australia. The papers address multiple and interconnecting aspects of lead emissions: identification of major sources emitting large volumes; measurement of lead in the environment and ongoing exposures; the impacts on the environment and consequences to human health. Additionally, this thesis examines the role of regulations and guidelines in protecting children from the harmful effects relating to the toxicity of lead.

The outcome of the studies in this thesis demonstrate that environmental lead emissions, depositions and exposures remain a cause for serious public health concern in Australia. Current lead emissions from mining and smelting operations continue to expose children to dangerous levels of toxic metals that result in blood lead levels above current guideline values. Quantification of lead emitted from petrol, at a quarter million tonnes, has revealed the enormity of this legacy source, even in relation to mining and smelting emissions. Although petrol emissions form an historical source, the findings in this thesis reveal its impact prevails in the environment. By providing a contemporary analysis on the issue of lead emissions, this thesis demonstrates that reliance on outdated regulations and guidelines are ineffective at reducing exposure to both historic and ongoing lead emissions in Australia. Therefore, in light of the globally accepted paradigm that there is no safe level of lead exposure, this thesis highlights the urgent need to revise existing strategies and regulations to limit preventable exposures.

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Notes regarding thesis format and author contributions to publications

This thesis is structured into five chapters. The studies contained within this thesis are presented in Chapters Two, Three and Four. Chapter Two, identifies the major sources of lead emissions in Australia, both historical and contemporary, quantifying the volumes of lead emissions and atmospheric lead in air levels. Chapter Three, includes studies conducted around Australia that measure historical and contemporary emissions of lead to the environment. Chapter Four, comprises studies that examine and evaluate the impacts and consequences of lead emissions to the environment and communities. These three chapters provide an all-encompassing study of the interlinking aspects and the current progression of lead emissions and pollution in Australia.

CHAPTER 2: Quantification and identification of sources of lead emissions

Paper One

Kristensen, L.J. (100 %) (2015). Quantification of atmospheric lead emissions from 70 years of leaded petrol consumption in Australia. *Atmospheric Environment*, 111, 195-201.

Paper Two

Taylor, M.P. (55 %), Davies, P.J. (10 %), **Kristensen, L.J.** (25 %), & Csavina, J.L. (10 %) (2014). Licenced to pollute but not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations. *Aeolian Research*, *14*, 35-52.

This paper was initiated by Taylor and developed by all authors. All authors were involved in data compilation and analysis. Writing was performed by all authors. Editing and reviewing was conducted by all authors.

CHAPTER 3: Measurement of lead emissions and exposures

Paper Three

Kristensen, L.J. (90 %), Taylor, M.P. (8 %) & Evans, A.E. (2 %) (2016). Tracing South Australia's anthropogenic lead history using lead isotope compositions in red wine. *Chemosphere*, DOI: 10.1016/j.chemosphere.2016.03.023.

This study was developed by myself and Taylor. Fieldwork and laboratory analysis was conducted by myself. The text was written by myself with editing and review done by Taylor and Evans.

Paper Four

Kristensen, L.J. (80 %), Taylor, M.P. (5 %), Odigie, K.O. (5 %), Hibdon, S.A. (5 %), & Flegal, A.R. (5 %) (2014). Lead isotopic compositions of ash sourced from Australian bushfires. *Environmental Pollution*, *190*, 159-165.

This concept for this study came from Taylor and was undertaken as my honours project. Initial fieldwork was conducted by myself and Taylor. Initial laboratory work was conducted by myself, Odigie and Hibdon. The study was then further developed during my PhD by myself and further fieldwork and laboratory work was conducted by myself. The text was written by myself with editing and reviewing conducted by Taylor and Flegal. More than half the work conducted in this study was completed during my PhD candidature.

Paper Five

Kristensen, L.J. (70 %), Taylor, M.P. (20 %), & Morrison, A.L. (10 %) (2015). Lead and zinc dust depositions from ore trains characterised using lead isotopic compositions. *Environmental Science: Processes & Impacts, 17*, 631-637.

The concept for this study came from Taylor. Fieldwork was conducted by myself and Taylor. The text was written by myself. Scanning electron microscope analysis and written section was performed by Morrison and edited by myself. Editing and reviewing was done by Taylor.

Paper Six

Kristensen, L.J. (80 %) & Taylor, M.P. (20 %) (2016). Unravelling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. *Environmental Geochemistry and Health*, DOI: 10.1007/s10653-016-9804-6.

This paper was developed by myself and Taylor. Fieldwork was conducted by myself and Taylor. Data analysis was conducted by myself. The text was written by myself. Editing and reviewing was done by Taylor.

Paper Seven

Taylor, M.P. (35 %), Camenzuli, D. (35 %), **Kristensen, L.J.** (15 %), Forbes, M. (8 %), & Zahran, S. (7 %) (2013). Environmental lead exposure risks associated with children's outdoor playgrounds. *Environmental Pollution*, *178*, 447-454.

The concept was developed by Camenzuli. Fieldwork was performed by myself and Camenzuli. The text was written and developed by Camenzuli and Taylor. Editing and reviewing was done by myself and Taylor. Statistical analysis was performed by Forbes and Zahran.

Paper Eight

Taylor, M.P. (40 %), Mould, S.A. (40 %), **Kristensen, L.J.** (15 %), & Rouillon, M. (5 %) (2014). Environmental arsenic, cadmium and lead dust emissions from metal mine operations: Implications for environmental management, monitoring and human health. *Environmental Research*, *135*, 296-303.

The concept for this study was developed by myself and Taylor. Fieldwork was conducted by myself, Taylor, Mould and Rouillon. The text was written by Mould and developed by myself and Taylor. Editing and reviewing was conducted by myself, Taylor and Rouillon.

CHAPTER 4: Impacts and consequences of lead emissions

Paper Nine

Taylor, M.P. (44 %), **Kristensen, L.J.** (25 %), Davies, P.J. (20 %), Csavina, J.L. (5 %), Mackay, A.K. (2 %), Munksgaard, N.C. (2 %), & Hudson-Edwards, K.A. (2 %) (2015). Omissions about the sources of contaminant emissions and depositions - A reply to comments on "Taylor, M.P., Davies, P.J., Kristensen, L.J., Csavina, J., 2014. Licenced to

pollute not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations. *Aeolian Research*, 14, 35-52." *Aeolian Research*, 17, 205-213.

This paper was in response to comments on Paper Two. Compilation of data was done by Taylor. Text was written by myself and Taylor. Editing was conducted by myself, Davies and Csavina. All authors reviewed the paper.

Paper Ten

Taylor, M.P. (35 %), Zahran, S. (30 %), **Kristensen, L.J.** (25 %), & Rouillon, M. (10 %) (2015). Evaluating the efficacy of playground washing to reduce environmental metal exposures. *Environmental Pollution*, 202, 112-119.

This study was proposed by Taylor as a follow up to Paper Eight. Fieldwork was conducted by myself and Rouillon. Laboratory work was conducted by myself. Statistical analysis was performed by Zahran. The text was developed by myself, Taylor and Zahran. All authors performed editing and reviewing.

Paper Eleven

Harvey, P.J. (42 %), Taylor, M.P. (20 %), **Kristensen, L.J.** (15 %), Grant-Vest, S. (5 %), Rouillon, M. (15 %), Wu, L. (2 %), & Handley, H.K. (1 %) (2015). Lead exposure risk in a former lead smelting community: assessment of a lead abatement strategy. *Environmental Geochemistry and Health*, DOI: 10.1007/s10653-015-9779-8.

Fieldwork was conducted by myself, Harvey, Taylor, Grant-Vest and Rouillon. Laboratory work was conducted by Harvey and Wu. Data anaylsis was conducted by myself, Rouillon, Taylor and Harvey. Text was written by Harvey and Grant-Vest and further developed by myself, Taylor and Rouillon.

Paper Twelve

Dong, C. (40 %), Taylor, M.P. (30 %), & **Kristensen, L.J.** (25 %) & Zahran, S. (5 %) (2015). The potential for environmental arsenic, cadmium and lead exposures to influence early childhood health and behavioural outcomes in an Australian mining community. *Environmental Pollution*, 207, 345-356.

The concept for this paper came from Taylor with development by Dong. Fieldwork was conducted by myself and Taylor. The text was developed by Dong. Statistical analysis was conducted by Zahran. Editing and reviewing was done by myself and Taylor.

Acronyms and Abbreviations

Australian Dureau of Statistics
Arsenic
Blood lead level
Cadmium
Centre for Disease Control and Prevention
Copper
Environment Protection Authority
Health Investigation Level
Inductively Coupled Plasma Mass Spectrometry
Intelligent Quotient
Lead Abatement Strategy
milligrams per kilogram
National Environmental Protection Council
National Environmental Protection Measure
National Health and Medical Research Council
National Measurement Institute
New South Wales
National Pollutant Inventory
Northern Territory
National Toxicology Program (United States)
Lead
portable X-Ray Fluorescence
Queensland
South Australia
Tasmania
Tetraethyl-lead
Targeted Lead Abatement Program
Micrograms per decilitre (units of blood lead measurement)
Micrograms per cubic metre (units of lead in air measurement)
United States
World Health Organisation
Zinc

CHAPTER 1: Introduction

Lead is a naturally occurring element in the earth's crust that is malleable, resistant to corrosion and has a low melting point (Callender 2003). As a result, the many uses of lead over the centuries have included water tanks and pipes, cooking pots, cosmetics, coinage, paints, pigments and glazes. Modern uses of lead include batteries, radiation protection and underwater cable protection. Evidence from the long history of lead production and the resultant lead emissions can be seen in historical environmental samples such as sediments, bogs, ice cores and corals around the world (Hong et al. 1994; Shotyk et al. 1998; de Callataÿ 2005; Kelly et al. 2009; McConnell et al. 2014). The toxic consequences of lead have also been known since antiquity (Nriagu 1983; Needleman 2008), yet it remains such an essential metal that it is still being mined and used today in increasing quantities (Figure 1.1) (Mudd 2007; International Lead Association 2015).



Figure 1.1: Global mine production and usage of lead (International Lead & Zinc Study Group 2015; International Lead Association 2015).

1.1 Toxicity of Lead

Exposure to lead and the associated health effects have been studied extensively. Elevated blood lead levels (BLL) from lead exposure result in neurological, cardiovascular, renal and nervous system health effects (Needleman 2008; National Toxicology Program 2012). As blood lead levels increase, so too does the range and severity of affected systems (Needleman 2004). Relevant to the current situation of lead emissions is that prolonged exposure to even low levels of lead has been linked to adverse health effects (Lanphear et al. 2005; National Toxicology Program 2012). It has been established that sufficient evidence exists linking blood lead levels below 10 μ g/dL as well as below 5 μ g/dL with adverse neurological affects causing greater incidence of attention-related and problem

behaviour disorders and decreased cognitive performance demonstrated through loss of IQ points, lower academic achievement and reduction in cognitive measures (National Toxicology Program 2012). Of particular concern is lead exposure to children as they are most susceptible to lead absorption, have behaviours that increase exposure risk (e.g. hand-to-mouth) and are developmentally vulnerable to toxic substances (Needleman 2004; Canfield and Jusko 2008). With the increased understanding of the effects of lead at low levels of exposure and that no safe level of lead can be identified, the Australian blood lead guideline was lowered from 10 μ g/dL to 5 μ g/dL in 2015 (National Health and Medical Research Council (NHMRC) 2015).

While some of the most significant consequences of lead are the detrimental neurocognitive affects in children, there is a wide spectrum of health effects from lead to both children and adults at blood lead levels below 10 μ g/dL as well as 5 μ g/dL (National Toxicology Program 2012; U.S. Environmental Protection Agency 2013). Increased blood pressure and cardiovascular related mortality has been associated in adults with blood lead levels less than 10 μ g/dL (Menke et al. 2006; National Toxicology Program 2012). Low birth weight, reduced postnatal growth and delayed puberty are all evident in children in blood lead levels below 5 μ g/dL (National Toxicology Program 2012; U.S. Environmental Protection Agency 2013). A health consequence common to both children and adults with low lead exposure is reduced kidney function due to decreased glomerular filtration rate (National Toxicology Program 2012). The severity of the consequences to human health due to low level blood lead exposure to lead.

1.2 Mining

Australia's lead emissions history dates back to the early days of mining in South Australia (SA) during the 1840s (Drew 2011; Mudd 2013). The initial period of lead mining was sporadic due to low tonnage, difficulties separating lead from zinc and more profitable copper mines nearby (Both 2011). Lead mining reached new levels of operation and production after the discovery of the world's largest lead-zinc-silver ore body in Broken Hill, New South Wales (NSW). This ore body has been mined continuously since 1885 with ore reserves projected to allow mining to continue over the next decade (Perilya Limited 2015). Discovery of other ore bodies rich in lead, such as in Mount Isa, Queensland (Qld) in 1924, has advanced Australia to being second in the world for lead production (U.S. Geological Survey 2015). Production of lead from Australian mining operations to date is in the order of 40 million tonnes (Mudd 2013) with Broken Hill responsible for half the lead produced followed by Mount Isa with approximately a quarter (Mudd 2007). The remaining lead produced has come in smaller quantities from more than 80 mines around Australia, the majority of which are no longer in operation (Geoscience Australia 2012). Current annual production of lead in Australia is 690,000 tonnes from over 20 active mines (Geoscience Australia 2012; Department of State Development 2014).

1.3 Smelting

Early smelting works coexisted with the first mining activities in South Australia in the 1840s (Smith 1988). These were characterised by small chimneys able to deal with the low volumes of ore produced. Smelting was initially conducted onsite at Broken Hill with many of the mining companies operating their own smelters, with 27 smelters in operation between 1886 and 1897 (Woodward 1965). Soon the increased production of ore and the lack of fuel for the smelters required alternative arrangements. The first smelter in Port Pirie opened in 1889 with all of Broken Hill's smelting works conducted in Port Pirie by 1897 (Figure 1.2) (Woodward 1965; Body 1986). The lead smelting facility at Port Pirie is currently one of the world's largest and presently ranks as the second biggest emitter of lead in Australia (NPI 2015a). Contamination from these long term emissions of large volumes of lead can be measured as far as 40-65 km around the Port Pirie lead smelter (Cartwright et al. 1976). Other smelting works emitting large volumes of lead in Australia include the Mount Isa lead smelter, Qld (1931 - ongoing), Hobart zinc smelter, Tasmania (Tas) (1916 – ongoing) Kalgoorlie nickel smelter, WA (1972 – ongoing) and Cockle Creek lead smelter, NSW (intermittent between 1897 - 2003). Emissions from smelters have caused widespread contamination to the environment together with population exposure to toxic substances, especially lead (Mackay et al. 2013; Kříbek et al. 2015; Li et al. 2015).



Figure 1.2: Lead smelting in Port Pirie from Broken Hill ore concentrates delivered in uncovered wagons, 1904 (Blainey 1968).

1.4 Leaded petrol

Lead in the organic form, tetraethyl-lead (TEL) was discovered as an antiknock agent in the United States (US) in the 1920s (Nriagu 1990). The rapid rise and domination of leaded petrol resulted in over 4 million tonnes of lead emitted into the atmosphere in the US (Mielke et al. 2011). While the US accounted for the majority of the market share of leaded petrol sales until the 1970s, global consumption was also on the rise (Nriagu 1990). Leaded petrol arrived on the Australian market in 1932 (Cook and Gale 2005). Following the

discovery of widespread contamination and evidence of the neurotoxic effects of lead, the long process of removing lead from petrol began in America in 1978 (Needleman 2008). Australia introduced unleaded petrol in 1985 and national regulations lowering the lead content in fuel throughout the 1990s, with the final ban on leaded petrol for cars completed in 2002 (McFarlane and Cass 1985; Office of Legislative Drafting and Publishing Attorney-General's Department 2002). As the major driver of petrol consumption was population, the emissions of lead during the leaded petrol era were therefore concentrated in Australia's populous capital cities (Farrington et al. 1981; Farrington and Australian Environment Council 1988).

1.5 Lead emissions

There are very few places in Australia that have not been affected by lead emissions, from mining and smelting towns to the consumption of leaded petrol in capital cities and all roads in between. Emissions of harmful substances such as lead went unmonitored and unregulated for many years (Figure 1.2) and only estimates can be placed on the total quantity. However, the consequences of these pervasive lead emissions can be observed through measurement of lead in air, water and soil and the harmful health issues associated with lead toxicity.

While there has been much action to reduce and eliminate sources of lead in recent decades through the removal of lead from paint and petrol, the worldwide demand for lead and Australia's resources has sustained mining and smelting operations. With the introduction of the *National Environment Protection (National Pollutant Inventory) Measure* in 1998, information on the quantities of harmful substances released into the environment has become available for evaluation. Although the emissions data is determined and reported by the industry operators, it is the best available data on toxic emissions in Australia. The goals and outcomes of the National Pollutant Inventory (NPI) include the improvement of air and water quality and minimisation of environmental impacts associated with the harmful substances (NPI 2015b). Yet despite this, significant volumes of lead continue to be emitted (Figure 1.3), from locations including Mount Isa, Port Pirie and Broken Hill.

The monitoring of lead in ambient air did not coincide with the advent of lead mining and smelting in Australia, nor did it start with the first sales of leaded petrol. Initially systematic measurement of lead in air concentrations was undertaken in the capital cities Sydney, Melbourne, Brisbane and Perth in the 1970s, with monitoring commencing in Canberra in 1990 (Department of the Environment and Heritage 2004). Regional monitoring of lead occurs in some locations, including Port Pirie and Mount Isa, where industry activities emit lead into the atmosphere surrounding local communities. Yet there are locations and time periods where no monitoring occurred despite the presence of lead emissions. Overall, the monitoring of lead emissions has been limited and a comprehensive understanding of the quantity, sources and impacts of lead emissions is lacking in Australia.



Figure 1.3: Distribution of Australia's largest lead emissions 2000-2014 (largest emitters determined from NPI data where at least one tonne was released within a given year).

1.6 Lead isotopic compositions

Lead isotopes have multiple applications and are now regarded as an environmental 'fingerprinting' tool. The measurement of lead isotopic compositions in environmental studies allows for a more precise and complete evaluation of contamination and its sources. The geochemistry of a particular location and system can provide a set of lead isotopic compositions that can be unique and identifying to a particular source (Sangster et al. 2000). Australia's geologically old ore bodies including Broken Hill and Mount Isa have low radiogenic lead isotopic compositions and are distinct in comparison to younger soil profiles in Australia and other domestic and international deposits of lead (Chiaradia et al. 1997; Bollhöfer and Rosman 2000). With knowledge of both the lead isotopic compositions of ore bodies and that the lead added to Australian petrol was sourced predominantly from Broken Hill and Mount Isa ore (Noden 1979; Gulson et al. 1981; Bollhöfer and Rosman 2000), it is possible not only to measure but also to identify the sources of lead contamination in the environment.

1.7 Australian research on lead

Lead contamination, and the consequent elevated BLLs in children, received attention in Australia throughout the 1980s and 90s which generated multiple studies. Despite this, investigation into environmental lead contamination was generally confined to Port Pirie (Cartwright et al. 1976; Merry and Tiller 1978; McMichael et al. 1988; Esterman and Maynard 1998; van Alphen 1999), Broken Hill (Gulson et al. 1994b; Gulson et al. 1995; Boreland and Lyle 2006), Boolaroo (Roy and Crawford 1984; Bately 1987; Gulson et al. 2004) and Sydney (Noller and Smythe 1974; Gulson et al. 1983; Roberts et al. 1983; Chiaradia et al. 1997). The majority of Australian blood lead studies have also been principally contained to Port Pirie (Calder et al. 1990; Baghurst et al. 1992; Tong et al. 1998; Maynard et al. 2003), Broken Hill (Gulson et al. 1994a; Phillips and Hall 1994; Gulson et al. 1996), Boolaroo (Ouw and Bisby 1976; Dalton and Bates 2005) and Sydney (Garnys et al. 1977).

Additional studies have been undertaken from other Australian capital cities (Wylie and Bell 1973; Farrington et al. 1981; Gulson et al. 1981; Lax et al. 1986; Tiller et al. 1987; Farrington and Australian Environment Council 1988; O'Connor et al. 1989; O'Connor et al. 1990; Simpson and Xu 1994) with very little from elsewhere in Australia (David and Williams 1975; Young et al. 1992; Willis et al. 1995; Chiaradia et al. 1997; Martley et al. 2004; Gulson et al. 2009; Taylor et al. 2010; Mackay et al. 2013). The only Australia wide investigation into sources of lead and childhood blood lead levels was carried out in 1995 (Donovan 1996). The average BLL of children sampled in Australia (n=1572) was determined to be less than the then Australian guideline of 10 μ g/dL. Since then there has not been any further Australia wide blood lead surveys.

After the removal of lead from petrol in 2002, the number of studies conducted on environmental lead contamination in Australia became less frequent. There was a perception that the problem of lead emissions and contamination had been resolved following decreases in lead in air and BLLs. This has led to the assumption that we now have a cleaner environment in the post leaded petrol era. It is well known that lead is a persistent pollutant and soil and dust are major pathways of lead into the body (Zahran et al. 2013; Gulson et al. 2014), yet studies in Australia that examine ongoing emissions and delineating historical depositions in a contemporary context are lacking. The studies presented in this thesis dismantle the many misconceptions relating to contemporary lead exposures by providing new insights into an old, but ongoing, problem.

1.8 Aims

While the guidelines for lead concentrations in air, as well as other health and environmental related guidelines, are generally met in Australia today, they have become outdated as the evidence of adverse health effects of low levels of lead increases. There are still locations that are producing significant volumes of lead emissions (as well as coemitters arsenic, cadmium and zinc) and while not all of these locations are populated, it is important to demonstrate the ongoing exposure to lead from historical and contemporary sources. Further, it is essential to develop current methods and strategies to evaluate rates of exposure, especially to children, along with the impact and consequences to the environment and human health resulting from lead emissions.

The aims of this thesis, culminating in the studies presented in the following chapters, include:

- Quantification, identification and assessment of major historical and ongoing lead emissions in Australia that continue to play a role in contamination and health exposure risks;
- Measurement of lead emissions to the Australian environment from multiple anthropogenic sources including leaded petrol consumption and mining and smelting activities;
- Apportionment of the lead measured in the environment to natural or anthropogenic sources using lead isotopic compositions;
- Assessment of the ongoing impacts and consequences of historical and contemporary lead emissions on the environment, human health and guidelines;
- Evaluation of the environmental regulations pertaining to lead emissions and exposures.

Drawing on these aims, it is anticipated that a more developed understanding of the contemporary environmental consequences of the two major contributing factors of lead emissions – leaded petrol and lead production from mining and smelting operations – will be achieved. Distinction between these two lead emitters has been confounded in the literature due to a paucity of emissions data from leaded petrol and a tendency of some mining companies to rely on the impact of leaded petrol and paint to deflect attention from their own significant lead emissions.

The aims of this thesis complement each other in addressing the overarching issue of contemporary lead emissions. Identification of lead sources, measurement of lead in the environment and assessment of the impacts and consequences all inform a thorough analysis of lead emissions in a contemporary context. Through encompassing the multi facets of lead emissions in the studies presented in this thesis, the overarching aim of this thesis is achieved by bringing further understanding and awareness to the forgotten legacy and ongoing exposure to lead in Australia.

1.9 Materials and Methods

The aims of this thesis have been achieved through the use of multiple materials and methods to evaluate a range of situations in Australia where lead emissions are occurring or have occurred in the past. The mixed methods approach provides a comprehensive and diverse set of information in relation to lead emissions and associated contaminants. Specific details of the materials and methods used for each part of this thesis are provided within each study publication.

Primarily, lead isotopic compositions have been utilised to determine the source of lead contamination in the environment. Lead isotopic compositions have enabled elucidation between different contemporary and historical emissions of lead and natural lead in the environment. Multiple elemental analyses including arsenic, cadmium, copper and zinc in conjunction with lead concentration measurements has been used to assess and confirm lead sources that co-emit multiple elements. This has been used to support lead isotopic compositions or to provide primary evidence when lead isotopic compositions could not be applied. Lead isotopic compositions could not be applied. Lead isotopic compositions could not be applied in Port Pirie or Boolaroo due to the mixed smelter feedstock sourced from Elura, NSW, Rosebery, Tas, Cannington, Qld (Department of State Development 2014) and ANGAS, SA ore (Jackson and Abbot 2008) in addition to Broken Hill ore.

A range of materials and matrices were collected and tested to develop the weight of evidence of sources of lead contamination. Soil samples were collected in depth profiles (0-2; 2-10; 10-20; 20-30; 30-40; 40-50 cm) to establish background concentrations and isotopic compositions of lead at depth and to measure contemporary and historical sources of lead emissions in the upper surface soils. Surface and hand dust wipes allowed for measurement of exposure to contemporary sources and air filters were used to establish temporal lead in air concentrations and isotopic compositions. In addition, more pioneering methods for Australia of measuring lead concentrations and isotopic compositions in bushfire ash deposits and historical wine provided data on the temporal impact of lead emissions to environments that are generally considered more pristine.

In addition to the environmental samples collected, historical information, together with mining and smelting data and government publications were compiled and incorporated into the studies in this thesis. This diversity of materials and methods has enabled the production of a comprehensive investigation into the sources, measurement, impacts and consequences of lead emissions into the Australian environment.

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CHAPTER 2: Quantification and identification of sources of lead emissions

Chapter Two presents the following two papers:

- Paper One: Quantification of atmospheric lead emissions from 70 years of leaded petrol consumption in Australia. Kristensen, L.J. (2015). *Atmospheric Environment*, 111, 195-201
- Paper Two: Licenced to pollute but not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations. Taylor, M.P., Davies, P.J., Kristensen, L.J., & Csavina, J.L. (2014). *Aeolian Research*, 14, 35-52.

The two papers in Chapter Two focus on the major sources and volumes of lead emissions in Australia. These papers are essential in understanding the full cycle of lead emissions, from the identified source(s) presented in this chapter, to measurement of the emissions in the environment, to human health and environmental impacts and consequences, regulation and remedial action. The identification and assessment of the sources presented in this chapter provide the basis on which further work has been conducted within this thesis.

This chapter presents research into quantifying both historical and contemporary sources of lead emissions in Australia. The papers in this chapter together quantify the largest contributors to lead emissions in Australia: leaded petrol consumption and mining and smelting activities. Quantifying the lead emissions from the various sources provides context to direct measurement of lead in the environment which is required to evaluate the overall impact and consequences resulting from lead emissions. This chapter on quantifying lead emissions is the first stage in the overarching investigation into lead emissions in Australia.

Paper One

Quantification of atmospheric lead emissions from 70 years of leaded petrol consumption in Australia

Kristensen, L.J. (2015) Atmospheric Environment 111, 195-201.

Supplementary Information in Appendix A

This paper fills a large and important gap in the literature regarding the volume of lead emissions across Australia as a result of leaded petrol consumption. While leaded petrol has long been associated with significant lead emissions, contaminated environments and elevated blood lead levels, no complete quantification of emissions has been undertaken. This paper contributes to this thesis by calculating the total volume of lead emitted through petrol consumption in Australia as well as compiling a comprehensive database of leaded petrol statistics to evaluate lead emissions on a state and territory level. This paper also provides context to contemporary lead emissions and a retrospective analysis of the largest lead emission source in Australia. Atmospheric Environment 111 (2015) 195-201



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Quantification of atmospheric lead emissions from 70 years of leaded petrol consumption in Australia



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ATMOSPHERIC ENVIRONMENT

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HIGHLIGHTS

- A complete compilation of leaded petrol sales figures for Australia.
- Lead emissions were calculated from leaded petrol concentrations and sales figures.
- Nearly one guarter million tonnes of lead released from petrol across Australia.
- Peak emissions of lead from leaded petrol occurred during the 1970s.
- Elevated ambient lead levels in cities were the result of leaded petrol.

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ABSTRACT

Lead is a persistent pollutant and the subject of many environmental studies, yet, in Australia, the extent of atmospheric lead emissions from the use of leaded petrol is unquantified. This paper details the first comprehensive account of leaded petrol sales and its lead concentrations over the 70 years of use in Australia. The resulting atmospheric lead emissions are calculated to provide the most complete understanding of the volume of lead released to the Australian continent from the consumption of leaded petrol. Atmospheric emissions of lead to the entire Australian continent from leaded petrol are calculated to total 240,510 tonnes over seven decades of use, peaking at 7869 tonnes in 1974. Total emissions for individual states and territories range from 1745 to 67,893 tonnes, with New South Wales responsible for the largest emissions. The effect of regulations on allowable concentrations of tetraethyl-lead additives are observed in the reduction of leaded petrol consumption in Australia's populous cities are examined against historical air quality data and blood lead levels.

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1. Introduction

The history of leaded petrol use has been described in detail (Nriagu, 1990; Needleman, 1998; Oudijk, 2010), from the discovery of lead (as tetramethyl- or tetraethyl-lead) as an antiknock agent, associated public health concerns, to the prohibition of its use in petrol. The use of leaded petrol resulted in the emission of large quantities of lead that are still present in the ambient environment, which may continue to cause concerns for health (Mielke et al., 2011). Although the United States was responsible for 80% of all leaded petrol sold globally prior to 1970 (Nriagu, 1990), Australia was a substantial consumer of lead petrol products. The use of leaded petrol in Australia over a 70 year period, from 1932 (Cook

and Gale, 2005) to 2002 (Fuel Standard (Petrol) Determination, 2001), was a major contributor to atmospheric lead levels (Australian State of the Environment Committee, 2001; Department of the Environment and Heritage, 2004). Leaded petrol emissions accounted for up to 90% of atmospheric lead (Department of the Environment and Heritage, 2004) (where no other major lead industry was present) as 75% of lead in petrol was emitted from engine combustion (Australian Bureau of Statistics (ABS), 1997; U.S. EPA, 1986) (with a further 2% emitted to the atmosphere from fuel tank evaporation (Australian Bureau of Statistics (ABS), 1997).

As Australia's population grew, from 6.5 million in 1932, to 10 million in 1959, to just shy of 20 million in 2002 (Australian Bureau of Statistics (ABS), 2008), so did the demand for leaded petrol in Australia (Donnelly, 1981), resulting in elevated ambient lead

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levels, particularly in metropolitan areas (Australian State of the Environment Committee, 2001; Abeeb et al., 2003). The adverse health effects of environmental lead have been thoroughly documented (Bellinger, 2008; Needleman, 2004; Rossi, 2008) along with the correlations of petrol-derived ambient lead levels and childhood blood lead levels in America (Annest et al., 1983; Lovei, 1998; Schwartz et al., 1985). With the introduction of unleaded petrol in Australia in 1985 (Australian Institute of Petroleum (AIP), 1986) and the subsequent phase out of leaded petrol by 2002 (Fuel Standard (Petrol) Determination, 2001), ambient lead levels have fallen in metropolitan urban centres to levels less than 10% of Australia's current guideline for lead in ambient air (0.5 μ g/m³) (Abeeb et al., 2003; National Environment Protection Council (NEPC), 1998).

Although leaded petrol has not been used in Australia in over a decade, environmental lead contamination persists. Understanding the history and extent of lead pollution is essential for evaluating long term environmental and human impacts (Cook and Gale, 2005). Studies quantifying emissions of petrol-derived lead in Australia are only available for limited years (Farrington and Australian Environment Council, 1988; Farrington et al., 1981) or locations (Abeeb et al., 2003; O'Connor et al., 1990; Gulson et al., 1983). The total volume of lead emitted into Australia's atmosphere from petrol consumption has never been determined despite multiple studies (Birch et al., 2011; Cooney et al., 1989; Cowie et al., 1997; Olszowy et al., 1995; Roberts et al., 1983) of the environmental and human health consequences. This study provides the first comprehensive compilation of Australian leaded petrol data, enabling calculation of the associated annual lead emissions. This new data allows consideration of the historical impact and future implications of leaded petrol consumption in Australia.

2. Methods and approach

Sales figures for leaded petrol from 1949 to 2002 were compiled from the Australian Bureau of Statistics (ABS) and Australian Institute of Petroleum (AIP) monthly bulletins and yearly reports. Sales figures are not available prior to 1949, instead ABS petrol import figures of petrol are used as surrogates because imports constituted the dominant proportion of petrol used in Australia until 1954 (Petroleum Information Bureau (Australia), 1960a). Sales and import figures for the years 1933-1957 are reported for the financial year (July 1st to June 30th) rather than the calendar year. Limited sales figures are also included in government reports (Berry et al., 1993; Cosgrove, June 2003; Trewin, 1997), but they do not always align with official sales figures reported by the AIP due to differing regional boundaries (Supplementary Fig. S1). Concentrations of tetraethyl-lead added to petrol have been reported by Associated Octel (Associated Octel, 1964; Associated Octel, 1968; Associated Octel, 1969; Associated Octel, 1975; Associated Octel, 1993; Octel, 1979), who was responsible for leaded petrol in Australia. Petrol regulations and actual average lead in petrol concentrations have been reported emission inventories and related studies (Nriagu, 1990; Farrington and Australian Environment Council, 1988; Farrington et al., 1981; O'Connor et al., 1990; Roberts et al., 1983; Trewin, 1997; Australian Institute of Petroleum, 1997; Australian Institute of Petroleum, 1998; Donovan, 1996).

Annual atmospheric lead emissions are calculated from leaded petrol sales data and the concentration of lead in each litre of petrol (data in Supplementary Tables S1 and S2) and the percentage of lead emitted from engine exhausts (Australian Bureau of Statistics (ABS), 1997; U.S. EPA, 1986; European Environmental Agency, 2013). Where the actual petrol lead concentration average is not known, the regulated maximum value of lead additives is used. Emissions from vehicles are calculated as follows:

$$E_{Pb/y} = Pb_{g/L} \times S_{L/y} \times 0.75$$

where $E_{Pb/y}$ is lead emissions from petrol per year, $Pb_{g/L}$ is the grams of lead per litre of leaded petrol, $S_{L/y}$ are the yearly sales of leaded petrol and 0.75 is the emission factor of lead emitted from petrol combustion (Department of the Environment and Heritage, 2004; Australian Bureau of Statistics (ABS), 1997; Brunekreef, 1984). Using this calculation method the correlation coefficient is 0.986 (Pearson correlation, p < 0.00001) between the calculated emissions of South Australia (SA) presented in this paper and those previously reported (Abeeb et al., 2003) (n = 12; largest available dataset), indicating the annual lead emission values calculated herein are robust and consistent with other studies.

3. Results and discussion

3.1. Leaded petrol sales

Sales figures (Supplementary Table S1) for total leaded petrol sales in Australia include both standard grade and super grade leaded petrol sales. Premium or "super" grade leaded petrol was introduced in June 1955 (Petroleum Information Bureau (Australia) and October, 1960b). Although sales figures are for states and territories, where available, sales figures for capital cities are provided. In New South Wales (NSW), Victoria (VIC), SA and Western Australia (WA), the sales figures for the capitals Sydney, Melbourne, Adelaide and Perth, are more than half the respective State annual total sales in 1976 (Donnelly, 1981; Farrington et al., 1981) and in 1985 (Australian Institute of Petroleum (AIP), 1986; Farrington and Australian Environment Council, 1988), with the exception of Sydney. For both these years, Queensland (QLD) capital, Brisbane, accounted for less than 50% QLD leaded petrol sales (Donnelly, 1981; Australian Institute of Petroleum (AIP), 1986; Farrington and Australian Environment Council, 1988; Farrington et al., 1981).

3.2. Lead petrol regulations

Initially, with the primary goal of achieving better fuel quality by increasing octane ratings, concentrations of lead in petrol were not regulated. However, it was not possible to raise the octane ratings indefinitely through the addition of greater quantities of tetraethyllead (Petroleum Information Bureau (Australia), 1959), with octane ratings plateauing at a lead concentration of 0.84 g/L (Michalski and Unzelman, 1980). As awareness that lead in petrol was a major environmental and health problem, the National Health and Medical Research Council recommended that yearly atmospheric lead emissions from petrol should not be permitted to rise above 1973 levels (National Energy Advisory Committee, 1978). Exhaust gases from leaded petrol combustion had a lead concentration of 75–80 mg/m³ based on 0.84 g/L petrol lead concentration, which was four times the then statutory limit for stationary lead sources discharged at height (Australian Environment Council, 1977) (instead of ground level as in the case of leaded petrol consumption).

In Australia, regulatory power is vested with state and territory governments to introduce legislation relating to motor vehicles (Faiz et al., 1996; Environment Australia, 2000). As such, legislation for the reduction of lead concentration in petrol was introduced by a number of states, but not nationwide and not simultaneously. Changes in petrol lead concentration across the states and territories are summarised in Fig. 1. While these changes detail the maximum allowable lead concentrations, the actual lead



Fig. 1. The reduction of maximum lead in petrol concentrations for state and territories of Australia.

concentrations in petrol may have differed from the maximum permissible standards. Additionally, there were two regulation levels for NSW, with tighter regulations implemented for the populous regions of Sydney, Newcastle, Wollongong and the Australian Capital Territory (ACT), with the rest of the State (population consisting of ~30%) retaining the original 0.84 g/L regulation (NSW 1 and NSW 2 respectively; Fig. 1). In addition, lead concentration in petrol can be highly variable depending on refinery, original crude oil and sources of imports (Oudijk, 2010).

Unleaded petrol was introduced nationally across Australia from July 1 1985 (Australian Institute of Petroleum (AIP), 1986; McFarlane and Cass, 1985) with certain states making unleaded petrol available from April 1985. However, the initial impact of unleaded petrol was minor as few vehicles were able to run on unleaded petrol (Australian Institute of Petroleum (AIP), 1986). Less than 2% of petrol sales comprised unleaded fuel in 1985 (Australian Institute of Petroleum (AIP), 1986) and only 6% in 1986 (Australian Institute of Petroleum (AIP), 1987). For all cars built from January 1 1986, it was mandatory they be able to run on unleaded petrol. The sales of unleaded petrol increased as Australia's vehicle fleet changed and parity between leaded and unleaded petrol sales was reached in 1994 (Australian Institute of Petroleum (AIP), 1994; Australian Institute of Petroleum (AIP), 1995a).

The phase out of leaded petrol in Australia under the *National Fuel Quality Standards Act 2000* (Fuel Standard (Petrol) Determination, 2001) implemented regulations of allowable lead concentrations in petrol for all states and territories (Supplementary Table S2). A lead concentration in petrol of 0.20 g/L was introduced in 1995 for NSW/ACT and QLD and 0.30 g/L for the rest of Australia (Australian Institute of Petroleum, 1995b). The 0.20 g/L regulation was met nationwide by January 1 1996 (National Environment Protection Council (NEPC), 1998) with the exception of SA which achieved the guideline by October 1 1996 (Australian Institute of Petroleum, 1996).

Western Australia introduced a "cleaner fuels" initiative through their *Environmental Protection (Diesel and Petrol) Regulations* 1999 that imposed a maximum lead in petrol concentration of 0.005 g/L from January 1 2000 (Environmental Protection, 2000). Queensland also implemented a faster phase out of leaded petrol requiring all petrol sales to be unleaded by March 1 2001 (Department of the Environment and Heritage, 2001). As the nationwide phase out deadline was drawing close, sales of leaded petrol reduced dramatically. Less than 4 ML of leaded petrol was sold in Australia from July to October in 2002 with no sales recorded in November and December 2002 (Australian Petroleum Statistics; Bureau of Resources and Energy Economics (BREE), 2014).

3.3. Emissions of lead associated with leaded petrol use

In Australian capital cities, 90% of atmospheric lead resulted from motor vehicle emissions during the era of leaded petrol (Department of the Environment and Heritage, 2004). More than 90% of the airborne lead was found in fine particulates ($<2.5 \mu m$) (Department of the Environment and Heritage, 2004), which are respirable (Australian Environment Council, 1977) and dangerous to human health (Ning and Sioutas, 2010; Csavina et al., 2011) as the fine particles are inhaled into the lungs and absorbed into the blood stream resulting in higher bioavailability and a higher lead dose (Csavina et al., 2012). Organo-lead compounds, tetramethyl- and tetraethyl-lead, that were used in leaded petrol are considered to be more toxic than inorganic forms of lead. However, >90% of lead emissions from leaded petrol combustion were in the form of halogenated lead compounds (eg. lead bromochloride [PbBrCl]) due to scavengers added to leaded petrol (Agency for Toxic Substances and Disease Registry (ATSDR), 2007; Fergusson, 1986). Halogenated lead compounds alter in the atmosphere to form products of lead carbonates (53%), lead oxides (12%) and lead sulphates (3%) (Ter Haar and Bayard, 1971).

The total lead loading from leaded petrol emissions in Australia is nearly one-quarter million tonnes over 70 years. The calculated yearly volumes of lead emissions in Australia as well as individual state and territory lead emissions are presented in Table 1.

The consequence of the rise and fall of leaded petrol use and the effect of regulations of lead concentration in leaded petrol in Australia are evident in the temporal changes in lead emissions (Fig. 2). Without the introduction of regulations for lead concentration in petrol, the growth in car ownership and demand for petrol would have resulted in ever increasing lead emissions. Key factors that influenced significantly the amount of lead emissions from leaded petrol were the implementation of regulations, the introduction of unleaded petrol and the phase out of leaded petrol. As NSW and VIC were the major consumers of leaded petrol in Australia, accounting for an average of over 60% of annual leaded petrol sales for the country, regulations of allowable lead in petrol had significant influence on emissions within the two states and for total leaded petrol emissions in Australia (Fig. 2). The introduction of unleaded petrol and the phase out of leaded petrol from the late 1980s to the beginning of the 2000s resulted in the decline of leaded petrol sales and consequent reductions of petrol lead emissions, especially in Australian cities (Department of the Environment and Heritage, 2004; Abeeb et al., 2003; Simpson and Xu. 1994).

Limitations in the calculation of lead emissions include the assumption that all petrol imports into Australia from 1933 to 1949 were leaded petrol. No distinction is made in the historical records as to the type of petrol imported during this period. However, considering the increase in octane rating received from leaded petrol, the improved fuel quality was favoured. Data detailing the actual concentrations of lead in petrol is the biggest limitation in the calculations of lead emissions in this study. Lead concentrations varied between super and standard grade petrol, although one grade was predominantly sold at any time. Actual lead concentrations (Fig. 1, Supplementary Table S2) and as such lead emissions may be slightly over estimated. No import or sales figures were reported for 1940–1941 resulting in an under calculation for total lead emissions in Australia. Nevertheless, the calculated values are the most

Table 1

Calculated volumes of lead emissions for each state or territory and totals for Australia (tonnes).

Year	Australia	Year	Australia	Year Au	ıstralia Year	Australia	a Year	Australia
		1936 ^c	695.6	1943 ^c 9	946.5 1948	1102.0	1953 ^c	1958.9
		1937 ^c	769.2	1944 ^c 10)14.7 1949 ^o	1236.8	1954 ^c	2179.4
1933 ^c	493.7	1938 ^c	907.8	1945 ^c 7	782.8 1950 ^o	1411.5	1955 ^c	2403.5
1934 ^c	567.4	1939 ^c	954.7	1946 ^c 10)12.0 1951 ^o	1731.6	1956 ^c	2604.3
1935 ^c	578.3	1942 ^c	722.8	1947 ^c 9	973.8 1952°	1868.8	1957 ^c	2747.7
Year	Australia ^a	NSW ^b	VIC	QLD	SA	TAS	WA	NT
1958	3028.7	1032.5	933.0	413.2	316.4	101.3	224.9	7.4
1959	3267.9	1116.7	1004.9	450.1	338.7	108.8	240.7	7.9
1960	3546.3	1228.2	1097.1	482.3	354.6	116.4	258.7	8.9
1961	3689.2	1287.3	1128.3	498.1	373.1	119.1	273.0	10.1
1962	3959.9	1390.3	1196.7	538.9	398.5	128.0	296.7	10.8
1963	4243.7	1485.7	1282.8	575.9	427.7	137.5	322.3	11.8
1964	4604.1	1611.7	1377.8	636.2	465.8	147.2	351.9	13.5
1965	4884.3	1704.7	1453.5	677.4	498.3	157.6	379.5	13.4
1966	5073.5	1765.3	1505.7	707.7	508.8	163.7	407.7	14.7
1967	5350.3	1864.5	1578.9	744.6	530.5	173.8	441.1	16.9
1968	5660.2	1978.5	1660.4	787.1	546.8	180.6	485.7	21.2
1969	6060.1	2106.5	1757.8	849.9	587.7	189.6	538.5	30.2
1970	6412.6	2245.8	1853.3	893.6	605.9	196.3	580.2	37.4
1971	6/44.9	23/5.4	1945.7	941.9	625.3	202.8	612.2	41.7
1972	7075.3	2469.3	2058.7	1007.2	648.6	211.3	635.0	45.2
1973	/615.8	2631.8	2188.9	1124.9	706.9	227.0	688.1	48.3
1974	7869.1	2/16.5	2240.2	1155.5	/51.6	234.5	/18.6	52.1
1975	7034.5	2322.4	1004.5	1231.0	770.7	237.8	/55.1	52.4
1976	/20/.8	2379.0	1/01.8	1288.8	/04.3	189.4	/05.1	59.0
1977	6/51.0	2038.1	1505.0	1358.0	δ11.1 916.2	154.7	822.1	61.4
1976	6000.0	2075.4	1334.0	1424.4	010.5 912.0	137.1	601.4 850.5	66.7
1979	6703.8	1086 1	1420.4	1489.0	812.9	144.0	850.3	69.0
1081	6851.6	2005.0	1/10/	1500.8	780.6	145.5	850.5	72.5
1987	6893.4	1975.8	1415.4	1664.8	700.0	137.7	803.8	72.5
1983	6871.7	1981.4	1425.0	1604.5	793.1	136.4	857.0	743
1984	6380.3	2018.9	976.3	1682.7	668.4	142.8	813.7	74.5
1985	6314.2	2010.5	980.1	1686.2	666.3	144.5	749.1	82.6
1986	6096.5	1939.3	951.8	1654.8	655.3	142.0	669.7	83.5
1987	5898.5	1828.7	906.5	1570.3	624.0	133.1	758.3	77.5
1988	5688.6	1750.7	870.4	1573.5	598.7	129.0	694.5	71.8
1989	5394.1	1616.8	830.9	1521.4	573.3	126.1	658.8	66.8
1990	4925.3	1463.5	748.9	1393.6	522.2	120.4	612.7	63.9
1991	4494.0	1335.9	673.8	1288.4	475.8	111.2	551.2	57.8
1992	4247.3	1245.1	632.0	1238.0	454.5	106.2	516.3	55.3
1993	3757.8	1148.1	599.1	1173.9	351.8	101.6	332.9	50.3
1994	2055.5	561.8	423.8	495.0	219.4	82.7	252.0	20.8
1995	1066.3	233.1	208.9	258.4	127.2	57.3	162.1	19.3
1996	847.0	225.1	188.9	187.3	111.7	36.0	89.3	8.7
1997	740.8	190.5	165.6	164.9	100.8	32.6	78.6	7.8
1998	502.4	142.0	132.5	102.4	47.8	18.9	52.3	6.6
1999	427.2	115.4	112.2	90.7	41.9	16.8	44.6	5.6
2000	333.6	88.6	87.8	73.6	33.8	14.0	31.7	4.1
2001	237.6	66.5	70.0	58.8	26.5	11.8	0.8	3.0
2002	98.8	26.4	30.1	24.4	11.5	5.1	0.3	0.8
Total ^a	240,510.6	67,893.3	49,443.3	41,858.8	22,190.2	5769.0	21,947.7	1744.8

^a Totals may differ due to rounding.

^b ACT included in value.

^c Fiscal year (July–June).

comprehensive estimate for total lead emissions during the full period of leaded petrol consumption in Australia.

3.4. Consequences of leaded petrol emissions

Given that 240,510 tonnes of lead from petrol were released into the Australian atmosphere, the pertinent question is where did it go and what was its impact? Fine particulates such as those lead particles released from engine exhausts, have a longer retention time in the atmosphere and as a result able to travel further (Csavina et al., 2012; Fergusson, 1986). Fallout rates from leaded petrol averaged 1 μ g/cm²/day in metropolitan Sydney with rates rising to 5 μ g/cm²/day in the inner city area (Davies, 1980). This equates to roughly 700 tonnes/year of lead in the CBD region of Sydney, approximately 20–30 % of lead emitted in NSW during the peak period of leaded petrol use. With roughly 50–60 % of leaded petrol consumed in metropolitan Sydney, it is possible that another 700 tonnes during peak emissions was deposited in Sydney outside the CBD with the remaining emitted lead being deposited over the rest of NSW, particularly in metropolitan Newcastle and Wollongong as well as the ACT.

Ambient lead levels around Australia during the period of leaded petrol consumption reached up to 40 times the current 0.5 μ g/m³ guideline (National Environment Protection Council (NEPC), 1998). A 1972 (Matoušek and Brodie, 1973) study showed ambient lead levels up to 6.2 μ g/m³ in Melbourne with lead levels



Fig. 2. Calculated lead emissions from leaded petrol combustion in Australia and within each state or territory after 1958.

reaching 6.5 μ g/m³ inside cars and 9.5 μ g/m³ in underground car parks (Matoušek and Brodie, 1973). Peak values during business hours in Sydney and Melbourne CBD's have been reported as high as 10 μ g/m³ and 19.6 μ g/m³, respectively (Davies, 1980). Twentyfour hour ambient air levels of up to 3.5 μ g/m³ were recorded in the CBD's of Adelaide (Steer, 1984), Brisbane (Department of the Environment and Heritage, 2004) and Perth (O'Connor et al., 1989). These ambient lead levels have resulted in elevated lead concentrations in soil and vegetation. Australian studies (Birch et al., 2011: Olszowy et al., 1995: Noller and Smythe, 1974: Wylie and Bell, 1973) have shown strong correlations of lead concentrations with proximity to major roads and high traffic density in Australia's major cities. The impacts of leaded petrol emissions in the accumulation of lead in soils has also been measured outside of Australia's capital cities (David and Williams, 1975; Rouillon et al., 2013) highlighting the extensive reach and impact of leaded petrol emissions in Australia. Although ambient lead levels are now well below guideline levels (Abeeb et al., 2003; Department of Environmental Protection (2001)), the fate of historic petrol lead in soil and dusts remains a health concern as a source of lead exposure in children (Laidlaw and Filippelli, 2008; Laidlaw and Taylor, 2011; Laidlaw et al., 2014).

In response to the lowering of lead concentrations in petrol and the phase out of leaded petrol, blood lead levels have declined internationally (Annest et al., 1983; Brunekreef, 1984; Thomas et al., 1999; Wu et al., 2011). A decrease in blood lead levels has also been observed throughout Australia from the 1990s (Taylor et al., 2014). Although very limited blood lead studies were conducted in Australia, a correlation (r = 0.970, p < 0.00001) can be established between lead emissions from petrol in NSW and blood lead levels of children in Sydney (Cooney et al., 1989; Cowie et al., 1997; Donovan, 1996; Garnys et al., 1979; Gulson et al., 2006, 2001; McBride et al., 1982; Mira et al., 1996; New South Wales (NSW) Health, 2002; Young et al., 1992) (Fig. 3). Notwithstanding the limited blood lead data and using NSW emissions as a surrogate for Sydney (which is approximately 70% of the population of the NSW State petrol marketing area), the association is consistent with previous studies.

Evidence that the lead has accumulated in soils around Australia, especially in major cities, means that environmental lead contamination and the risk to human health from leaded petrol is an ongoing issue (Juhasz et al., 2011). These environmental consequences of leaded petrol emissions affected human health with a body burden as a result of unregulated leaded petrol in the 1970s ranging between 120 and 480 mg (Schroeder and Nason, 1971). The current body burden of lead due to leaded petrol is harder to evaluate as historic lead in soils and dust is now the primary source of historic lead from petrol and is intermixed with additional sources of lead (e.g. paint). Awareness of the health hazards of lead resulted in tightening of regulations and guidelines further



Fig. 3. Lead emissions from NSW sales of leaded petrol and Sydney blood lead levels (Cooney et al., 1989; Cowie et al., 1997; Donovan, 1996; Garnys et al., 1979; Gulson et al., 2006; Gulson et al., 2001; McBride et al., 1982; Mira et al., 1996; New South Wales (NSW) Health, 2002; Young et al., 1992).

lowering the current body burden of lead from petrol and other sources of lead contamination in Australia such as paint, mining and smelting. However, with increasing evidence of negative impacts on health below 5 μ g/dl (Jusko et al., 2008; Lanphear et al., 2005; U.S. EPA, 2013), the significant historic lead depositions from leaded petrol remain substantial sources of lead, especially to children. The total quantification of leaded petrol emissions provided by this paper will be essential to further assess the requirements in reducing current and future exposure to lead in Australia.

Lead isotopic compositions can be used to apportion atmospheric lead to specific sources, such as lead petrol emissions. For example, the lead used in petrol in Turin, Italy, was switched to lead from Broken Hill in 1975, which possessed a distinctly different lead isotopic composition to previous lead additives (Facchetti, 1989). The atmospheric lead isotopic composition in Turin altered from ²⁰⁶Pb/²⁰⁷Pb: 1.19 to match precisely the Broken Hill sourced lead petrol additive (²⁰⁶Pb/²⁰⁷Pb: 1.04) almost instantaneously (Facchetti, 1989). The lead isotopic compositions of Turin residents' blood lead altered to reflect the new atmospheric lead source. The limited information relating to the lead isotopic compositions of Australian petrol (Gulson et al., 1983; Bollhöfer and Rosman, 2000; Chiaradia et al., 1997), makes it difficult to account for all of the specific sources of environmental contamination. However, it has been reported that Associated Octel used lead derived primarily from Broken Hill ore (Bollhöfer and Rosman, 2000; Chen et al., 2005). In addition to lead from Broken Hill, Australian lead from Mount Isa. OLD as well as ores from USA and Canada were used to make tetraethyl-lead for Australian petrol (Gulson et al., 1981).

4. Conclusion

Leaded petrol was consumed in Australia for 70 years during which time 240,510 tonnes of lead was released into the environment. This study shows that almost half of the petrol-derived lead was released in NSW and VIC, which comprise almost 60% of Australia's population. Given that this is the first complete quantification of leaded petrol emissions to the Australian environment, it is now possible to evaluate more comprehensively the effects of past actions on its resident population and the environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.04.012.

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Paper Two

Licenced to pollute but not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations

Taylor, M.P., Davies, P.J., **Kristensen, L.J.**, & Csavina, J.L. (2014). *Aeolian Research, 14*, 35-52.

Supplementary Information in Appendix B

This paper addresses the difficulties in regulating and reporting emissions of toxic substances including lead in Australia. After petrol, mining and smelting operations account for the largest volumes of lead emissions, especially in a contemporary context. Australian guidelines, to protect environmental and human health are overridden by special licences for Australia's top two lead emission facilities, located in Mount Isa and Port Pirie. This paper contributes to this thesis by outlining the arrangements that allow for lead and other toxic contaminants to be continually emitted into the atmosphere in proximity to communities and the lack of transparency in reporting lead in air concentrations affecting children in these locations.
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Licenced to pollute but not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations



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ABSTRACT

This article details and examines the impact of significant inconsistencies in pollution licencing, monitoring and reporting from Australia's leading mining and smelting communities of Mount Isa in Queensland and Port Pirie in South Australia. Although emissions to the environment are regulated according to Australia's national air quality standards, significant atmospheric point source toxic emissions of arsenic, lead and sulfur dioxide continue to contaminate Mount Isa and Port Pirie communities.

Short-term atmospheric contaminant emissions across residential areas from the Mount Isa Mines operations are significant: in 2011, 24-h maximum suspended particulate (TSP) values for lead-in-air and arsenic-in-air were 12.8 μ g/m³ and 2973 ng/m³, respectively. The relevant Queensland air quality objectives for lead and arsenic are 0.5 μ g/m³ (TSP) and 6 ng/m³ (PM₁₀), respectively, averaged over a year. Mount Isa is also blanketed by elevated sulfur dioxide concentrations, with the Australian and Queensland 1-h air quality standard (0.2 ppm) being exceeded on 27 occasions in 2011. At Port Pirie, contamination of the urban environment is arguably worse with 24-h maximum TSP values for lead-in-air and arsenic-in-air of 22.57 μ g/m³ (2011) and 250 ng/m³ (2009), respectively. Port Pirie has an annual average lead-in-air standard of 0.5 μ g/m³ (TSP) but there are no set values for arsenic. In 2012, the national 1-h standard for sulfur dioxide was exceeded 50 times in Port Pirie.

Despite chronic childhood blood lead exposures in both communities, there is a history of denial and downplaying of the source and impact of the contamination. A contributory factor to this pattern of behaviour is the fragmented and inconsistent delivery of data as well as its interpretation in relation to environmental and health impacts from exposures. This study reviews available data sources and makes inference to the impacts from contamination and in doing so, explains why the current regulatory framework fails to protect the impacted communities.

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1. Introduction

This paper examines and evaluates the effectiveness of environmental management policy to regulate atmospheric pollution from Australia's two primary lead producing facilities at Mount Isa Mines Ltd, Queensland and Nyrstar Port Pirie Pty Ltd, South Australia. In this study of emissions regulation and control, we focus on lead, arsenic and sulfur dioxide because of their known adverse effects on human health. Lead and arsenic are well known neurotoxins and carcinogens (e.g. ATSDR, 2004; NTP, 2012; USEPA, 2013) while sulfur dioxide adversely affects respiratory condition (Smargiassi et al., 2009). Although environmental assessments of the impact of the two facilities have been compiled in recent studies (Taylor and Hudson-Edwards, 2008; Noller et al., 2009; Taylor et al., 2009, 2010, 2011, 2013; Mackay et al., 2013), the usefulness of the monitoring and regulation regime for minimizing environmental harm and protecting public health has not been subject to the same sort of analysis. This paper assembles, analyses and reviews critically the existing air quality monitoring data for Australia's primary lead mining and smelting operations at Mount Isa and Port Pirie. Further, in the adjoining communities, existing pollution licence, environmental legislative instruments and health data are evaluated to ascertain their efficacy for achieving appropriate environmental and human health protection.

The Mount Isa mine is located in a remote area of north-west Queensland, 1800 km from the state capital city of Brisbane and

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Fig. 1. Air quality sample sites at Mount Isa (Queensland) and Port Pirie (South Australia). The Mount Isa air quality samples sites include a combination of industry sites (XMIM, 2013) and the two Queensland Government air quality-monitoring sites at Menzies and the Gap, which are used for NEPM reporting (sulfur dioxide at both and leadin-air only at The Gap) (EHP, 2011). The air quality monitoring used at Port Pirie incorporates the South Australia's Environment Protection Authority monitoring network (red circles), the licence monitoring regime for the smelter owned Nyrstar Port Pirie Pty Ltd (comprised of separate licencee monitoring at the same 4 locations plus the Boat Ramp site). The sites used for NEPM monitoring are those at Oliver Street (lead- and sulfur dioxide-in-air concentrations) and Frank Green Park (lead-in-air concentrations). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

900 km from the nearest major town of Townsville on the northeast coast of Australia (Fig. 1). Mount Isa Mines Ltd is the largest copper-lead-zinc mining operation in Australia. The mine is owned and operated by Glencore Xstrata Mount Isa Mines¹ and operates under the Environmental Authority No. MIN102700011, granted by the Queensland Government under the *Environmental Protection Act 1994* (Qld (Queensland)) (Supplementary data S1). The mine employs around 5,000 people and contributes around AUS\$1 billion to the economy per annum (Mount Isa Mines (MIM) 2014a). The mine is co-located immediately adjacent to the largest outback city in Australia – Mount Isa, whose population was 21,237 in 2011 (ABS Census, 2011; Xstrata, 2012). In 2012, lead production from Mount Isa was 153,116 tons (Xstrata, 2012).

The Port Pirie smelting facility is located 220 km north of the state capital city, Adelaide in South Australia (Fig. 1). The smelter is operated by Nyrstar Port Pirie Pty Ltd and operates under a licence approval EPA 775 granted by the South Australian Environment Protection Authority under the *Environment Protection Act* 1993 (South Australia) (EPASA, 2012). The smelting facility supports 2500 jobs in South Australia making up around 15% of Port

Pirie's workforce (Russell, 2013). Nyrstar produced 158,000 tons of lead in 2012 (Nyrstar, 2013).

2. Mining in Australia

Australia has a long history of mining. Following European settlement in 1788, coal was discovered as early as 1797 (Hargraves, 1993). However, the exploration and mining of minerals did not occur until the 1840's following the discovery of silver–lead and copper ores in South Australia, which resulted in a mining boom in this State (AMHA, 2011). Some of the world's largest silver– lead–zinc ores were discovered in 1883 at Broken Hill, New South Wales (NSW) and in 1923 at Mount Isa, Queensland (QLD), both of which continue to be Australia's premier lead mining towns. Mining is a major industry in Australia and contributes approximately 8–9% of Australia's annual gross domestic product (Roarty, 2010; Geoscience Australia, 2013).

3. Environmental emissions and public health

The mining and smelting operations at Mount Isa, Queensland, and the smelting facility at Port Pirie, South Australia, are known to be significant point sources for the atmospheric emission of metals and gases to the environment. Estimates of individual facility emissions to the environment are reported to Australia's National

¹ The name for the smelting operations at Mount Isa has changed over the last few years due to changes in company ownership. Therefore, the names Mount Isa Mines (MIM), Xstrata Mount Isa Mines (XMIM) and Glencore Xstrata Mount Isa Mines all relate to the same facility. These names are used according to the correct name at the time of reference in this document.

 Table 1

 Atmospheric emissions estimates from Mount Isa and Port Pirie 2011–2012 (NPI, 2013a,b).

Location	Arsenic (kg)	National Emission Ranking	Lead (kg)	National Emission Ranking	Sulfur dioxide (kg)	National Emission Ranking
Mount Isa	33,000	1st	120,000	1st	220,000,000	1st
Port Pirie	1,300	13th	46,000	2nd	66,000,000	4th

Pollutant Inventory. Table 1 summarizes the most recent data for atmospheric emissions of arsenic, lead and sulfur dioxide from the Mount Isa Mines Ltd and Nyrstar Port Pirie Pty Ltd facilities (National Pollutant Inventory (NPI) 2013a,b). In terms of point source emissions, Mount Isa Mine is Australia's leading emitter of arsenic, lead and sulfur dioxide. The Nyrstar Port Pirie Pty Ltd lead–zinc smelter facility ranks 13th for arsenic, second for lead and fourth for sulfur dioxide emissions in Australia (NPI, 2013b). The emission inventories are estimated using one of several estimation techniques, and facilities may use one, or a combination of estimation techniques, which might vary between reporting periods, producing inconsistencies (Ellson and Johnston, 2005; Weng et al., 2012). The National Pollutant Inventory is the only available tool for assessing emissions to the environment in Australia.

Although Australia ranks first in the world in economic lead resources (Geoscience Australia, 2013), there is limited research into associated human or environmental health impacts, particularly with respect to the Australian public health issue of childhood lead exposure from industrial and domestic sources (Taylor et al., 2011, 2012a,b, 2013; NHMRC, 2009). While the current accepted goal for Australian blood lead is <10 µg/dL (NHMRC, 2009), several major international reviews indicate that blood lead concentrations well below this level may result in permanent impairment of neurocognitive functioning in children (e.g. NTP, 2012; ACCLPP, 2012; Health Canada, 2013a,b). Fresh concerns have been raised about the impact of chronic, low-level lead exposure on children across a number of Australian mining and smelting towns including Mount Isa and Port Pirie (Taylor, 2012; Taylor et al., 2011, 2012a,b). As a result of the international research and concomitant lowering of blood lead intervention values (Taylor et al., 2012a,b), in 2012 the Australian NHMRC elected to review the national guideline for blood lead (NHMRC, 2013).

In lead mining and smelting towns, environmental exposure to toxicants are typically not just limited to lead; significant amounts of arsenic and cadmium, for example, are also present in aerosols, dusts and soils (ATSDR, 2004; Csavina et al., 2011, 2012; Sorooshian et al., 2012). Although less well studied than lead, a number of studies have shown that arsenic exposure in children and adults can also result in neurocognitive impairment (Calderón et al., 2001; Rocha-Amador et al., 2007; Rosado et al., 2007; von Ehrenstein et al., 2007; O'Bryant et al., 2011; Roy et al., 2011). Studies examining the interaction of metal exposures are limited, though some indicate that arsenic, manganese and lead can have an additive or synergistic neurotoxic effect (e.g. Yáñez et al., 2002).

The smelting of ores for the production of refined sulfide metals such as copper, lead and zinc also produces significant sulfur dioxide emissions to the environment. Communities exposed to elevated sulfur emissions have been shown to be associated with increased problematic respiratory symptoms, disease and mortality as well as hospital admissions for asthma (NEPM, 1998; Smargiassi et al., 2009). The most recent summary of respiratory data for Mount Isa shows that between 2002 and 2006 there were significant disparities in asthma rates for Mount Isa compared to the rest of Queensland (Fig. 2, Queensland Health, 2009). Hospitalization rates (n = 109) were significantly higher (80%) compared to the rest of Queensland, and asthma mortality rates (n = 5) were similarly greater, being 322% higher than the rest of the State.



Fig. 2. Direct age standardised hospital asthma separation rates for Mount Isa Health Service District and Queensland by sex, 2002/03–2005/06 (redrawn from Queensland Health, 2009).

4. Legal and policy framework for the environmental protection

The Australian legal system has two sources of environmental legislation: the Federal (Commonwealth) Government of Australia and State Governments. The Federal Government's function in environmental management is to "coordinate enquiry, general policy formulation and standard setting, and specifying budget priorities" with the States having the bulk of the responsibilities for regulation and administration (Sawyer, 1974). This arrangement leads to a lack of consistency for environmental management in Australia, except where matters of national significance can be triggered under the external affairs power in s.51(xxix) of the *Commonwealth of Australia Constitution Act 1901*.

The inability of the Commonwealth to coordinate the management of the environment, in particular pollutants, has been the subject of numerous enquiries and cooperative arrangements between the States (see Fowler, 1984, 1994). The *Intergovernmental Agreement on the Environment* (1992) (Australian Government, 2010) aimed to create harmonization of environmental standards across all States. Schedule 4 of this agreement outlines a number of matters relevant to National Environment Protection Measures including, *inter alia*, air quality:

- The Commonwealth and the States acknowledge that there is benefit to the people of Australia in establishing national environment protection standards, guidelines, goals and associated protocols (hereinafter referred to as 'measures') with the objectives of ensuring:
 - 1. that people enjoy the benefit of equivalent protection from air, water and soil pollution and from noise, wherever they live;
 - that decisions by business are not distorted and markets are not fragmented by variations between jurisdictions in relation to the adoption or implementation of major environment protection measures.

Any proposed measures must be examined to identify economic and social impacts and to ensure simplicity, efficiency and effectiveness in administration.

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Australian Federal Government, State (Queensland (Qld)) and South Australia (SA) air quality guidelines and Mount Isa Mines and Nyrstar Port Pirie smelter mandated maximum air quality values.

Contaminant Federal Legislation ^a		Queensland ^b measured	South Nyrstar Port Pirie Pty Ltd		Mount Isa Mines Environmental Authority conditions ^{c,d}	
	– measured at 0 °C and in μg/m ³ unless stated	at 0 °C and in µg/m³ unless stated	Australia	Licence conditions (µg/m³)	Timeframe	Concentration – measured at 0 °C and in $\mu g/m^3$ unless stated
Arsenic	None	6 ng/m ³ (annual, total in PM_{10})	None	None	2011 [°] 2012 2013 2014 2015 2016 2017	0.023 (annual – total in PM_{10}) 0.021 (annual – total in PM_{10}) 0.020 (annual – total in PM_{10}) 0.018 (annual – total in PM_{10}) 0.017 (annual – total in PM_{10}) 0.015 (annual – total in PM_{10}) 0.006 (annual – total in PM_{10})
Cadmium	None	5 ng/m ³ (annual, total in PM_{10})	None	None	2011 [*] -2013 2014-2016 2017	0.008 (annual – total in PM_{10}) 0.007 (annual – total in PM_{10}) 0.005 (annual – total in PM_{10})
Lead	0.5 (annual, TSP)	Follows Federal guideline	Follows Federal guideline	0.5 (annual, TSP) at Pirie West PS; Oliver St (enforceable limit); 1.6 and 0.6 (annual TSP) non-enforceable target at Ellen St and Boat Ramp, based on daily measurements of TSP lead.	2011 onwards	0.5 (annual, TSP)
Sulfur dioxide	1 h – 0.2 ppm 24 h – 0.08 ppm Annual – 0.02 ppm	1 h – 0.2 ppm (570 µg/m ³) 24 h – 0.08 (230 µg/m ³) ppm Annual – 0.02 ppm (57 µg/m ³)	Follows Federal guideline	None	February 2012 – end of 2016 when compliance with Qld/ NEPM air quality standards is required	1 h – 2,500 μ g/m ³ (0.9955 ppm) measured at 25 °C 24 hr – 230 μ g/m ³ at a commercial or sensitive place Annual – 57 μ g/m ³ at a commercial or sensitive place

The air quality objectives for arsenic and cadmium are expressed as ng/m^3 in the Qld legislation, which is 10^{-3} of the units expressed as $\mu g/m^3$. TSP – total suspended particulates. PM_{10} – particulate matter < $10 \mu m$ (microns).

Queensland values are for health and wellbeing see Environmental Protection (Air) Policy 2008 (Qld).

^a NEPM – National Environmental Protection Measure.

^b Environmental Protection (Air) Policy 2008 (Qld).

^c TEP – Transitional Environmental Program.

^d EA – Environmental Authority.

* Value proposed for 2011 in the May 2011 Mount Isa Mines Environmental Management Plan.

In spite of this agreement, there remain significant inconsistencies in emission standards across States and with respect to specific facility pollution control licences (Table 2).

In 1998, the National Environment Protection Council was established to set national ambient air quality standards for key pollutants (National Environment Pollutant Measure (NEPM) 1998). These standards have since been expanded and revised to reflect contemporary knowledge of environmental and health concerns relating to air quality including the monitoring and advisory levels for PM_{2.5} (fine particle matter <2.5 µm) (NEPM, 2003; NEPC, 2011).

In an additional effort to create consistency across all of the States, the Council of Australian Government (COAG) Standing Committee on Environment and Water was formed in 2010 to address the following priority issues (*inter alia*) of national significance (COAG, 2012):

1. Pursuing seamless environmental regulation and regulatory practice across jurisdictions . . .

5. Developing and implementing a National Plan for Clean Air to improve air quality and community health and wellbeing

These priorities also reflect a long-standing goal to create cohesive regulation of certain industries and their associated emissions.

5. Licence and legislation arrangements in Queensland and South Australia

Each State has the ability to legislate and regulate certain proposals and activities that reflect the priorities of the respective governments. This is particularly relevant to mining and ancillary activities given their economic impact arising from revenue raised for their State budgets (SA Government, 2011; Queensland Department of State Development, Infrastructure and Planning, 2012).

In Queensland, mining is an 'exempt development' under the *Sustainable Planning Act 2009* (Qld), and any such activities are coordinated by the Department of Natural Resources and Mines. Approvals are required through the *Mineral Resources Act 1989* (Qld) for the purpose of prospecting, exploration or extraction. The *Environmental Protection Act 1994* (Qld) deals with regulation of the environmental impacts and is administered by the Department of Environment and Heritage Protection (EHP). This planning and approval process has been the subject of recent streamlining to enable a more timely progression of mining and petroleum approvals inline with the State's priority to grow the economy (Queensland Government, 2011), which is enforced through the *Mines Legislation (Streamlining) Amendment Act 2012* (Qld).

Major mining projects in South Australia are coordinated by the Department of Primary Industries and Resources through the Mining Act 2011 (SA (South Australia)) and, in limited situations, the Development Act 1993 (SA) (cf. Leadbeter and Wawryk, 2013). The Mining Act 1971 and Mining Regulations 2011 (SA) sets the framework for a broad range of mining activities including their environmental impact. The Development Act 1993 (SA) (s 46 (1)) enables the assessment of projects of major environmental, social or economic importance. This provision has been used recently for the proposed upgrade of the Port Pirie smelter (The South Australian Government Gazette, 2013). Pollution licensing is governed by the State's Environment Protection Authority (EPA) (constituted under the Environment Protection Act 1993 (SA)). Environmental and development authorizations for certain activities are issued by the South Australian EPA under Part 6 of the Environment Protection Act 1993 (SA). This extends to some activities related

to the processing of mining products (section 2 and 7 of Schedule 1 of the *Act*) although mineral extraction is not specifically included in the Schedule.

The Australian Commonwealth government (Federal Government) has set strict air quality standards for a range of atmospheric pollutants including lead and sulfur dioxide (NEPM, 1998; Table 2), which are required to be met by all States, Territories and other localities under their jurisdiction (Australian Government, 2010). Although no national guidelines exist for arsenic and cadmium, the Queensland State Government has set their own air quality objectives for these and other contaminants under the *Environmental Protection (Air) Policy 2008* (Qld). In contrast, South Australia's State Government only report on the guidelines set by Australia's Federal Government, of which lead and sulfur dioxide are relevant here.

The current 2012 Mount Isa Mines Transition Environmental Program (TEP), (Table 2; Supplementary data S2), reveals that the permissible values for atmospheric sulfur do not match those stipulated in the national guidelines (NEPM, 1998). The Mount Isa Mines TEP allows for significant variation of atmospheric arsenic and cadmium concentrations (see Table 2; Supplementary data S2) with respect to the values stipulated in the *Environmental Protection (Air) Policy 2008* (Qld), which are applicable to the rest of Queensland.

In addition to the Queensland State's guidelines, the mining and smelting operations at Mount Isa Mines (now owned by Glencore Xstrata plc - MIM), previously had their own special pollution legislation, the Mount Isa Mines Limited Agreement Act 1985, 1997 (Qld) that exempted them from meeting the air quality standards set out in the NEPM (1998). The Mount Isa lead-in-air limit was set to not exceed 1.5 μ g/m³ averaged over 90 days measured as PM₁₀ (particle matter sized 10 µm in diameter or less) as compared to the NEPM (1998) standard of 0.5 µg/m³ averaged over a year and measured as total suspended particulates (TSP). Sulfur dioxide air quality values in the special pollution legislation were set at a maximum of 1300 μ g/m³ (0.5 ppm) for a 3-h running average; $365 \,\mu\text{g/m}^3$ (0.14 ppm) for the 24-h running average maximum; 80 µg/m^3 (0.03 ppm) as the annual arithmetic mean. These standards contrast significantly the values set in the NEPM (1998) and for the rest of Queensland under the Environmental Protection (Air) Policy 1997 (Qld) for sulfur at 570 μ g/m³ (0.2 ppm) for 1 h; 230 μ g/m³ (0.08 ppm) for a 24-h period and 57 μ g/m³ (0.02) ppm for the annual average value (Table 2). The special agreement for air pollution values under the Mount Isa Mines Limited Agreement Act 1985, 1997 (Qld) was repealed on December 31, 2011 when the Environmental Protection (Air) Policy 2008 (Qld) came into force on January 1, 2012.

Under the air quality objectives in the Environmental Protection (Air) Policy 2008 (Qld), the new 2012 XMIM Environmental Authority agreement (Queensland Government Environmental Authority No. MIN102700011, 13 December 2012, Supplementary data S1) for atmospheric lead is in accordance with the Federal and State government legislation (i.e. $0.5 \,\mu g/m^3$ averaged over a year). In contrast, arsenic and cadmium ambient concentrations continue to have transitional arrangements (the Transitional Environmental Program (TEP), Supplementary data S2) that allow XMIM to exceed the standards for the rest of Queensland until January 1, 2017 (Table 2). In the case of arsenic, the Environmental Authority permits 3.5 times the annual average air concentration as provided for in the Environmental Protection (Air) Policy 2008 (Qld) (6 ng/m³) in 2012 and 3.3 times the value for the rest of Queensland in 2013 (Table 2). Even in 2016, the final year of the TEP agreement, arsenic air emission concentrations are permissible at more than double the Queensland statutory air quality objective (Table 2). While the TEP for cadmium emissions are closer to the Environmental Protection (Air) Policy 2008 (Qld), concentrations in excess of the

Queensland State air objective for cadmium of 5 ng/m^3 (averaged over a year) remain permissible until the end of 2016.

Assessment of the XMIM Environmental Authority for allowable sulfur dioxide emissions shows that in a commercial or sensitive place (essentially the city of Mount Isa) the annual and 24-h values are the same as those stated in the NEPM (1998) and the *Environmental Protection (Air) Policy 2008* (Qld). However, under the XMIM TEP until the end of 2016, the allowable limits for the sulfur dioxide 1-h values are a lot less stringent, being around five times higher than those set for elsewhere in Queensland or Australia as a whole (Table 2, NEPM, 1998).

Xstrata Mount Isa Mines have stated that by January 1, 2017, they will be able to meet the Environmental Protection (Air) Policy 2008 (Qld) guidelines. In May 2011, XMIM announced they will decommission their copper smelter by the end of 2016 because the economic viability of smelting and refining is not sustainable financially in the long-term (MIM, 2014a,b). It would appear, though it is not stated explicitly, that XMIM can only attain their environmental obligations for air quality under the Environmental Protection (Air) Policy 2008 (Qld) upon decommissioning the existing copper smelter. This implies pollution control is subordinate to the economic cost of proper filtration of the existing system. While the provision of transitional arrangements (TEP) is permissible under the Environmental Protection (Air) Policy 2008 (s 8(4)) (Qld), the concentrations for the purpose of enhancing and protecting human health and wellbeing are seemingly compromised as set forth in s7 (b) of the aforementioned act:

The qualities of the air environment that are conducive to human health and wellbeing.

6. Environmental emissions compared to guidelines values – Mount Isa, Queensland

According to the Queensland Department of Environment and Heritage Protection, the Environmental Authority for XMIM (Supplementary data S1) issued under the Environmental Protection Act 1994 (Qld), has set maximum limits for arsenic, cadmium, lead and sulfur dioxide emissions (inter alia) (Table 2). The air quality parameters collected by the XMIM monitoring network (Fig. 1) are provided directly to the Queensland Government's Department of Environment and Heritage Protection (EHP) for compliance assessment. While the Environmental Protection Act 1994 (Old) requires a register to be kept by the EPA (s540a of the Environmental Protection Act 1994 (Qld)), it is not explicit that the register must contain all monitoring reports and data. Accordingly, the data collected under this legislation can be difficult to access. For example, the limited access to monitoring data is not confined to XMIM operations as highlighted in the submission by Leck and Kindleysides (2013) to the review of the Port of Gladstone operations in North Queensland. It would seem that both the Environmental Protection Act 1994 (Qld) and the Right to Information Act, 1999 (Qld) are clearly inadequate in supporting an open and transparent system that enables public access to monitoring reports and data in spite of the legislative intent of these acts. In essence, the data required by the regulator and collected for a public health issue, on public land and provided to a publicly funded body are not readily accessible to the public. The Environmental Protection Act 1994 (Qld) also contains a provision at s542 for the register to be available for inspection by members of the public and for them to be able to make copies of extracts from the register. Interestingly however, when we made enquiries to access data collected under XMIMs Environmental Authority in March 2013 we were informed by Rob Lawrence, the Executive Director, Northern Region Department of Environment and Heritage Protection that: "Under the Environmental Protection Act 1994, EHP cannot provide the mine's data to external sources without consent, however, applications for such information could be made through the Right to Information process." Clearly, our experience in relation to data access concurs with that described by Leck and Kindleysides (2013).

Lead, arsenic and sulfur dioxide are also monitored using near real-time equipment at The Gap monitoring site at Mount Isa by Queensland Government's Department of Environment and Heritage Protection (EHP, 2014c; Fig. 1). Sulfur dioxide is also monitored at the Menzies site (Fig. 1). The data on the Department of EHP website contains close to real-time air quality data (EHP, 2014c) for a range of cities in Queensland, but Mount Isa is the only location with real-time lead and arsenic measurements. The values for lead and arsenic from the on-line system are only available as 'non-validated' TSP data, while sulfur dioxide concentrations are available as validated measurements after verification by the Department of EHP. Lead-in-air measurements are available subsequently as validated data via the monthly air quality bulletins for northern Queensland (EHP, 2014a) and the annual NEPM reports (EHP, 2014a). The validated NEPM monitoring data for atmospheric lead is collected separately at The Gap station using EHP's high-volume TSP monitor (EHP, 2011). The returned data is used only for NEPM reporting (EHP, 2014a) and in the monthly air quality bulletins (EHP, 2014a) but not for compliance with respect to the XMIM Environmental Authority (licence) requirements, which have separate arrangements and standards for atmospheric metals and sulfur dioxide (Table 2, Supplementary data S1 and S2).

Validated air quality information with respect to arsenic or cadmium air concentrations was not available to the public until November 2013 even though the Mount Isa Mines Limited Agreement Act 1985, 1997 (Qld) and the Environmental Authority for XMIM requires that air concentrations for these elements were measured and after January 2012 had set maximum values (Table 2). By comparison, atmospheric arsenic and cadmium values have been reported for Townsville for many years, where there are two refineries: a zinc refinery owned by Sun Metals Corporation Pty. Ltd. and the Xstrata Copper-Townsville Operations refinery owned and operated by Glencore Xstrata plc. Thus until recently, the only detailed daily publicly available data for arsenic at Mount Isa was EHP's on-line 'non-validated' data, which is collected using X-ray fluorescence (XRF) equipment (EHP, 2013). The air quality data available from the continuous XRF metals monitoring equipment is based upon TSP, whereas the value set in the Environmental Protection (Air) Policy 2008 (Qld) objectives is for PM₁₀ arsenic, not TSP arsenic. Therefore, the values available via the on-line air quality system are likely to be conservative given that higher concentrations of metals typically occur in finer particulates (Csavina et al., 2011; EHP, 2014a). Section 6.1 provides more detail on the air sampling equipment used at Mount Isa (XRF and high-volume) and the measurement of arsenic- and cadmium-in-air.

6.1. Arsenic-in-air: Mount Isa

In 2011, for the month of April, the maximum 24-h average arsenic-in-air emissions (calculated using available hourly data on the EHP website) in Mount Isa was 2973 ng/m³ (TSP) (EHP, 2014c). The maximum monthly 24-h average arsenic-in-air concentrations during 2011 exceeded the Queensland annual air quality objective of 6 ng/m³ in all months except for May (Fig. 3).

In the 2011 XMIM Environmental Management Plan, the proposed arsenic-in-air annual average value was 23 ng/m³ (Table 2). This air quality value may well have been exceeded based upon the available rolling 24-h average arsenic on-line 2011 data (EHP, 2014c), but the raw data is not available to calculate the actual annual mean value. However, in the final agreed Environmental Authority, including the transition arrangements (Table 2), no



Fig. 3. 2011 monthly maximum 24-h average arsenic-in-air (As-in-air) concentration TSP data (μ g/m³) recorded at The Gap monitoring station, Mount Isa. Data is based upon non-validated TSP data from the Queensland Government Department of Environment and Heritage Protection online monitoring station (EHP, 2014c). In 2011, no formal TEP (Transition Environmental Program) arsenic-in-air value guideline was set for Mount Isa, although a value of PM₁₀ 23 ng/m³ (0.023 μ g/m³) was proposed in the XMIM Environmental Management Plan (see Table 2 and Supplementary data S2).



Fig. 4. 2012 monthly maximum 24-h average arsenic-in-air (As-in-air) concentration TSP data (μ g/m³) recorded at The Gap monitoring station, Mount Isa. Data is based upon non-validated TSP data from the Queensland Government Department of Environment and Heritage Protection online monitoring station (EHP, 2014c). In the 2012, the TEP (Transition Environmental Program) arsenic-in-air value for Mount Isa was set at PM₁₀ 21 ng/m³ (0.021 μ g/m³) (see Table 2 and Supplementary data S2).

limits were enforced for 2011. Monitoring arrangements in 2011 were still captured by *Mount Isa Mines Limited Agreement Act* 1985, 1997 (Qld), which only specified air maximum values for lead and sulfur dioxide.

Although air quality was markedly better in 2012 with lower maximum 24-h average arsenic-in-air TSP values (Fig. 4), a significant number of short-term high values were evident, including 109 ng/m³ in November 2012 (see Fig. 4). While the Queensland *Environmental Protection (Air) Policy 2008* stipulates compliance is to be averaged over a year at 6 ng/m³, the transitional arrangements agreed under the XMIM Environmental Authority states values of 21 and 20 ng/m³ averaged over a year were to be applied for 2012 and 2013, respectively (Table 2).

Air quality is measured following the procedures set out in the Standards Australia (2003) document. The procedure for measurement of atmospheric lead contaminants (and other metal and metalloid contaminants) is based on a 24-h period every 6th day, the values of which are then averaged over a year. Thus, short-term emissions (over a day or less) identified here (Figs. 3 and 4) may

not be captured by the existing regulatory regime or by application of the air sampling approach set out in Standards Australia (2003). Hot vapours emitted from smelting and slag dumps produce ultrafine particulates (<0.1 μ m) that have an atmospheric residence time of minutes to hours (Csavina et al., 2012) before they coagulate into larger particles $(0.1-1.0 \,\mu\text{m})$. Coarser particles $(>1 \,\mu\text{m})$ that are generated by ore crushing and grinding and wind erosion of mine tailings are large enough to be deposited out of the atmosphere in minutes to hours (Csavina et al., 2012). Particulates that reside in the middle of these ranges, referred to as 'accumulation mode' particles $(0.1-1.0 \,\mu\text{m})$ are dependent on the hydrological cycle for their removal and are considered to have average residence time of 10 days in the atmosphere (Hinds, 1999; Csavina et al., 2012). Given that the atmospheric residence time for the short-term, high-concentration fine particulate plumes is less than 6 days, and that these emissions occur for only for a few hours or days, it is unlikely that they will be captured using the standard sampling procedure of 24 h every 6th day. Further, Csavina et al.'s (2011) analysis of mining and smelting emissions in Arizona showed quite clearly that the ultra-fine (<0.1 µm) particulate component of aerosols were the most contaminated size fraction. Concentrations were extremely variable according to wind patterns and also between seasons, with the winter period having up to an order of magnitude higher values.

Averaging of the every 6th day atmospheric contaminant concentrations over a year does not capture short-term maximum pollution concentration events that are associated with acute environmental health effects. As a result, the current regulatory approach does not provide maximum protection for environmental health in the adjoining community. The Mount Isa community provides the perfect example for this point where wind patterns influence significantly pollution concentrations. Although airflow is primarily from the east and south-east for \sim 80% of the year (Taylor et al., 2010), short-term seasonal airflows (mainly in the Australian summer months) result in the flow of industrial emissions across the city causing deposition of contaminants (Taylor et al., 2010; Mackav et al., 2013). Examining the 24-h period on November 22, 2011 illuminates the effect of short-term emissions and the reliance on wind flow to protect the community. During this period the average 24-h arsenic-in-air concentration recorded at The Gap EHP monitoring station was 348 ng/m³, with the airflow coming from the west, towards the direction of the community (EHP, 2014c). However, given the approach detailed in the Standards Australia (2003) air quality monitoring guidelines, it is





Fig. 5. 2012–13 validated, monthly maximum 24-h average arsenic-in-air concentrations in the PM_{10} fraction as published by the Queensland Government (EHP, 2014a). Data is calculated from TSP arsenic values measured at the Queensland Government Department of Environment and Heritage Protection online monitoring station at the Gap, Mount Isa, (Fig. 1, EHP, 2014c). TEP = Transition Environmental Program (see text and Supplementary data S2).

feasible that a day such as November 22, 2011 would not be recorded; the consequences of which would reduce the apparent average emissions to the environment making it easier to attain the values set in legislation or licence arrangements.

Short-term elevated pollution events are also likely to apply to lead and other contaminants. Indeed, data provided in the 2011 XMIM Environmental Management Plan that was collected from the Mine's own monitoring network confirms the values extracted from the EHP online network are not anomalous. The 2011 XMIM Environmental Management Plan document revealed maximum 24-h arsenic-, cadmium- and lead-in-air values recorded at the XMIM BSD station were 2700 ng/m³, 70 ng/m³ and 3.5 μ g/m³, respectively (see Fig. 1 for the location of the BSD site). Similarly, at the RSL monitoring location, the maximum recorded 24-h arsenic-, cadmium- and lead-in-air values were 150 ng/m³, 230 ng/m³ and 12.8 μ g/m³, respectively (see Fig. 1 for the location of the RSL site).

Subsequent to the construction of this article, the Queensland government issued arsenic and cadmium PM₁₀ concentration data for the first time in November 2013, with monthly maximum 24-h average concentrations available back to August 2012 (Figs. 5 and 6). The data are derived using a two-step process (Air Quality Monitoring, Queensland Government, pers. comm.). Firstly, although the continuous XRF monitoring instrument measures metal concentrations in TSP, the Queensland Government Air Sciences had to benchmark the XRF TSP values for lead-in-air against their colocated high-volume sampler at the Gap monitoring site (Fig. 1). This is because the airflow intake rates are different between the instruments (the XRF sampler has a BGI louvered TSP inlet operating at a flow rate of 0.017 m³/min whereas the TSP high-volume sampler operates at a flow rate of 1.3 m³/min (Air Quality Monitoring, Queensland Government, pers. comm.) Second, the derivation of the PM_{10} fraction of TSP values for arsenic- and cadmium-in-air concentrations was derived using co-located TSP and PM₁₀ highvolume samplers at the nearby XMIM monitoring sites at Miles Street and Racecourse (Fig. 1). This determined that the ratio of PM₁₀ to TSP for arsenic is 0.88:1 and for cadmium 0.76:1 (EHP, 2014a). The final values published in the Government Air quality bulletin were adjusted for the lower airflow volumes on the continuous metals monitoring instrument as described in the first step. Notwithstanding these conversions, the recently published monthly maximum 24-h average PM₁₀ concentrations are not inconsistent with our analysis and interpretations of the on-line continuous TSP metals data.

6.2. Lead-in-air: Mount Isa

The allowable lead-in-air was set previously at $1.5 \,\mu g/m^3$ per quarter year under the Mount Isa Mines Limited Agreement Act 1985, 1997 (Qld), but was reduced to match the Australian Federal Government limit of 0.5 μ g/m³ following the enforcement on January 1st 2012 of the Environmental Protection (Air) Policy 2008 (Qld). The source and isotopic composition of Mount Isa's leadin-air is detailed in Mackay et al., (2013), with some additional, relevant information available in the Queensland EPA (2008) lead management report. Additional information about temporal variations in the monthly lead-in-air measurements and annual values are available in the air quality bulletins and the annual NEPM reports (EHP, 2013, 2014a). Details of the depositional impact of emissions on environmental quality and its link to lead exposures are detailed in a suite of recent studies (Taylor et al., 2010, 2011; Munksgaard et al., 2010; Mackay et al., 2013). The evidence shows that the contemporary emissions are impacting the urban environment and influencing blood lead outcomes in children (Queensland Health, 2008, 2010). However, there have been some incorrect and misleading arguments disseminated by the Queensland



Fig. 6. 2012-13 validated, monthly maximum 24-h average cadmium-in-air concentrations in the PM_{10} fraction as published by the Queensland Government (EHP, 2014a). Data is calculated from TSP cadmium values measured at the Queensland Government Department of Environment and Heritage Protection online monitoring station at the Gap, Mount Isa, (Fig. 1, EHP, 2014c). TEP = Transition Environmental Program (see text and Supplementary data S2).



Fig. 7. Monthly maximum 24-h lead-in-air (Pb-in-air) TSP data compiled for the years 2010–2012 from the Queensland Government North Queensland Air Quality Bulletins (EHP, 2014a). The red line represents the annual average maximum value $(0.50 \ \mu g/m^3)$ as set by both the Australian Federal and Queensland governments, in their respective air quality criteria documents. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

government and industry with respect to the source of the environmental lead problem in the city and why up to one child every 9 days presents with a blood lead > 10 μ g/dL (Munksgaard et al., 2010). These arguments have stated that the childhood lead exposures in the city have occurred due to lead naturally occurring in the city's soils or that the elevated blood lead levels have been caused by other means such as ingestion of fishing sinkers or possible lead paint sources (Queensland Health, 2008, 2010; Taylor and Schniering, 2010; Taylor et al., 2010; Munksgaard et al., 2010: Mackay et al., 2013). The recent data shows XMIM meets its Environmental Authority restrictions for lead-in-air and, by default, the NEPM (1998) lead-in-air standard of 0.5 μ g/m³ averaged over a year. Nevertheless, the true picture of the impact from the mining activities cannot be understood properly by a simple annual average assessment of lead-in-air concentrations. Fig. 7 shows there are significant monthly variations in ambient concentrations of lead, with the peaks occurring in the Australian



Fig. 8. A view looking north along the fence of the lease of Xstrata Mount Isa Mines on February 22nd 2012 with the emission plume from the copper smelter stack (red and white stripes, 155 m high) blowing across the urban area. The centre stack is the Incitec Pivot plant that converts sulfuric acid into ammonium phosphate fertilizer. The stack obscured partly by smoke is the lead smelter stack (270 m high). The photograph was taken at 10 am in the morning. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

summer, when the monsoon winds blow from the north and west (winds blowing from the mine site across the town). Other data extracted from the (2011) Mount Isa Mine Environmental Management Plan (not publicly available) confirms these impacts, with very high short-term lead-in-air values of $12.8 \ \mu g/m^3$ recorded over a 24-h period at the XMIM RSL site, located in the city (Fig. 1).

Contrary to the argument that the city's air, soil, and dust contains predominantly naturally occurring lead is the visual evidence of the smelter plumes blowing contaminated emissions across the city (Fig. 8). Taylor et al., (2010) and Mackay et al., (2013) showed that soils, dusts and aerosols were not only higher closer to the facility, but that they were sourced from the deposition of particulates from smelter emissions. Such events occur despite the fact that XMIM's air quality control (AQC) system is instructed to minimize the impact of emissions on the city when winds are blown from the north/west direction. However, this system is not automated and is reliant on operator judgment, providing greater potential for short-term air pollution events. Indeed, XMIM (2010) stated the following:

"It is important to note that westerly winds will generally result in the shutdown of operations at the lead and copper smelters and the



Fig. 9. Sulfur dioxide air quality data (ppm) as reported for the National Environment Protection (Air Quality) Measures for the Menzies site in Mount Isa for the years 2000–2011 (EHP, 2014a).

Incitec Pivot acid plant. However, the AQC system will allow westerly winds to blow emissions from the stacks over the city at night time and during early mornings when there is a cool air inversion at low level, which minimises the chances of the plume reaching the ground."

Csavina et al., (2011) found atmospheric contaminants around a USA copper smelter reside primarily in the fine size fraction of particle matter (PM) (>70% of the lead and arsenic concentrations in the <PM_{1.0} fraction). An AQC system reliant on wind direction and inversion cannot provide effective protection against the deposition of fine metal-rich aerosol particles. This is because atmospheric contaminants can reside in the ambient environment for an average of 10 days, allowing for the possibility of the air mass containing the accumulated emissions to be blown back across the community. Therefore, the AQC system and the current air quality sampling program is probably insufficient for ~70% of the contaminants coming out of the stack.

Thus is it is clear that source and cause of contemporary emissions and exposure are directly traceable to the activities at MIM. Even though the annual lead-in-air concentrations are below the Environmental Authority limits ($0.5 \ \mu g/m^3$), it is clear the mine and smelter are impacting air, dust and soil quality, and by deduction are the cause of elevated blood lead levels in the community (see Taylor et al. (2010), Munksgaard et al. (2010), Mackay et al. (2013)).

6.3. Sulfur dioxide-in-air: Mount Isa

In addition to the measurement of atmospheric sulfur dioxide and metals at The Gap (Fig. 1), ambient sulfur dioxide is also monitored by Queensland Government at its Menzies site in Mount Isa (Figs. 1 and 9). This data is also used in Queensland's NEPM air monitoring report each year (EHP, 2014a) and in their monthly air quality bulletins (EHP, 2014a). The latest available NEPM report from 2011 provides exceedence data on 1-h, 24-h and annual average sulfur dioxide emissions from 1983 onwards. While the annual sulfur dioxide guideline of 0.02 ppm (57 μ g/m³) has been met since the implementation of the NEPM in 1998 (NEPM, 1998), the 1-h and 24-h guidelines have not. The NEPM guidelines allow for 1 day exceedence per year for each of the 1-h and 24-h sulfur dioxide standards (NEPM, 1998).

The 1-h sulfur dioxide air quality standard of 0.2 ppm (NEPM, 1998) was breached on a minimum of 16 days per year between 1998 and 2011. In particular, the years 2002 and 2005 each have 49 days where the 1-h sulfur dioxide emissions were in non-compliance. Given that the NEPM (1998) air quality standard specifies only the number of daily exceedences at a specified concentration, it does not demonstrate the frequency of exceedences within a single day, which would provide a better understanding of the impact of smelting emissions on the community. For example, during the year 2011, although 22 days were recorded with hourly sulfur dioxide emissions over the NEPM guideline level, there were in fact, 27 hourly exceedences recorded at the Menzies monitoring station (Air Quality Sciences, 2012). No other monitored location in Queensland had any exceedences for the NEPM 1-h sulfur dioxide in 2011 (Air Quality Sciences, 2012). The Queensland Government (Oueensland Health, 2009) health indicators study showed significant disparity between asthma hospital separations and mortality events in Mount Isa versus the rest of Queensland (Fig. 2). However, Donoghue and Thomas's (1999) study concluded that there was no evidence of any positive relationship between peak sulfur dioxide concentrations and hospital presentations or admissions for asthma, wheeze, or shortness of breath. Nevertheless, given the magnitude and frequency of peak atmospheric sulfur dioxide concentrations at Mount Isa along with other pollutants including PM₁₀, lead, arsenic and cadmium, it is difficult to not associate the reduced air quality with significant potential adverse respiratory function as has been identified elsewhere (Smargiassi et al., 2009).

7. Environmental emissions compared to guidelines values – Port Pirie, South Australia

Air quality is monitored by the South Australian Environment Protection Authority (EPASA) at four stations in Port Pirie (Fig. 1). In addition, Nyrstar Port Pirie Pty Ltd has an extensive network of its own monitors at 13 sites across the city with four of these co-located next to the EPASA sites (Fig. 1). As part of its licence requirements (EPASA, 2012), Nyrstar provides data from their air monitor located at the Boat Ramp along with those at Pirie West Primary School, Oliver Street and Ellen Street (Fig. 1, Table 1). A recent review showed that there was no statistical difference between the air quality data collected over equivalent 24-h time periods by EPASA and Nyrstar (personal communication – Rob Mitchell, Manager Air Science, Air & Noise Branch, EPASA).

In terms of NEPM reporting, the EPASA relies on data collected at the Frank Green Park and the Oliver Street sites for lead-in-air and Oliver Street only for sulfur dioxide. Data is collected and reported in the annual NEPM statements according to Standards Australia (2003), i.e. every 6th day. During 2011, the EPASA also collected lead-in-air data from West Pirie Primary School and Oliver Street on a daily basis, which is discussed below.

Monthly data is available from the EPASA (2014) under their air quality monthly summary reports. These reports provide more detail than is available in the annual NEPM reports. The rolling 365 day average for lead in TSP is available for the two Port Pirie NEPM sites of Frank Green Park and Oliver Street and for the two non-NEPM sites of Ellen Street and Pirie West Primary School (Fig. 1). In addition, the daily 1-h maximum sulfur dioxide and the daily average sulfur dioxide are available for each month in the air quality reports (EPASA, 2014). The data for the 13 Nyrstar smelter sites is not available to the public, but the four EPASA monitoring stations for lead-in-air provide a reasonable coverage of the impact of the smelting operations across the city (Taylor et al., 2013).

7.1. Arsenic-in-air: Port Pirie

The EPASA does not collect arsenic or other metal data as part of its normal monitoring. Filters from the air quality monitoring equipment were analysed occasionally in the past (1970s–2010) for a range of heavy metals and metalloids including arsenic, cadmium, manganese and zinc. The most recent data available from EPASA includes TSP arsenic concentrations from the Ellen Street monitoring site (Fig. 1), and indicates air quality in Port Pirie is also impacted by elevated arsenic and cadmium concentrations (Table 3).

Air quality measures for arsenic appear to be similar to Mount Isa ambient concentrations. However, there are no arsenic-in-air concentration values provided for in South Australian legislation, but the data shows that values exceed significantly the annual average concentration of 6 ng/m³ (arsenic) proscribed in the *Environmental Protection (Air) 2008 Policy* (Qld). In addition, these recent air quality values are not dissimilar to older EPASA data from Port Pirie, which exceed the World Health Organisation (WHO, 2000) statement that the lifetime risk level for arsenic is determined at 1:100,000 for an atmospheric concentration of 6.6 ng/m³.

7.2. Lead-in-air: Port Pirie

The problems of environmental contamination and associated lead poisoning due to the smelting operations at Port Pirie have been known for over 80 years (South Australia Royal Commission on Plumbism, 1925). The Royal Commission study revealed that the principal cause of plumbism (lead poisoning) was due to fine lead rich dust emanating from the smelting operations. The smelting operations have been active since 1889, when the Broken Hill and Associated Smelters were constructed in order to process the ore being produced at Broken Hill in NSW, some 400 km to the north-east. However, despite this prior knowledge, along with a suite of studies examining the spatial and temporal impacts of lead around Port Pirie (Body et al., 1991; Baghurst et al., 1992; Calder et al., 1994; Cartwright et al., 1976; Esterman and Maynard, 1998; Maynard et al., 2003, 2006; van Alphen, 1999), the South Australian government continued to imply the historical (but not contemporary) lead-smelter dust-emissions held in the city's soils and home environments were the primary cause of elevated blood lead in children (Body et al., 1991; Sara, 2012; Taylor, 2012). Indeed, very recently, the local State parliamentary member, Mr. Geoff Brock, continued with this line of argument when defending

Table 3

Air quality values for TSP arsenic and cadmium from Port Pirie's Ellen Street monitoring site (Fig. 1). The Port Pirie values are benchmarked against the *Environmental Protection* (*Air*) 2008 Policy (Qld) for arsenic (6 ng/m³) and cadmium (5 ng/m³) because no equivalent guidelines exist within the South Australian legislation or in the NEPM (1998).

Date	Arsenic		Times over arsenic	Cadmium		Times over cadmium	
	μg/m ³	ng/m ³	Qld Air Policy (2008)	μg/m ³	ng/m ³	Qld Air Policy (2008)	
15/03/10	0.05	50	8.33	0.02	20	4	
27/11/09	0.1	100	16.67	0.18	180	36	
16/09/09	0.25	250	41.67	0.17	170	34	
8/01/10	0.11	110	18.33	0.08	80	16	



Fig. 10. Lead-in-air measurements in 2011 for the Environmental Protection Authority South Australia's (EPASA) four monitoring sites in the city of Port Pirie, South Australia. The dashed line represents the Australian (NEPM, 1998) lead-in-air standard of 0.5 µg/m³. Ellen Street and Pirie West Primary School are monitoring every day for 24 h, whereas the Frank Green Park and Oliver Street sites are monitored every sixth day for 24 h (data supplied by EPASA).

the negative image being portrayed about the impact of smelter emissions of children's blood lead levels (Sara, 2012):

"I think it is unwarranted, quite frankly. We have got that stigma of, I call it a polluted city, and we are not a polluted city. It is an inherited issue through the lead smelter over many, many years."

Esterman and Maynard (1998) and van Alphen's (1999) studies of air quality showed elevated concentrations of atmospheric lead dust (and other metal contaminants) from smelter emissions were the dominant source of elevated blood lead levels in Port Pirie children. Additionally, Taylor et al.'s (2013) study of lead dust on playgrounds and on hands after timed play (with a maximum hand dust lead value of 49,432 µg/m²) confirmed atmospheric lead concentrations were related to surface deposition. However, while Esterman and Maynard's (1998) and van Alphen's (1999) studies were important fundamentally in terms of addressing the source and cause of the environmental lead problem in Port Pirie, significant intervention on lead-in-air emissions did not occur until 2012 when the EPASA revised the smelter licence causing the government and industry to start on a process of 'transformation'. On December 12th 2012 Nyrstar Australia Pty Ltd announced a commitment to an in principle transformation and replacement of the smelter with assistance from the South Australian Government and the Australian Federal Government at a cost of AUS\$350 million (Nyrstar, 2012). In addition, AUS\$35 million is to be allocated for lead abatement in the city to help address the current problem of 24.9% of children having a blood lead > 10 μ g/dL (excluding surrogate maternal blood lead values, Simon et al., 2013). Blood lead values < 10 μ g/dL is the current goal for all Australians to be under (NHMRC, 2009). The recent soil lead study (SA Health, 2013)

showed 20% of samples from community spaces contained lead concentrations above the NEPM (2013) public open space guideline of 600 mg/kg. However, the smelter transformation process is not yet complete and questions have been raised over the viability of the future operations (O'Shea, 2013).

Although the 2012 smelter licence revision did not lower the maximum annual lead-in-air value from the national standard of $0.5 \,\mu\text{g/m}^3$, it did implement a new, more stringent daily monitoring clause than is applied at Mount Isa or elsewhere in Australia (s3 (335-61), EPASA, 2012). Nevertheless, recent surface and hand dust studies (Simon et al., 2007; Taylor et al., 2013) as well as the current percentage (24.9%) of children with blood levels > 10 μ g/dL illustrates the licence does not protect children adequately from the effects of the very elevated, but short-term pollution events that blanket the city with lead contaminated dust (Fig. 10; Taylor et al., 2013). The implementation of the new licence maximum lead-in-air requirements only pertain to two of city's EPASA sites - Oliver Street and Pirie West Primary School (EPASA, 2012). The other two monitoring locations detailed in the licence, Ellen Street and the Boat Ramp site (Fig. 1), which are closer to the smelter have non-enforceable targets for maximum lead-in-air concentrations of 1.6 and 0.6 μg/m³, respectively (EPASA, 2012). In February 2014, Kemp (2014) revealed that Nyrstar exceeded its mandated maximum limit (0.5 μ g/m³) at the Pirie West Primary School site with a 24-h 365-day rolling average of 0.508 μ g/m³ (measured using its own instrumentation), which may result in a small fine of \$120,000 or a warning. It is worth noting that according to the only available public data for Port Pirie (EPASA, 2014) 365-day rolling average lead-in-air concentration at December 31st 2013 at Pirie West Primary School was ~ 0.7 and $\sim 2.9 \,\mu\text{g/m}^3$ at the Ellen Street Site (Fig. 1). The Ellen Street monitoring site has only a



Fig. 11. Sulfur dioxide air quality data (ppm) as reported for the National Environment Protection (Air Quality) Measures for the Oliver Street site in Port Pirie for the years 2002–2012 (data supplied by EPASA).

non-enforceable target value of $1.6 \ \mu g/m^3$ and any exceedences at this site cannot be enforced (Table 2). The point here is that despite the significant body of information relating to the adverse effects of lead exposure and the significant emissions from the facility, there appears to be relatively little effective action that the regulatory agencies have or will do.

7.3. Sulfur dioxide-in-air: Port Pirie

Sulfur dioxide emissions at Port Pirie are only measured at a single site by the EPASA. This monitoring occurs at the Oliver Street site, located at the south-east edge of the city (Fig. 1). The data available via the NEPM reports (Hunt and Mitchell, 2012) and the monthly air quality reports (EPASA, 2014) show Port Pirie has the worst air quality with respect to sulfur dioxide for anywhere in South Australia. In 2010, Port Pirie had 44 exceedences of the 1-h sulfur dioxide standard. In addition, the 24-h PM₁₀ standard was also exceeded on three occasions. Analysis of the 1-h sulfur dioxide concentrations suggests median values have been stable (Hunt and Mitchell, 2012) but the maximum recorded sulfur dioxide concentrations have trended upwards since 2002 (Fig. 11). The lowest maximum atmospheric sulfur 1-h concentration (0.44 ppm) from 2002 to 2012 data period occurred in 2004, with peaks of 1.26 and 1.18 ppm occurring in 2009 and 2012, respectively (Fig. 11). The frequency of hourly events exceeding the national 1-h standard show a similar pattern over the same time period with a peak of 56 exceedences in 2011 (Fig. 11).

The Social Health Atlas for South Australia contains separation rates for respiratory diseases, which is inclusive of asthma (PHIDU, 2013). Figures from 2007/2008 show that the Port Pirie City district area had hospital separations for respiratory illness at a rate of 3774 per 100,000 population, compared with 2036 per 100,000 population for the remainder of South Australia. While these figures do not demonstrate causation, they are in line with those identified for Mount Isa and are consistent with chronic, poor air quality in the city of Port Pirie.

As with Mount Isa, the NEPM 1-h standard for sulfur dioxide cannot be enforced because there is no existing legal mechanism for that to occur. Despite the smelter licence being recently revised, the known issues around sulfur dioxide were left unaddressed and the licence was silent on the enforcement of the national standard (EPASA, 2012). This was clearly a missed opportunity that needs to be addressed as part of the Port Pirie transformation and smelter replacement project (South Australian Government, 2013).

8. Discussion

8.1. Clarity of information available to the public

In Mount Isa, the public is unable to make fully informed and independent decisions about the risks of exposure due to the lack of availability of the full suite of air quality information. In addition, assessment of the online data from the Queensland Department of EHP system shows that there is evidence of misleading advice. For example, the online monitoring network data located at The Gap, as provided by the Queensland Government's EHP Department, shows that the guideline values (demarked by a red line) are 0.3 μ g/m³ (300 ng/m³) for arsenic and 2.0 μ g/m³ for lead per 24-h (Supplementary data S3 and S4). However, there are no 24-h values set within the XMIM Environmental Authority or by the NEPM (1998), or in the Queensland legislation. The sources of these values are detailed in the latest North Queensland air quality bulletins (EHP, 2014a). As a result, the use of these non-statutory values is misleading, particularly with respect to arsenic whose annual average air quality objective is set to 6 ng/m³ for Queensland and at 18 ng/m³ for 2014 under the transition arrangements for XMIM (Table 2). With respect to lead, the red line value of 2.0 μ g/m³, is four times higher than the annual average limit of 0.5 µg/m^3 . Even where graphics are constructed using the online system for the whole year the red line values remain unchanged. which, to the untrained eye, suggests air quality is much better than the required value (see Supplementary data S3 and S4).

To assist in interpreting air quality data, the Queensland Government provides an air quality index for the online reporting system, which is determined as follows:

 $Index = \frac{pollution \ concentration}{pollutant \ goal \ concentration} \times 100$

The index value used for the goal concentration is expressed as a percentage of the National Environment Protection Measure for Ambient Air Quality (NEPM, 1998) standard or the *Environmental Protection (Air) Policy 2008* (Qld) objective (EHP, 2014b). Values in excess of 100 indicate air quality exceeds the relevant standard or goal for that given contaminant. Air quality is expressed in six categories depending on the calculated index: Not available; Very good (0–33); Good (34–66); Fair (67–99); Poor (100–149); Very poor > 150.

Analysis of the data from the online systems reveals the pollutant goal concentration used to determine an air quality index does not reflect the NEPM standard or Queensland air quality objectives and as a result misleads the public about air quality. This serious misinformation arises because the contemporary air quality is benchmarked against the non-statutory 24-h 'red-line' values as described above (Supplementary data S3-S5). For example, the 24-h rolling lead-in-air average value recorded on the online air quality system on 15/01/2013 is identified as 'Good' at 0.895 µg/ m³ (Supplementary data S6). It is defined as 'Good' even though the 24-h value significantly exceeds both the NEPM (1998) and Environmental Protection (Air) Policy 2008 objective at 0.5 µg/m³ averaged over a year. Using the Queensland Government's air quality index equation above as per the instructions on their website shows the air quality index should be 179 ('Very poor'). The arsenic-in-air on the same day is also shown as 'Good' based upon a concentration of 0.186 μ g/m³ (24-h rolling average) rather than a properly derived index score of 3100 (20 times the Government's 'Very poor' guideline). The 24-h rolling average for arsenic-in-air on April 25th 2011 at 9 am-10 am of 2973 ng/m³ is the highest on record, producing an air quality index of 49,550.

Therefore, the near-time air quality information available misinforms the public, in contradiction to the Queensland Department of EHP who stated that the "website is designed to keep the community informed on local air quality conditions" (Rob Lawrence, email communication, Department of EHP, 13th March 2013). By contrast the guideline on the sulfur dioxide is correct at 0.2 ppm for the NEPM 1-h averaging period (Supplementary data S5), which shows the maximum monthly atmospheric sulfur concentration breached the NEPM (1998) 1-h average value in eight of the 12 months in 2012.

At the time of writing, the Queensland Government's high-volume lead-in-air monitoring equipment at The Gap (Fig. 1) had not been operating for more than 9 months since the end of 2012. According to a Queensland Government media statement from Dr Julia Playford, Director, Science Delivery, Department of Science, Information Technology, Innovation and the Arts (August 30 2013) the high-volume lead-in-air monitoring equipment at The Gap (Fig. 1) could not be attended to every six days as required because when the "EHP relocated its Mount Isa office to Cairns after key positions were unable to be filled within the region, despite sustained recruitment efforts since 2008." The Gap site provides the only independent, validated data on lead-in-air concentrations that are available to the public. Although XMIM collect similar data from its five high-volume TSP monitoring stations (XMIM, 2013, Figure 1), this information is not available to the public. The online hourly air quality data is available to the public, but for lead and arsenic and other metallic elements, the data is provided as 'Non-Validated Data' (EHP, 2014a; Supplementary data S3, S4, S5). The failure to collect independent measurements compounds data clarity and availability issues and exposes MIM to further uncertainty because there is no independent data to scrutinize their operations.

8.2. Inadequacies of the current Environmental Authority and licence arrangements

According to Federal Government information on "national standards for criteria air pollutants in Australia" (Australian Government, 2005), the air quality standards are legally binding on each level of government, with the goal that all standards were to be met by all States and Territories by 2008. This should have required the regulation of sulfur emissions in Mount Isa to comply without the benefit of the transition period. However, while these standards are legally binding, there is no mechanism for enforcement unless the relevant values have been stipulated in an environmental authority or in licence arrangements such as those for the Mount Isa Mines or Nyrstar's operations. Therefore, in practical terms, it is clear that the individual States of the Australian Commonwealth retain significant discretion in terms of enforcement of the NEPM (1998) air quality standards.

Currently, the EPASA uses air monitoring data from the sites at Frank Green Park and Oliver Street to report lead-in-air quality to Australia's National Environment Protection Council (Hunt and Mitchell, 2012). The selection of the sites Frank Green Park, Oliver Street and West Pirie Primary (sites 2, 3, 4, Fig. 1) for use in national air quality reporting and the smelter licence arrangements, is problematic for three reasons: (1) Although the whole city is impacted by emissions this is not properly captured in the reported data or by the data used to manage the smelting facility, a situation that is advantageous to the polluter. (2) The use of the two most distant sites in the annual national air quality reporting arrangements downplays the impact of the industry on the city's air quality. (3) The use of a rolling annual average for the determination of acceptable lead-in-air results in a numerical dilution of the impact arising from significantly elevated short-term pollution events that blanket the city, which are evident in the air monitoring data (Fig. 10).

As part of the Port Pirie smelter transformation project, the SA Government agreed to introduce new legislation and to take on new obligations with respect to the management of the smelter. These new obligations include some important benefits for the company with respect to their environmental obligations and liabilities. The State Government announced an agreement to provide a guarantee/indemnity of up to AUS\$115 million for potential environmental, health and property liabilities to assist the attraction of external financing for the proposed Port Pirie smelter upgrade (Weatherill, 2013). In addition, the government also tabled a new piece of legislation, the *Port Pirie Smelting Facility (Lead-in-Air Concentrations) Bill* in July 2013, designed to provide environmental certainty for the operation of the new smelter. Of particular concern, *inter alia*, are the following sections in the *Bill*:

4 – Provisions relating to reduction of maximum lead-in-air condition by Environment Protection Authority

- (1) The Environment Protection Authority may not, during the period commencing on the project completion date and ending on the commencement day, vary a maximum lead-in-air condition in a way that would have the effect of reducing the maximum specified in the condition unless the Environment Protection Authority has consulted with –
 - (a) the Manufacturing Minister; and
 - (b) the Company.

5 – Maximum lead-in-air condition not affected by other laws of State

- The law of the State is modified so that any requirement applying (whether directly or indirectly) to the Company under-
 - (a) a law of the State; or
 - (b) a relevant authorisation,
 - that would have the effect of reducing the maximum permissible air concentrations of lead at a location or locations in Port Pirie specified in a condition of a relevant environmental authorisation (a **relevant requirement**), is taken not to apply (but only to the extent that the relevant requirement has that effect and except as provided in subsection (3)) to the Company during the prescribed period.

Finally, consistent with the South Australian Government's decision to provide limited, but significant (AUS\$115 M) indemnity for the company, the new legislation also includes protection for the Minister and related staff to any future litigation in respect of the functions of the *Port Pirie Smelting Facility (Lead-in-Air Concentrations) Bill* (2013):

6 – Immunity provision

No act or omission undertaken or made by the Manufacturing Minister or any other person engaged in the administration of this Act with a view to exercising or performing a power or function under this Act gives rise to any liability (whether based on a statutory or common law duty to take care or otherwise) against the Manufacturing Minister or other person or the Crown.

In all cases these administrative and legal decisions appear to place the operations of the smelter company and functions of government ahead of the rights and interests of the public. Indeed, the limitation applied to the EPASA under the *Port Pirie Smelting Facility (Lead-in-Air Concentrations) Bill 2013* contradicts the legislation (*Environment Protection Act* (SA) 1993) that was enacted to define EPASA's functions and powers. The Objects of the *Environment Protection Act* (SA) 1993 contain several relevant items including:



Fig. 12. Percentages of Port Pirie children 0–4 years of age presenting with blood lead (PbB) values > 10 µg/dL covering the period from January 2006 to December 2010. The annual monthly mean data used in this figure (supplied by SA Health Port Pirie Environmental Health Centre) contains repeated blood lead test measures collected in a single calendar year on children with blood lead results > 10 µg/dL, whereas children with values < 10 µg/dL are tested only once per year. The SA Health annual data was extracted from Simon et al. (2013).

10 - Objects of Act

- (1) The objects of this Act are -
 - (a) to promote the following principles (principles of ecologically sustainable development):
 - (i) that the use, development and protection of the environment should be managed in a way, and at a rate, that will enable people and communities to provide for their economic, social and physical wellbeing and for their health and safety while-
 - (A) sustaining the potential of natural and physical resources to meet the reasonably foreseeable needs of future generations; and
 - (B) safeguarding the life-supporting capacity of air, water, land and ecosystems; and
 - (C) avoiding, remedying or mitigating any adverse effects of activities on the environment;
 - (ii) that proper weight should be given to both long and short term economic, environmental, social and equity considerations in deciding all matters relating to environmental protection, restoration and enhancement; and
 - (b) to ensure that all reasonable and practicable measures are taken to protect, restore and enhance the quality of the environment having regard to the principles of ecologically sustainable development;
 - (iii) to facilitate the adoption and implementation of environment protection measures agreed on by the State under intergovernmental arrangements for greater uniformity and effectiveness in environment protection;

Although not stated explicitly, section 10 (1) (b) (iii) appears to relate to Schedule 4 of the Intergovernmental Agreement on the Environment (1992) (Australian Government, 2010). This agreement states that not only should there be harmonization of legislation but that all Australians, irrespective of where they live, should have equal protection from environmental pollution. Thus, the construction of the Port Pirie Smelting Facility (Lead-in-Air Concentrations) Bill 2013 (SA) is designed to limit that right and the formulation of the wording is tantamount to a gift to the industry, which will not be bestowed on any other industry or location in the State. There are clear analogies with this piece of South Australian legislation to those in the now rescinded Mount Isa Mines Limited Agreement Act 1985, 1997 (Qld) as well as the current transitional arrangements in Mount Isa. In each case, the

needs of a specific industry are placed ahead of known environmental and health concerns. The special arrangements, in effect, provide a business advantage by virtue of not requiring more stringent and immediate environmental management controls on pollution.

8.3. Tricks with statistics – downplaying the extent of the Port Pirie blood lead problem

The data in Fig. 12 shows three values for the annual number of children < 5 years old returning a blood lead > 10 µg/dL. The line showing the 'Annual mean of monthly PbB (blood lead) results' is derived from the monthly percentages of children aged 0-4 years old who return a blood lead test > 10 μ g/dL. These results contain all blood lead tests in any 1 year that produced a value > 10 μ g/dL and contain repeat measures on a single child. If a child presents with an elevated blood lead level, they are usually tested multiple times in a year as part of a follow up program to help lower the exposure levels. The line showing the 'SA Health annual PbB results - with surrogates' are defined as the inclusion of the mother's blood lead level in place of that of a child's at birth (Simon et al., 2013), which occurs when a child is less than 9 months old and has not been blood lead tested (David Simon pers comm.). The line on Fig. 12 showing the 'SA Health annual PbB results - without surrogates' contains the same data as that used in the aforementioned line but does not include maternal surrogate values.

In the SA Health's annual reports on blood lead in children at Port Pirie and related media releases, the preference is to report the percentage of children with a blood lead > 10 μ g/dL that includes the maternal surrogate values. Data that excludes surrogate measures is also provided within the same report but its use is predominantly secondary to statistics relying on surrogate measures (Simon et al., 2013). The monthly data, expressed in Fig. 12 as the annual average percentage of children with blood lead values > 10 μ g/dL is not presented in SA Heath technical reports on blood lead. For the purposes of the quarterly or annual blood lead reports, only the last blood lead result collected from a child (even where a child has been tested multiple times in a year) is included in the calculations of the percentage of children above or below > 10 μ g/dL. The effect of using selective data sets is clear in Fig. 12. The non-inclusion of all results coupled to the use of the surrogate reduces the apparent annual percentage value of children who present with a blood lead > 10 μ g/dL during any single year. This discrepancy is evident for all years between 2006 and 2010 (the only years with available comparable data), with a difference of 5.8-13.6% between the annual mean value using the surrogate data and versus the annualized monthly data (Fig. 1).

The rationale for this approach is that SA Health and the smelter company want to establish a population estimate of childhood lead exposure at a point in time. This approach allowed the population impact from atmospheric smelter lead emissions to be measured against the now disbanded 'tenby10' project target, which set a target that 95% of all children living in Port Pirie would have a blood lead level below 10 μ g/dL on the 31 Dec 2010 (Thumbs up for low levels, 2014). This desire to have a 'point in time' estimate means that *only* the most recent blood lead test result of a child is used in the annual analysis of blood lead data (Simon et al., 2013).

The collective body of evidence with respect to the different health and environmental assessments, management and reporting of the environmental pollution problem in Port Pirie suggests not only significant inadequacies in the arrangements but a flagrant disregard for the interests of public health over the needs of industry. Given the pervasive and frequent elevated lead-in-air concentrations across the city, currently the highest in Australia, it is not surprising that approximately one child every three days presents with lead poisoning (i.e. a blood lead level > 10 μ g/dL) in Port Pirie (Simon et al., 2013; Taylor et al., 2013).

9. Monitoring but not regulating

This discussion highlights the need for significant reform to the roles, responsibilities and legislation governing the Commonwealth and States with respect to environmental approvals and regulation. Specifically, this paper has focused on two mining and smelting operations that have a significant history of discharging atmospheric pollution that is known to be potentially harmful to human health. In completing the analysis, this study has revealed several deficiencies in the approval, regulation, and oversight provisions as well as the misleading and limited data available to the public to make informed decisions about their place of residence.

One of the primary objectives of environmental agencies is to protect the environment while enabling certain activities or development to occur under regulation such that they do not compromise ecological sustainability and human health (e.g. Environmental Protection Act 1994 (Qld) s3 and Environment Protection Act 1993 (SA) s10). State environmental agencies ability to function independently within the existing planning and approval frameworks and to accommodate economic development and related government priorities appears to result in a conflict of interest, as detailed in the examples reviewed in this study. Two prime examples of this are evident from our analysis: first, the generous transitional environmental arrangements at Mount Isa with respect to compliance against State and national standards. Second, the ability of the States to set specific emission standards that exceed agreed standards in the interests of enabling and sustaining economic growth. In both cases, major industry seems to be able to leverage or have captured the regulatory process for its own benefit.

In the case of Mount Isa, the generous transitional environmental arrangements fits the description of giving primacy to economic interests and ensuring continuity of the operations at XMIM. With respect to the Nyrstar smelter at Port Pirie, the support and funding by State and Federal Government for the upgrade of the facility to be classified as a Major Development (Division 2) under the *Development Act 1993* (SA) also fits into this category. The extent of South Australia mining industry regulatory capture on government is discussed by Leadbeter and Wawryk (2013), who concluded that the independence of the EPASA does not always occur nor is capable of operating within its statutory objectives.

The critical question therefore, is how can the development, assessment and related mining approval process be separated meaningfully from the environmental licencing approval process? While certainty in terms of government approval is a desirable outcome in the interests of economic growth, the capacity of the environmental regulators to require industry to meet known and previously determined emission standards should be a non-discretionary process. Similarly, where science identifies health or environmental implications linked to a pollutant, regulatory systems must be robust and responsive to demand upgrades to pollution control systems. Alternatively, it may be necessary to withdraw a licence or environmental authority to pollute, in effect suspending or retracting the planning consent and conditions of approval therein.

Environmental regulators should not be asked to take into consideration the economic impacts of an industry in terms of the cost to implement and maintain pollution control equipment. This is a planning matter. Applicants have prior knowledge of emissions standards, and accordingly should factor the costs of meeting any such requirements into project planning and economic viability assessment. The environmental regulator's focus should remain on whether emission standards are appropriate with respect to the protection of the environment and public health and if industry is meeting these standards via the appropriate licencing provisions. If industry does not meet the agreed standards, the regulator should regulate. The regulators independence to provide specific environmental and public health advice to government should not be muddied with matters better dealt with from a planning perspective, such as the cost of pollution control. However, such recommendations are at odds with the provisions of the Environment Protection Act 1993 (SA), which requires the agency to take into account reasonable and practical measures that also include the costs of regulation (s10(1)(b)(i)(B)).

The final recommendation from this analysis relates to public access to information. All environmental agencies should maintain a functional, accessible and accurate database of pollution licencing and monitoring data. Data should be verified independently and be assessed regularly to ensure the public can access the necessary information and inform themselves of any potential risk of harm in their local area. Environmental standards and units of measure should be consistent within and between jurisdictions and licences. While over-arching freedom of information provisions exist at a Federal and State level, it is not unreasonable to expect public-funded environment, health and other relevant agencies to have their own statutory and functional processes to enforce and facilitate the dissemination of accurate and timely monitoring data. An example of such an approach operates in NSW as part of the recent reforms to the Protection of the Environment Legislation Amendment Act 2011 (NSW). This amendment requires the relevant licencee's pollution monitoring data to be made available to the public (see s66(6) of the Protection of the Environment Legislation Amendment Act 2011 (NSW)). Supporting this amendment, the NSW EPA (2012) issued a document outlining the requirements for publishing monitoring data that included, inter alia:

- Monitoring data must be made available within 14 days of obtaining the data.
- The data must be available on the licencee's web site or must otherwise supply the data to those who request a copy.
- The data must be available in a format that is easy for the general public to understand.
- Data tables must be provided and be in a form that can be exported to common data analysis programs and may include graphs and charts, but these on their own are not acceptable.

By contrast, this is not the case with respect to the reporting of environmental data from Mount Isa, either via the online system (EHP, 2014c) of the monthly bulletins (EHP, 2014a).

In the interests of public health, environmental quality and economic equality, emission standards must be a national responsibility and enforced equally across all States and Territories. Shortterm economic advantage by way of favourable emission limits and worse, legislative immunity, will lead to a legacy of problems for future governments and their communities. While industry may seek certainty to operate, communities affected by industrial pollution must also have certainty that their health and environment is a priority and cannot be negotiated or used as a *de facto* subsidy in the interests of economic growth.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.aeolia.2014. 03.003.

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CHAPTER 3: Measurement of lead emissions in the environment

Chapter Three presents the following six papers:

- Paper Three: Tracing South Australia's anthropogenic lead history using lead isotope compositions in Australian red wine. Kristensen, L.J., Taylor, M.P. & Evans, A.E. (2016). *Chemosphere*, DOI: 10.1016/j.chemosphere.2016.03.023.
- Paper Four: Lead isotopic compositions of ash sourced from Australian bushfires.
 Kristensen, L.J., Taylor, M.P., Odigie, K.O., Hibdon, S.A., & Flegal, A.R. (2014).
 Environmental Pollution, 190, 159-165.
- Paper Five: Lead and zinc dust depositions from ore trains characterised using lead isotopic compositions. Kristensen, L.J., Taylor, M.P., & Morrison, A.L. (2015). *Environmental Science: Processes & Impacts, 17*, 631-637.
- Paper Six: Unravelling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. **Kristensen, L.J.** & Taylor, M.P. (2016). *Environmental Geochemistry and Health*, DOI: 10.1007/s10653-10016-19804-10656.
- Paper Seven: Environmental lead exposure risks associated with children's outdoor playgrounds. Taylor, M.P., Camenzuli, D., Kristensen, L.J., Forbes, M., & Zahran, S. (2013). *Environmental Pollution*, 178, 447-454.
- Paper Eight: Environmental arsenic, cadmium and lead dust emissions from metal mine operations: Implications for environmental management, monitoring and human health. Taylor, M.P., Mould, S.A., Kristensen, L.J., & Rouillon, M. (2014). *Environmental Research*, 135, 296-303.

Following on from Chapter Two which identified and quantified lead emissions to the atmosphere in Australia, the papers in Chapter Three focus on various methods utilized to measure historical and contemporary lead depositions to the environment. The studies in Chapter Three all have similar aims, namely to measure and analyse the effect of emissions on surface dust loadings, surface soil depositions and anthropogenic influences in comparison to natural lead found in the environment. The measurement of lead in the environment conducted in the studies in Chapter Three link the sources and volumes of lead emissions with the corresponding impacts and consequences.

A wide range of media are used in this chapter to demonstrate the pervasiveness of lead emissions to various aspects of the environment. An array of methods have been used to reveal the extent of lead emissions seen in the environment, from small volumes of emissions measured locally, to large volumes of emissions seen in remote pristine environments. This chapter includes studies that measure the historical as well as contemporary lead emissions to the environment.

Paper Three

Tracing changes in atmospheric sources of lead contamination using lead isotopic compositions in Australian red wine

Kristensen, L.J. Taylor, M.P. & Evans, A.J. (2016) *Chemosphere*, DOI: 10.1016/j.chemosphere.2016.03.023.

Supplementary Information in Appendix C

The paper utilises the yearly harvesting and bottling of wine to reconstruct and measure historic emissions of lead in South Australia. It contributes to this thesis as it extends the understanding of atmospheric lead levels beyond the period of lead in air monitoring and the effect of deposition to nearby agriculture. The correlation between lead in the wine and available atmospheric data reveal further information with which a more complete understanding of the changing concentrations and sources of lead in the atmosphere can be developed. The concentrations and lead isotopic compositions reveal the dominant source of lead in the wine to be from leaded petrol which demonstrates the pervasiveness of leaded petrol emissions to the environment.

Tracing changes in atmospheric sources of lead contamination using lead isotopic compositions in Australian red wine

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Abstract

Air quality data detailing changes to atmospheric composition from Australia's leaded petrol consumption is spatially and temporally limited. In order to address this data gap, wine was investigated as a potential proxy for atmospheric lead conditions. Wine spanning sixty years was collected from two wine regions proximal to the South Australian capital city, Adelaide, and analysed for lead concentration and lead and strontium isotopic composition for source apportionment. Maximum wine lead concentrations (328 µg/L) occur prior to the lead-in-air monitoring in South Australia in the later 1970s. Wine lead concentrations mirror available lead-in-air measurements and show a declining trend reflecting parallel reductions in leaded petrol emissions. Lead from petrol dominated the lead in wine (²⁰⁶Pb/²⁰⁷Pb: 1.086; ²⁰⁸Pb/²⁰⁷Pb: 2.360) until the introduction of unleaded petrol, which resulted in a shift in the wine lead isotopic composition closer to vinevard soil (²⁰⁶Pb/²⁰⁷Pb: 1.137; ²⁰⁸Pb/²⁰⁷Pb: 2.421). Current mining activities or vinification processes appear to have no impact with recent wine samples containing less than $4 \mu g/L$ of lead. This study demonstrates wine can be used to chronicle changes in environmental lead emissions and is an effective proxy for atmospherically sourced depositions of lead in the absence of air quality data.

Keywords

Atmospheric emissions; lead monitoring; leaded petrol; mining; strontium

Introduction

Australia's lead mining history dates back to 1841 in South Australia (SA) (Drew 2011) but was sporadic and ceased by the early 20th century as the deposits were generally of low tonnage. Mining operations in the region south of Adelaide, SA, including the ANGAS zinc-lead-silver mine, have seen a recent resurgence. Multiple smelting operations commenced with early mining, but it is the lead smelters in Port Pirie, SA, continuous since 1889, that have released the largest volumes of lead in SA (NPI 2015b). In addition to emissions from mining and smelting activities, approximately 22,000 tonnes of lead were released from the combustion of leaded petrol in SA (Kristensen 2015). Lead emissions from petrol consumption reached peak levels in the 1970s and declined from 1981 following regulation of the concentration of lead in fuel followed by the introduction of unleaded petrol in 1985 (Kristensen 2015). Despite well-established prior knowledge of the adverse effects of lead toxicity (Needleman et al. 1979), monitoring and analysis of lead emissions into the Australian environment was limited. Outside of Port Pirie, availability

of the lead-in-air data is limited to the state capital, Adelaide, and is only publically available between 1982-2001 (Australian State of the Environment Committee 2001).

Lead emissions in Australia have inevitably altered the continent's atmospheric lead levels over the last 150 years, as has been the case elsewhere in the southern hemisphere (Bollhöfer and Rosman 2000). Given the deficiency of lead-in-air measurements, trends in long term air quality have not been captured, and monitoring commenced after peak emissions from leaded fuels. Although current mining operations in SA are small, there is a long history of mining and smelting. With the established link between lead-in-air concentrations and blood lead levels (Annest et al. 1983), particularly from leaded petrol and mining and smelting operations (Thomas et al. 1999; Hilts 2003; Taylor et al. 2014), a complete analysis of lead-in-air would assist in evaluating the long term health effects from lead emissions in Australia.

To address the limited data for assessing the historic impact of anthropogenic lead emissions to Australia's atmosphere, proxies have good potential to provide suitable substitute information. Wine is a rarely used proxy but its seasonal production and bottling has obvious potential for re-tracing emissions and depositions over the recent industrial past. Lead in wine is sourced in part by plant uptake from soil lead but also from anthropogenic sources (Almeida and Vasconcelos 2003). Temporal analysis of European wines has shown that the pattern of lead concentration in wines follows the consumption of leaded petrol in Europe (Lobiński et al. 1994; Rosman et al. 1998; Médina et al. 2000; Mihaljevič et al. 2006).

Lead isotopic analysis of wines from Bordeaux, France has shown that lead in the wines changed over time to reflect the dominant atmospheric lead pollution in southern France (Médina et al. 2000). Other European studies have found that lead isotopic compositions in wine may not always reflect those of leaded petrol, but reflect the isotopic signature of local, dominant metallurgical industries (Larcher et al. 2003; Mihaljevič et al. 2006). These studies confirm atmospheric deposition as being the dominant contributor to the lead content and isotopic composition of wine. Some studies have shown that contamination from tin-lead foil capsules in the presence of corrosion and cork disintegration can dominate the source of lead in wine (Gulson et al. 1992). Other studies have attributed the lead in wine to machinery or additives used during the vinification process where environmental contamination is a minor source of lead (Almeida and Vasconcelos 2003).

Given the paucity of air quality data in Australia, this study evaluates whether historic wine samples can be used to provide reliable surrogate information in the absence of traditional air quality data. In order to determine whether age-dated wine can be used as a proxy for atmospheric emissions, lead isotopic composition of wines and local vineyard soil were measured to apportion atmospheric lead depositions to their anthropogenic origins. Wine-derived lead concentration and isotopic data was also evaluated against leaded petrol emissions data for SA (Kristensen 2015) and the isotopic compositions of available archive air filters from South Australia Environmental Protection Authority (SAEPA). Strontium

isotopes have also been employed to provenance wine, sometimes in conjunction with lead isotopes (Balcaen et al. 2010). In contrast to industrial emissions of lead, there are no known anthropogenic sources of strontium in wine, indicating the potential to use strontium isotopes to establish the influence of natural soil on wine composition, including that of lead.

Methods and Materials

Field methods

Wine samples were collected from wineries established in the viticulture regions of McLaren Vale and Langhorne Creek in SA (Figure 3.1) spanning the years 1963-2012 (n=60; Appendix C, Supplementary Table S1). To limit potential confounding factors, wine samples were all of a red variety (Shiraz or Cabernet Sauvignon), produced from known vineyards within the same wine region, and were free from blending with wine from other regions. Soil samples (n=12; Appendix C, Supplementary Table S2) were collected from vineyards that provided wine samples for the study. Surface soils (0-2 cm) were collected to characterise the effect of atmospheric depositions and a sub-surface sample (below 20 cm dependant on bedrock depth) were taken to characterise background soil concentrations. Soil samples were sieved to < 2 mm to remove rocks and course particulates.



Figure 3.1: Locations of McLaren Vale and Langhorne Creek wine regions in relation to the main sources of lead emissions in Adelaide (petrol) and Port Pirie (lead smelter).

Air filter papers were collected from SAEPA who had sampled in central Adelaide city (Parkside: April 1997-June 2003). The city air filters provide a measure of aerosol composition during the later years of leaded petrol emissions, while those from an area in north Adelaide (Osborne: January 2002-December 2004), represent local industrial emission sources (Figure 3.1). No filter papers were available prior to 1997. Given the fact that sampled wine regions are located either side of ANGAS zinc-lead-silver mine (Figure 3.1), ore samples were sourced directly from the mine in 2012 to characterise this contemporary source.

Laboratory methods

Wine, soil and air filter samples were subject to acid extractable digestion and measurement at the National Measurement Institute, North Ryde, Sydney. Wine samples (5 mL) were digested on a hot block with 16 M HNO₃ (3 mL) after evaporating the alcohol. In order to test the homogeneity of a wine bottle, six separate 5 mL samples were taken from one bottle and analysed, returning a lead concentration of 1.10 μ g/L (SD 0.13; n=6). The homogeneity in sampling wine for lead was tested by replicate analysis (n=10) of multiple bottles of the same wine from a single vineyard in the same year (2011), which returned a lead concentration of 1.13 μ g/L (SD 0.11). Soil samples (1 g) and air filter samples were digested in concentrated HCl (3 mL) and HNO₃ (3 mL). Lead concentrations and isotopic compositions were determined on a Q-ICP-MS (PerkinElmer ELAN DRCII). Matrix spikes of wine samples returned recoveries of 82-84% for wine samples and a correction factor applied. Replicate analysis returned RSDs <4.7% for wine samples and <5.0 % for soil samples. Soil sample matrix recoveries were 85-90% with recoveries of internal reference materials AGAL-10 (Hawkesbury River Sediment) 100% and AGAL-12 (biosoil) 99%.

Lead concentrations were optimised for isotopic analysis. Pre-concentration of wine samples was required for concentrations <70 µg/L (lead) and was achieved by digesting 200 mL wine. Concentration matched NIST SRM 981 (natural lead isotope composition standard) bracketed each sample to correct for mass fractionation. Precision (RSDs) was 0.13% for 206 Pb/ 207 Pb, 0.14% for 208 Pb/ 207 Pb and 0.22% for 206 Pb/ 204 Pb. Measurement uncertainty was 0.0004 for 206 Pb/ 207 Pb, 0.0007 for 208 Pb/ 207 Pb and 0.01 for 206 Pb/ 204 Pb. Strontium isotopes were measured after separation from rubidium using ion exchange chromatography and complexing with EDTA following the methods outlined by Vorster et al. (2008). Concentration matched NIST SRM 987 bracketed each sample measured on a HR-ICP-MS (Thermo Element 2) with 0.11% RSD for 87 Sr/ 86 Sr. Although no corrosion was evident in the corks, testing by X-ray fluorescence (Olympus Delta Premium 40 kV) confirmed there was no evidence of lead migration through the cork into the wine where tin-lead capsules were used (n=5; Appendix C, Supplementary Table S3).

Results and Discussion

Lead concentrations

Concentrations of lead in the sampled wine ranged from 1-328 μ g/L with an average concentration of 33 μ g/L (Appendix C, Supplementary Table S1). Lead concentrations of surface soil samples (n=6) ranged from 5–27 mg/kg with an average of 11 mg/kg. Subsurface soil samples (n=6) were only slightly lower, ranging from 4–14 mg/kg with an average of 10 mg/kg. Atmospheric lead concentrations for Adelaide city ranged from 0.02-1.75 μ g/m³ for the period 1982-2001 (Department of the Environment and Heritage 2004). Lead isotopic compositions of Adelaide aerosols from 1994 measured by Bollhöfer and Rosman (2000) were used to supplement the air filter data measured here.

Although the availability of wine samples prior to 1985 are sporadic, wine lead concentrations show a decreasing trend over the six decades of sampling (Table 3.1). A study of Australian wines in 1955 found an average lead concentration of 200 μ g/L (n=24)

with red wines having a range of 40-390 μ g/L (Rankine 1955). These concentrations are significantly higher than more recent decadal averages found in this study. A later assessment of a range of Australian wines from 1991 returned average concentrations of 40.7 μ g/L (n=96) (Lee et al. 1991), which is more than double the 1990s average recorded in this study. However, a random selection of Australian wine varieties and regions were used in these previous studies to determine if lead in wine guidelines set by the International Organisation of Vine and Wine (OIV) were being met.

Direct comparisons of lead contents in wine from different regions cannot be made as the volumes and sources of lead have varied in different regions (Kristensen 2015; NPI 2015a). Proximity to cities during the period of leaded petrol use and industrial operations would contribute in differing degrees to wine lead concentrations. Additionally, vinification processes including the use of fertilisers, pesticides, wine additives and machinery may have contributed to lead concentrations in wine in the absence of large emissions of lead (Mihaljevič et al. 2006). It is for this reason that comparisons of lead concentrations in wine in this study cannot be made with values returned in international studies. What can be compared is the overall pattern of declining lead concentrations in wine, which is consistent with the decline in leaded petrol emissions from the mid-20th century (Lobiński et al. 1994; Kaufmann 1998; Rosman et al. 1998; Médina et al. 2000). This trend in wine lead concentrations also fits with other environmental archives of lead emissions such as peat bogs (Marx et al. 2010) and Antarctic ice cores (Planchon et al. 2003) but provides a greater level of sensitivity to yearly variations, particularly within smaller regions of Australia.

Decade	Average lead \pm SD	Range (µg/L)	OIV lead guideline
	(µg/L)		(µg/L)
1960s (n=4)	96 ± 25	75-123	600 (1953)
1970s (n=7)	125 ± 109	22-328	500 (1975)
1980s (n=6)	46 ± 24	29-92	300 (1987)
1990s (n=17)	18 ± 10	6.8-46	250 (1993); 200 (1996)
2000s (n=18)	5.3 ± 4.9	1.9-14	150 (2007)
2010s (n=6)	2.7 ± 0.88	1.0-3.4	150 (2007)

Table 3.1: Lead concentrations in wine for each decade from McLaren Vale and Langhorne Creek wine regions.

All lead levels measured were below corresponding concurrent wine guidelines, which have been lowered progressively over the last six decades (Table 3.1) (International Organisation of Vine and Wine (OIV) 1995). Wines post-dating 2000 also fall below drinking water guidelines for lead (10 μ g/L) as set by the National Health and Medical Research Council (NHMRC) (2011). Lowering of the maximum allowable lead concentration in wine (International Organisation of Vine and Wine (OIV) 1995, 2013) was in response to the falling global atmospheric lead concentrations, rather than health concerns. Elevated lead concentrations in wine samples from the 1970s coincide with the highest consumption of leaded petrol within SA and across Australia (Farrington et al. 1981; Kristensen 2015). In 1993 'normal' lead levels in Australian wines were deemed to be less than 100 μ g/L (Gulson et al. 1998). Analysis of 20 years of younger wines, post

leaded petrol, shows that levels of lead in contemporary wine are 50-100 times lower at 1-2 μ g/L. This recent wine data indicates current wine lead concentrations are more likely to reflect 'normal' lead levels, sourced naturally from vineyard soil.

Peak wine lead concentrations occur in the mid-1970s and a decline in the wine lead concentrations are observed from the mid-1980s onwards (Figure 3.2; Appendix C, Supplementary Table S1). Peak lead emissions from leaded petrol occurred in SA in 1980 (Kristensen 2015) and decline following the introduction of unleaded petrol and petrol regulations to reduce the maximum allowable concentration of lead permitted to be added to petrol. Lead in air levels declined from the mid-1970s (Figure 3.2) and only fell below the current lead in air guideline of 0.5 μ g/m³ (National Environment Protection Council (NEPC) 1998) in 1994. Although it cannot be determined if the increase in the wine lead content measured in earlier samples of wine (Table 3.1) is similarly associated with elevated ambient air lead due to the lack of monitoring data, the correlation (Pearson correlation r=0.815, p < 0.01, excl. outlier value for 1986) for year-matched wine and aerosol lead concentrations indicate grapes and wine respond to local atmospheric lead concentrations. The strong association between lead in wine and atmospheric lead provides evidence to support the argument that atmospheric depositions were the dominant contributor to wine quality. The year to year variance is affected by the limited number of samples. Higher correlations between wine concentrations and aerosols would likely be achieved with more samples. Although it cannot be discounted, the extremely low concentration values recorded in recent wine samples indicate negligible influence from the vinification process, in contrast to arguments advanced in previous studies (Almeida and Vasconcelos 2003; Stockley et al. 2003).



Figure 3.2: Lead concentration in wine (this study) compared to lead-in-air data for Adelaide city (1977-1979: Vehicle Emissions and Noise Standards Advisory Committee and Australian Environment Commission (1980); 1980-1981: SAEPA personal communication and 1982-2001: Department of the Environment and Heritage (2004)) and

lead emissions from petrol combustion (Kristensen 2015). Dashed lines indicate non-continuous data.

Wine lead concentrations from McLaren Vale and Langhorne Creek correlate with peak atmospheric levels measured in the 1970s and decline in tandem thereafter. Given that petrol emissions were the predominant source of lead-in-air (Adeeb et al. 2003), deductive reasoning implies that these parallel shifts can only be ascribed to changes in leaded petrol consumption and related emissions (Figure 3.2). Although the largest lead emissions in SA are from the smelter in Port Pirie approximately 230 km north of the studied wine regions (47 tonnes in 2013/14 (NPI 2015c)), there is no evidence of any significant contribution to lead in contemporary wines. Had there been wine samples available between 1900-1920, lead emissions from the Port Pirie smelter may have been measured in the wine as these large unregulated lead emissions from this time have been measured in Antarctic snow (Van de Velde et al. 2005). However, as the northerly wind only blows in Port Pirie during the winter months (Bureau of Meteorology (BoM) 2014) when the wine grapes have already been harvested, the wine samples may not be subject to significant depositions from the Port Pirie smelter. Further, the decade-by-decade decline in lead concentrations is not consistent with an argument that states the smelter was the dominant source of lead. Indeed, earlier studies in Adelaide have shown the pervasive effect of automotive exhaust lead depositions, which contaminated the rural landscape up to 50 km downwind of the city (Tiller et al. 1987).

The human health risks associated with elevated lead levels in wine are unlikely to affect children who are most at risk from the toxic effect of lead (National Toxicology Program 2012) because of the prohibitive alcohol content of wine. Further, the measured concentrations of lead from the last decade of samples show that all samples were significantly below Australian drinking water guidelines (National Health and Medical Research Council (NHMRC) 2011) indicating consumption of contemporary wines poses little overall risk to human health. Nevertheless, atmospheric deposition is a potential source of lead as part of the diet (World Health Organisation (WHO) 2010), which suggests that grapes or other food grown in areas located near to contemporary sources of lead emissions (or other harmful substances) should be subject to careful scrutiny. This route of potential exposure is relevant given the evidence that blood lead levels in adults below 10 μ g/dL are associated with increased blood pressure, risk of hypertension and cardiovascular-related mortality (National Toxicology Program 2012). Similar health risks have also been associated, independently, with excessive consumption of alcohol (O'Keefe et al. 2007).

Lead isotopic composition

Decade averages of lead isotopic compositions (²⁰⁸Pb/²⁰⁷Pb; ²⁰⁶Pb/²⁰⁷Pb; ²⁰⁶Pb/²⁰⁴Pb) of wine samples in relation to vineyard soils and Adelaide air filters are presented in Figure 3.3. Chronological changes to lead isotopic compositions in wine (Appendix C, Supplementary Table S1) compared to contributing lead sources are presented in Figure 3.4. Lead isotopic compositions of the air filters have low lead compositions relative to the

isotopic compositions of the vineyard soils, which reflect more strongly natural source inputs. The disparity in lead isotopic compositions between surface and sub-surface soils (Figure 3.3), is due to the effect of atmospheric deposition on surface soils (Tiller et al. 1987). Wines sampled from the 1960s and 1970s have lead isotopic compositions that correspond to Adelaide aerosols, reflecting lead sourced from petrol emissions. After the 1980s, lead isotopic compositions of wine trends towards natural vineyard soils (Figure 3.3) and 3.4), which corresponds to the introduction of unleaded fuel in 1985 followed by the drawdown of leaded petrol consumption from that time onwards (Kristensen 2015).



Figure 3.3: Average (mean) decadal lead isotopic composition of wine samples and Adelaide lead-in-air compared to vineyard soils demonstrate clearly the change in lead over time.

The time-series of mean decadal wine lead isotopes (Figure 3.3) demonstrates a shift in composition through the sixty years of McLaren Vale and Langhorne Creek wine analysed. Figure 3.4 demonstrates the chronological evolution of lead isotopic compositions in the wines with reference to local background soil and Adelaide air lead isotopic compositions. The most marked shift in isotopic composition of the wines does not occur until the 1980s (Figure 3.4), reflecting two significant factors influencing atmospheric composition. Firstly, in 1984, South Australia reduced via regulation the allowable concentration of lead in petrol from 0.80 g/L to 0.65 g/L (Kristensen 2015). Secondly, a year later in July 1985, unleaded petrol was introduced across Australia.

The influence of atmospheric deposition in driving the source of lead in the wine is observed in the isotopic compositions of samples from the 1960s and 70s. The single sample from 1979 has the lowest lead concentration of these leaded petrol decades (22 μ g/L) and corresponding isotopic composition that reflect soils from the local vineyards. This anomaly may have arisen from the effect of washing of the grapes or rain prior to harvest, removing surficial atmospherically deposited lead and resulting in a higher

influence from soil lead. Washing of wine grapes has been shown to reduce lead in the grape juice up to 75 % (Stockley et al. 1997), although is not common practice.



Figure 3.4: Temporal shifts in a) ²⁰⁶Pb/²⁰⁴Pb, b) ²⁰⁸Pb/²⁰⁷Pb, and c) ²⁰⁶Pb/²⁰⁷Pb of McLaren Vale and Langhorne Creek wine and Adelaide air filters. Isotopic range of multiple samples indicated within each year. The 1994 Adelaide air isotopic composition is from Bollhöfer and Rosman (2000).

The removal of leaded petrol in 2002 and the consequent changes in atmospheric composition, opened up the potential for other more dominant contemporary industrial lead emission sources to influence the lead content in wine, particularly where vineyards and industry coexist. One such region is Langhorne Creek, where the ANGAS lead-silver-zinc mine operated from 2007-2013. Mine operations are located only 7 km from the vineyards of Langhorne Creek (Figure 3.1), and although only a small and principally an underground operation, are potentially responsible for even the low levels of lead seen in wine produced in Langhorne Creek since commencement of operation.

The ANGAS mine emitted an estimated maximum of 320 kg of lead a year, totalling 1300 kg since operations began (NPI 2014). Deposition of lead in dust produced from mining operations averaged 1.3 μ g/m²/day (457 μ g/m² total annual loading in 2012) at monitoring locations outside and within 1 km of the mining lease (Terramin Australia Limited 2013). Values declined rapidly from the lease to outmost samples sites implying limited spatial depositional effects. The average dust lead loading values are well below Australian acceptable lead in surface dust limit (Standards Australia 1998) of 8000 μ g/m² and international daily limits standards of 100 μ g/m²/day (TA Luft (Technical Instructions on Air Quality Control) 2002).

From the measurement of the lead isotopic compositions, it appears the lead in the wine from 2000 was sourced predominantly from vineyard soil. However, the advent of the ANGAS mine may have caused a lag in the lead isotopes in wine being sourced entirely from vineyard soils (Figure 3.4). The upward recovery of isotopic composition values towards matching natural values as measured in local vineyard soils appears to have stabilised during the period of the operation of ANGAS mine (2007-2013). During this period ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁷Pb/²⁰⁸Pb ratios remain offset from the natural local soil lead sources (Figure 3.4). However, the limited time period between the cessation of leaded petrol and the advent of the ANGAS mine does not allow for definitive conclusions to be drawn as the data may reflect inherent natural variations. The ANGAS mine was closed in 2013 as ore reserves were depleted (Terramin Australia Limited 2015) and future analysis of wines from the region may reflect another shift in lead isotopic compositions.

The spread of lead isotopic composition values measured in the air filters (Figure 3.4) correspond to the reducing influence of leaded petrol through the decade of the 1990s as leaded petrol was phased out and the lead concentration of petrol was reduced concomitantly. As such, other sources from Adelaide are likely to have become a more significant component in the aerosols resulting in the range in isotopic compositions seen from 2002 (Figure 3.4). Port Adelaide (EPA air monitoring station Osborne), 14 km north of Adelaide city centre, imports and exports commodities (including ore concentrates from the ANGAS mine (Jackson and Abbot 2008)) as well as hosting industrial companies, which produced collectively almost 200 kg of lead emissions in the 2003/2004 reporting period (NPI 2015b). Although the emissions are less than the ANGAS mine, its influence on the wine samples cannot be discounted.

Quantifying the contribution of anthropogenic sources such as leaded petrol to environmental samples can be achieved by application of isotopic mixing models (Komárek et al. 2008). A recent improvement of the model by Larsen et al. (2012) has allowed for two dimensional quantification (²⁰⁶Pb/²⁰⁷Pb vs. ²⁰⁸Pb/²⁰⁶Pb) and analysis of the variance of samples from the two end member mixing line. A variance of more than 20 % would indicate there are more than two contributing sources of lead and a variance of more than 40 % indicates a more dominant lead source than the selected anthropogenic end member (Larsen et al. 2012).

Applying Larson et al.'s (2012) model, the percentage of anthropogenic lead from leaded petrol can be determined for the wine samples (Table 3.2). In the absence of lead isotopic compositions for Adelaide's leaded petrol, we have used the oldest available isotopic composition for Adelaide aerosols collected in 1994 (Bollhöfer and Rosman 2000). This isotopic composition is similar to Broken Hill ore, which was the dominant lead source used in Australian leaded petrol resulting in a conservative model. Quantifying source contributions from the ANGAS mine is complicated by the fact that the lead isotopic composition of the ore lies on the mixing line between Adelaide aerosols and natural vineyard soil. This limitation in the model has restricted our application to quantifying the contribution from leaded petrol for the relevant years.

Decade	Percentage anthropogenic	Variance
1960s	81.0% petrol	6%
1970s	83.9% petrol	2%
1980s	78.4% petrol	2%
1990s	64.8% petrol	3%
2000s	52.3% petrol	4%

Table 3.2: Percentage of lead from leaded petrol found in the wine samples per decade.

The model apportioning the source of lead in the wine to leaded petrol is further evidence of the significance of leaded petrol consumption on atmospheric quality and composition. The percentages relating to lead from petrol in the wine correspond with previously reported variations in emissions (tonnes) from leaded petrol in SA (Adeeb et al. 2003; Kristensen 2015). Governmental reductions of lead in petrol and the implementation of unleaded petrol have significantly reduced atmospheric lead, a fact that is demonstrated clearly in the wine samples from this study and from Europe (Médina et al. 2000) as well as in other environmental archives including peat bogs (Marx et al. 2010), ice cores (McConnell et al. 2014) and corals (Lee et al. 2014).

Strontium isotopic composition

The strontium isotopic composition ⁸⁷Sr/⁸⁶Sr was measured in all wine samples and subsurface soils from vineyards where the origin of wine was known (Wineries A, B and C) (Table 3.3). The strontium isotopes were determined for the wine and soil samples to evaluate possible changes to isotopic compositions due to the uptake of metals through the vines or due to the vinification process. Conserved strontium isotopic composition between soil and wine supports the finding that the changes in the lead isotopic compositions in the wine are a result of anthropogenic lead sources. In addition to acting as an isotopic control, strontium isotopic composition ⁸⁷Sr/⁸⁶Sr was measured to provide further geochemical information on these wine regions for future provenance studies.

Age range	Wine ⁷ Sr/ ⁸⁶ Sr		Soil ⁸⁷ Sr/ ⁸⁶ Sr
of wines	Average	Range	
1994-2012	0.710	0.707-0.713	0.710
1973-2010	0.714	0.708-0.727	0.721
1988-1995	0.712	0.709-0.715	0.710 ^a ; 0.721 ^b
1963-1983	0.711	0.710-0.712	
1979-2011	0.711	0.709-0.714	
	Age range of wines 1994-2012 1973-2010 1988-1995 1963-1983 1979-2011	Age range of winesWine ⁷ Sr/ ⁸⁶ Sr1994-20120.7101973-20100.7141988-19950.7121963-19830.7111979-20110.711	Age range of wines Wine ⁷ Sr/ ⁸⁶ Sr 1994-2012 Average Range 1993-2010 0.710 0.707-0.713 1973-2010 0.714 0.708-0.727 1988-1995 0.712 0.709-0.715 1963-1983 0.711 0.710-0.712 1979-2011 0.711 0.709-0.714

Table 3.3: Strontium isotopic compositions in wine and soil for McLaren Vale and Langhorne Creek

a Vineyard 1 b Vineyard 2

The average strontium isotopic composition from the wine reflects soil from McLaren Vale. The use of strontium isotopic compositions is effective for attributing wine to the McLaren Vale wine region. By contrast, the single Langhorne Creek winery returned a slightly larger range of strontium isotopic compositions. This wine region is located on a floodplain, which may account for the naturally higher variability in strontium levels due to soils receiving deposits from a wider range of catchment sources or may be a result of mixing the wine with McLaren Vale grapes. Nevertheless, the conserved strontium isotopic composition between the soil and wine from the McLaren Vale wine region provide evidence that the different lead isotopic compositions in the wine are of anthropogenic (atmospheric) origin and not a consequence of plant uptake from the soil.

Measurement of the strontium isotopic composition ⁸⁷Sr/⁸⁶Sr has been used as a tracer of geochemical origin for food authentication as no fractionation of the isotopes occurs during plant uptake from soil (Balcaen et al. 2010). Studies assessing whether the wine making process affects the strontium isotopic composition have been conducted previously in Europe. These studies determined no statistical difference in strontium isotopic composition between the vineyard soil and corresponding wines, indicating that the method can be utilised for provenance purposes (Almeida and Vasconcelos 2003; Petrini et al. 2015).

The combination of strontium isotopes with lead isotopic compositions has significant potential for establishing wine provenance determination in this region. However, a broader library of wine strontium isotopic compositions from across Australia and international wines is needed to make this approach viable. Multi-elemental analysis has shown to be successful in discriminating wine from different regions across Australia, except for regions in close proximity such as McLaren Vale and Langhorne Creek (Martin et al. 2012). Combining lead and strontium isotopic compositions with multi-elemental analysis can provide a robust enough approach to accurately identify the provenance of wine, which could be used to enhance product security and limit counterfeiting. Counterfeiting is not an insignificant concern for the Australian wine industry, whose fastest growing market is China where an estimated 70 % of wines are fake (Fitzgerald 2014; Sage 2015). This study also demonstrates that wine has significant potential for application as an environmental proxy for the construction of atmospheric conditions in the absence of conventional air monitoring. The measurement of baseline environmental quality and source apportionment can be employed in other regions where pollution generating industry and vineyards are co-located.

Conclusion

Lead concentrations and isotopic compositions measured in the wine samples demonstrate atmospheric depositions from leaded petrol was the primary source of lead in wine in the regions surrounding Adelaide. Temporal shifts over the last six decades in lead concentration and isotopic composition in the wine correspond closely to the decreased concentrations of lead used in petrol and the decline of leaded petrol consumption. Further, the use of strontium isotopes supports our conclusion that atmospheric depositions and not *in situ* sources of lead in soil are the prevailing source of wine contamination. The analysis of historic wine presented in this study demonstrates that it is a viable proxy for understanding historic atmospheric lead concentrations and associated depositions. The results suggest that with an adequate library of wines and their corresponding elemental

and isotopic compositions, there is potential for successful provenance and authentication of Australia wines.

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Paper Four

Lead isotopic compositions of ash sourced from Australian bushfires

Kristensen, L.J., Taylor, M.P., Odigie, K.O., Hibdon, S.A., & Flegal, A.R. (2014). Environmental Pollution, 190, 159-165.

Supplementary Information in Appendix D

This paper investigates historic lead emissions, in particular leaded petrol, to pristine environments in Australia and their potential for remobilisation during fire events. This study measures and characterises the significant volume of historic lead emissions from petrol affecting regions removed from the expected emissions footprints. This study also demonstrates the ability of historic lead emissions to be re-emitted and thereby contribute to the overall burden of lead emissions and contemporary exposures in Australia. Environmental Pollution 190 (2014) 159-165

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Lead isotopic compositions of ash sourced from Australian bushfires

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1. Introduction

Lead, which has been used extensively for industrial applications for thousands of years (Nriagu, 1983), is the most pervasive and ubiquitous elemental pollutant in the world – including Australia (Bollhöfer and Rosman, 2000, 2001). Australia has a long history of lead mining, dating back to 1841 in Glen Osmond, South Australia, and now ranks second in the world in lead mining, processing and production (Guberman, 2012). In addition to the impact of mining and smelting activities, significant amounts of lead were released in Australia from the combustion of leaded petrol. Between 1932, when the first documented sale of leaded petrol occurred in Australia, and 2002, when leaded petrol was completely phased out (Cook and Gale, 2005; NEPC, 2001), it is estimated that leaded petrol emissions contributed up to 90% of the atmospheric lead in urban areas in the country (NEPC, 2001). In two national assessments of petrol lead emissions, it was determined that 3842 tonnes of lead were emitted in 1976 in Australian capital cities (Farrington and Boyd, 1981) and 2388 tonnes of lead were emitted in 1985 (Farrington, 1988), despite mandated reductions of allowable lead in petrol (NEPC, 2001). Therefore, over the 70-year period of leaded petrol use in Australia tens, if not hundreds, of thousands of tonnes of lead was released into the ambient environment.

ABSTRACT

This study identifies natural and industrial lead remobilized in ash deposits from three bushfires in relatively pristine areas of Australia in 2011 using lead isotopic compositions ($^{208}Pb/^{207}Pb$; $^{206}Pb/^{207}Pb$). Lead concentrations in the ash ranged from 1 to 36 mg/kg, bracketing the range of lead (4–23 mg/kg) in surface soils (0–2 cm), subsurface (40–50 cm) soils and rocks. The lead isotopic compositions of ash and surface soil samples were compared to subsurface soils and local bedrock samples. The data show that many of the ash and surface soil lead isotopic compositions were a mixture of natural lead and legacy industrial lead depositions (such as leaded petrol combustion). However, some of the ash samples at each of the sites had lead isotopic compositions that did not fit a simple two end-member mixing model, indicating other, unidentified sources.

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These industrial lead emissions have adversely impacted environmental and human health in Australia (Laidlaw and Taylor, 2011). Although industrial lead exposures have declined over the past three decades with the elimination of leaded petrol, as they have elsewhere (Annest et al., 1983), the environmental legacy from those emissions remain a source of potential exposure (Harris and Davidson, 2005; Laidlaw et al., 2012). Moreover, recent studies have determined that relatively low blood lead levels that were previously considered innocuous have been associated with adverse human health problems (ACCLPP, 2012; Lanphear et al., 2005). The most commonly reported health effects of lead exposure in children are reduced intelligence, increased behaviour problems, reduced attention, hyperactivity and cognitive impairment (NTP, 2012).

Consequently, events that remobilize historic lead depositions are an environmental and human health concern. These include fires, which pose potential health risks due to smoke and particulate emissions (Weinhold, 2011) along with their role in redistributing elements such as mercury (Finley et al., 2009) and lead (Nriagu, 1989). Given that fluctuations in atmospheric lead emissions have been linked to changes in blood lead levels (Annest et al., 1983) and that there is still no established safe level for lead (NHMRC, 2009; WHO, 2010), the likelihood that bushfires mobilise historic lead depositions (Odigie and Flegal, 2011) warrants investigation. Previous studies have shown that heavy metals can become enriched in the residues formed from the burning of biomass (Nzihou and Stanmore, 2013). Up to 11.7% of the lead stored in the original biomass may remain as bottom (*in situ*) ash,





POLLUTION

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Fig. 1. The location of the three bushfire sample sites and Australia's two major lead mines of Broken Hill (New South Wales) and Mount Isa (Queensland).

with the remainder forming airborne component (fly-ashes and dust) that can be widely dispersed (Narodoslawsky and Obernberger, 1996).

The potential for the re-release of historic anthropogenic lead emissions is a particular concern in Australia because hazard reduction burning (controlled burning) of urban bushland is a standard fire risk-reduction strategy. Furthermore, the Australian continent is prone to frequent and uncontrolled wildfires, and their incidence and severity are predicted to increase due to climate change (Hennessy et al., 2006). Therefore, the primary goal of this study was to ascertain if historic depositions of industrial lead were being released back into the environment during bushfires.

Fortunately, tracing lead contamination in Australia is often rather simple because almost all of its industrial lead came from a few large, geologically old (~1700 million years) ore deposits that have relatively unique isotopic fingerprints (Gulson, 2003). The principal Australian lead ore deposits are in Broken Hill (New South Wales) and Mount Isa (Queensland), which are among the largest in the world and have distinctive lead isotopic compositions (e.g., ²⁰⁶Pb/²⁰⁷Pb: ²⁰⁸Pb/²⁰⁷Pb: 1.0390-1.0432; 2.3102 - 2.3197) (Chiaradia et al., 1997; Cooper et al., 1969; Cumming and Richards, 1975; Gulson, 1985; Gulson and Mizon, 1979; Townsend et al., 1998; Table S2, Supporting Information). Relatively small amounts of leaded petrol, with more radiogenic isotopic compositions, were imported from Singapore and the US prior to 1998, but sales of those imports were restricted to northern Australia, thousands of kilometres from the field sites analysed in this study. Consequently, we hypothesized that lead isotopic compositions of soil and ash samples collected for this study would be composed primarily of natural lead and Australian industrial lead.

2. Methods

2.1. Sample collection sites

Ash and soil samples were collected at three sites across Australia shortly after three large, uncontrolled and intense bushfire events in relatively pristine areas in the first week of February 2011 (Fig. 1). These were in the Waygara State Forest (Tostaree Fire) in Victoria, ~340 km east of Melbourne; the Darling Range Regional Park (Red Hill Fire), ~ 20 km northeast of Perth; and the Banyowla Regional Park (Kelmscott Fire), ~20 km east of Perth. In all cases, ash samples were collected from the burnt remains at the base of large old eucalypt trees that had been destroyed during the fire events. This targeted sampling approach differs from that used in Odigie and Flegal (2011) who relied on the collection of ash samples accumulated at the surface of soils in the burnt area. Older trees were the focus of the sampling because we hypothesized that these trees would be more likely to contain signatures of historic lead depositions compared to smaller, younger trees that would have grown in period following the introduction and domination of Australian unleaded petrol for all new vehicles from 1986 (Australian Government, Department of Environment, 2001). Sampling of the ashed trees was undertaken using a semisystematic sampling pattern spread out across the burnt area. While the collected samples were spread widely across each of the locations (Tostaree Fire 110 km²; Red Hill Fire 11.7 km²; Kelmscott Fire 10 km²), the occurrence of ashed older trees dictated individual sample locations (Table S1, Supporting information). The ash was collected in plastic bags, using established trace metal clean procedures (Odigie and Flegal. 2011)

Soil samples were collected from depths of 0-2 cm (surface) and 40-50 cm (deepest), using comparable trace metal clean procedures (Taylor et al., 2010). Additional soil and rock samples were collected from Kelmscott and Red Hill in 2012. The deeper soil samples were used to determine local natural background soil lead concentrations and isotopic composition as no natural lead isotopic compositions had been reported in the literature for the study sites. This assumption was based on previous studies using a similar approach to determine successfully both local natural background lead concentrations and isotopic compositions. Subsurface sampling of soils at depths > 30 cm has been demonstrated previously to be a robust technique for characterizing the natural lead signature of a location (Gulson and Mizon, 1979; Gulson et al., 1981; Mackay et al., 2013; Taylor et al., 2010). Soil and rock samples were collected close to, but outside of, the bushfire areas with the footprint of the samples enveloping the ash sample areas.

Locations of the three fires studied, along with those of the Broken Hill and Mount Isa lead mines and sites referenced in the report are shown in Fig. 1. Therefore in order to establish the lead isotopic compositions and concentrations of ash sourced from Australian bushfires this study analyses 56 ash samples, 8 surface soils, 7 subsurface soils and 6 local rocks, giving a total dataset of 77 environmental samples (Supporting information Table S1).

2.2. Sample preparation

Samples (n = 77) were prepared by air drying and sieving to remove materials > 2 mm at Macquarie University, Sydney, prior to acid digestion and analysis of lead concentrations and isotopic compositions at the University of California at Santa Cruz (UCSC) (n = 64, Table S1) and Australia's National Measurement Institute, Sydney (n = 13, Supporting information Table S1).

2.3. Analytical methods

Sample processing at UCSC was undertaken in a HEPA (Class 100) filtered air hood, within a trace metal clean laboratory. Approximately 0.5 g of each ash and soil sample was oven dried at 65 °C. Ash samples were digested by refluxing twice in concentrated, trace metal grade HNO₃ as per the methods detailed in Flegal et al. (2010). Soil samples were processed using the digestion procedure detailed in Soto-Jimenez et al. (2006), and were refluxed once using trace metal grade aqua regia (HCl:HNO₃ 3:1 v/v). Both ash and soil solutions were analysed for lead concentrations using a Thermo Scientific XSeries 2 Quadrupole ICP-MS. Rhodium was used as an internal standard to correct for instrumental drift, which was also monitored by multiple analyses of a 1 ppb lead consistency standard. The consistency standard returned a mean concentration 0.90 ppb \pm 7.7% RSD. Concentrations were calculated using the natural abundance of the calibration standards. The calibration accuracy was ascertained with multiple (n = 10) analyses of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1640a (trace elements in natural water), with a mean recovery concentration of 0.22 ppb \pm 7.2% RSD. The completeness of sample digestion and remobilization of lead was determined by concurrent digestion and analysis of SRM 1547 (peach leaves, n = 3) and SRM 1633b (coal fly ash, n = 4). Recovery for SRM 1547 was 91% (RSD 3%) while for SRM 1633b, recovery was 47% (RSD 8.5%). The former (SRM 1547) provides the best estimate of lead recoveries in ash samples because they are derived predominantly from vegetation and organic soil material, as observed previously (Odigie and Flegal, 2011). The soil samples were digested concurrently with NIST SRM 2704 (Buffalo River Sediment) and National Research Council Canada (NRCC) PACS-1 (British Columbia Harbor Sediment), which had recoveries of 43% (RSD 4%) and 76% (RSD 7.4%), respectively. The instrument detection limit, 3 \times the standard deviation of blanks (n = 3) was 0.005 ng/g. The use of a concentrated HCl/ HNO₃ digestion method in this study measures the acid-leachable (labile) levels of lead in the samples. The derived values are conservative relative to those achieved via a concentrated HF digestion, which would also extract natural lead within refractory aluminosilicates (Odigie and Flegal, 2011).

Lead isotopic compositions were measured with a Finnigan Element 2 High-Resolution ICP-MS, after optimizing sample volumes based on their lead concentrations. Analyses were conducted with concurrent measurement of 1 ppb SRM 981 (common lead), which was used to correct for isotopic fractionation. To determine the precision within each sample, two ash samples and two soil samples were digested in triplicate. Three separate measures of the same sample were weighed into separate Teflon vials for triplicate analysis. The analytical precisions (RSD) for ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁴Pb were 0.23%, 0.25% and 0.31%, respectively.

Lead isotopic composition analysis of additional soil and rock samples was carried out in 2013 at the National Measurement Institute, Sydney, using comparable digestion and analysis methods (Evans, 2013). Each sample was bracketed by concentration matched SRM 981 (common lead) and also run on a Finnigan Element 2 High-Resolution ICP-MS. The analytical precisions (RSD) for ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁶Pb/²⁰⁴Pb were 0.39%, 0.31% and 0.55%, respectively.

3. Results

3.1. Lead concentration and isotope composition

Lead concentrations and isotopic compositions of the ash and soil samples from the three bushfires are listed in Table S1, Supporting information. Lead concentrations of the soils, which ranged from 4 mg/kg to 23 mg/kg (dry weight), were bracketed by those of the ash samples, which ranged from 1 to 36 mg/kg. However, the isotopic composition (²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁴Pb) of most of the ash samples and many of the surface soils differed measurably from those of the deepest (40–50 cm) soil samples and rock samples, which were assumed to represent the natural or baseline values for the three study sites. For comparison,

the lead isotopic composition of Broken Hill and Mount Isa ore bodies and Australian leaded petrol are provided in Table S2, Supporting information.

3.2. Tostaree, Victoria

Fig. 2 shows that the lead isotopic composition of 80% of ash samples from Tostaree are less than 2% different with respect to the local background soils (*t*-test p = >0.05 for both 206 Pb/ 207 Pb and ²⁰⁸Pb/²⁰⁷Pb), indicating influence from leaded petrol depositions in the forest is minimal. Given that Tostaree, a rural location with a population of <1000, is ~340 km east of the state of Victoria's major city Melbourne (population ~ 4 million), it is not surprising that local lead is dominant in the ash samples. However, some of the Tostaree ash samples (in particular TS_2A, TS_4A, TS_13A, Table S1) have lead isotopic compositions that are comparable to those used in Australian leaded petrol (Table S2, Supporting information), particularly petrol used in the 1990s (Gulson, 2003). The isotopic composition of ash sample TS_2A plots closer to the lead isotopic composition of aerosols recorded in Victoria in the 1990s (Bollhöfer and Rosman, 2000) than the local lead signature (Fig. 2). Although the total lead concentration is low (1.6 mg/kg) in ash sample TS_2A, its lead isotopic composition indicates that Australian leaded petrol was the predominant lead source in this ash, even though the relatively pristine site is \sim 340 km from the nearest city. Local surface soil samples (0-2 cm) collected immediately adjacent to the burnt bushland also have an isotopic composition distinct from that of background soil. The surface soils and majority of the ash samples fit a simple two end-member mixing model between the natural lead of the area and the lead isotopic compositions of leaded petrol used in Australia (Table S1; Fig. 2). Isotopic compositions of ash samples that do not fit within the two end-member mixing model may reflect either a wider range of natural lead isotopic compositions in the area or another, as yet unidentified, source of industrial lead.

3.3. Red Hill, Western Australia

Isotopic compositions of ash and surface soils (0–2 cm) differ from those of background soil (40–50 cm) and rock from the Red Hill Fire (Fig. 3, Table S1). Analysis of the isotopic composition of the ash samples shows that 80% of ash samples are >2% different compared to local background soil and rock, with the two samples groups being statistical different for only 208 Pb/ 207 Pb (*t*-test, *t*(17) = 3.912 *p* = 0.001). These differences are partially attributed to leaded petrol emissions from the Perth region, which was Australia's third largest consumer of petrol in 1976 (Farrington and Boyd, 1981) and the fourth largest in 1985 (Farrington, 1988). The isotopic compositions of those legacy inputs are characterized by aerosols in the region during that period (Fig. 3) (Bollhöfer and Rosman, 2000).

However, isotopic compositions of the ash and surface soil samples indicate they do not fall within a simple two end-member mixing model of natural lead and petrol lead (Fig. 3), evidencing other sources of lead in the ash and surface soils. These could include atmospheric depositions from the Red Hill Quarry, operating since 1963, and the Red Hill Waste Management Facility, operating since 1981. The quarry produces granite and diorite/ dolerite aggregate (EPA, 2011) while the waste management facility accepts Class I to IV waste, which can include contaminated soils (EPA, 1997). The isotopic composition of the Red Hill ash lead does not reflect the lead smelted at the former Fremantle Smelting Works (closed 1920), located 6 km south east of Perth city (Fig. 1). Red Hill is ~40 km downwind of Freemantle, in the track of one of the most energetic sea breeze systems in the world (Masselink,



Fig. 2. The lead isotopic composition of ash and soil samples collected from Tostaree, Victoria, Australia. Australian leaded petrol lead isotopic composition is indicated by the dotted and dashed lines. Shaded area indicates lead isotopic signature of 1990s Victorian aerosols (Bollhöfer and Rosman, 2000). The standard error inset represents ²⁰⁶Pb/²⁰⁷Pb: 0.004 and ²⁰⁸Pb/²⁰⁷Pb: 0.009.



Fig. 3. Lead isotopic composition of ash and soil samples collected from the Red Hill, Perth, Western Australia. Australian leaded petrol lead isotopic composition is indicated by the dotted and dashed lines. Shaded area indicates lead isotopic signature of 1990s Perth aerosols (Bollhöfer and Rosman, 2000). The standard error inset represents ²⁰⁶Pb/²⁰⁷Pb: 0.024 and ²⁰⁸Pb/²⁰⁷Pb: 0.013.

1996). The Fremantle Smelting Works sourced lead from the Western Australian Eastern Goldfields ($^{206}Pb/^{207}Pb$: 0.933; $^{208}Pb/^{207}Pb$: 2.289, Cumming and Richards, 1975) and North-ampton Complex ~ 500 km north from Perth ($^{206}Pb/^{207}Pb$: 1.145; $^{208}Pb/^{207}Pb$: 2.465, Richards et al., 1985). In both cases, the smelted lead has isotopic compositions distinct from the environmental samples analysed in this study (Fig. 3).

Atmospheric inputs of industrial lead emissions may also have come from the Fremantle Ports, which has been processing international cargo for over 100 years (Fremantle Ports, ND) (Fig. 1). As a result, uncovered and exposed contaminants could easily have been transported by the strong, seasonal, southwesterly summer winds that occur along the coast of Western Australia that can extend up to 100 km inland (Masselink, 1996). Unfortunately, we are not aware of any information that could be used to identify those different potential sources of lead, much less their isotopic compositions.

3.4. Kelmscott, Western Australia

Lead isotopic compositions of the ash and soils collected from the Kelmscott Fire, along with those of rocks from the area, are plotted in Fig. 4. Comparison of the sample sites to the local geology shows that the variability of samples reflect the variability of the underlying geology of the area. Samples KR_9A - KR_12A were sampled from an area underlain by gneissic rocks of the Darling Scarp, which are associated with the Archaean eon to the east of the site. Samples KR_1A - KR_8A were collected on the western side of the site area on Quaternary alluvium, which was deposited over laterite of the Darling Range (Baxter et al., 1980). The different surface geologies are reflected in the two separate background lead isotope envelopes (Fig. 4). Previous measurement of soils from the Perth region returned ²⁰⁶Pb/²⁰⁷Pb ratios of 1.2127 and a ²⁰⁸Pb/²⁰⁷Pb ratio of 2.508 (Bollhöfer et al., 1999), which is similar to the background soil and rocks collected from the Quaternary aged, western side of the field site (Fig. 4). Ash and surface soil lead compositions from Kelmscott cannot be ascribed categorically to the influence of leaded petrol. The spread of the isotopic composition data in Fig. 4 indicates that the lead in surface soils and some of the ash samples have come from more than one other external source. Analysis of all of the ash samples from Kelmscott shows that 25% are >2% different compared to local background soil and rock. Overall however, they are not statistically different (*t*-test 206 Pb/ 207 P: 208 Pb/ 207 Pb, p = >0.05). Only the lead isotopic compositions for the surface soils from the western side of the Kelmscott (Fig. 4) are statistically different from the corresponding local background soils and rock (t-test, t(4) = 3.530, p = 0.024 for ${}^{206}Pb/{}^{207}Pb$ and t(4) = 4.851, p = 0.008 for ²⁰⁸Pb/²⁰⁷Pb).

Similar to the Red Hill site, the isotopic compositions of the Kelmscott ash lead does not reflect the lead types smelted at the former Fremantle Smelting Works. Other potential sources of lead in the ash and surface soils could include emissions from the Kwinana Bulk Terminal, an industrial port ~25 km directly south west of Kelmscott. The port ships and stores slag, metal ores and other bulk commodities into and from Western Australia (Fremantle Ports, ND). Kwinana Bulk Terminal is also the location of several refineries, including a former leaded petrol refinery (Rankin, 2011; Fig. 1). As with Red Hill, Kelmscott is directly in the trajectory of strong, seasonal southwesterly winds that have the potential to transport aerosols from the Kwinana Port to inland areas such as Kelmscott (see Fig. 1).

Although the ash lead compositions from Kelmscott cannot be ascribed categorically to any one industrial lead source, it is clear that the lead released in ash from fire events is not sourced entirely from natural lead found in local soils and rocks. Regrettably, there are no available data that could be used to identify the lead isotopic compositions of the other potential sources definitively. Nevertheless, it is clear that the surface soils (0-2 cm) collected at Kelmscott have a lead isotopic composition that is akin to historic leaded petrol emissions (Fig. 4).

3.5. Significance of findings

The results obtained from this study show that lead is remobilized in ash during bushfire events. The environmental lead isotope compositions measured in this study demonstrate that lead contained within ash deposits does not correspond entirely to the respective natural soil or rock lead isotopic compositions and that remobilization of historic, industrial lead depositions is occurring. Although the characterization of natural lead isotopic compositions in subsurface soils and rocks from the study sites is limited (n = 13), the data show that the lead remobilization process is demonstrated most clearly in the samples from Red Hill, Western Australia, which is ~20 km north west of the Perth city centre. While ash total lead concentrations are low compared to those measured in soils and dusts from Australian mining and smelting towns such as Broken



Fig. 4. Lead isotopic composition of ash and soil samples collected at the Kelmscott, Perth, Western Australia. Australian leaded petrol lead isotopic composition is indicated by the dotted and dashed lines. Lead isotopic signature of 1990s Perth aerosols (Bollhöfer and Rosman, 2000) and soils (Bollhöfer et al., 1999) indicated by shaded regions. The standard error inset represents ²⁰⁶Pb/²⁰⁷Pb: 0.018 and ²⁰⁸Pb/²⁰⁷Pb: 0.015.

Hill (Gulson et al., 1995) and Mount Isa (Taylor et al., 2010), it is worth noting that environmental samples analysed in this study were collected from what are considered to be relatively pristine environments of national and regional parks, in a large, sparsely populated continent. However, because this study measured in situ ash (akin to bottom ash sensu Narodoslawsky and Obernberger, 1996), it is likely to be a conservative estimate of the effect of wildfires on the re-release of lead to the environment because most of the lead is mobilised in an aerosol-ash component. Therefore, given the pervasive effect of industrial lead emissions on the environment (Bollhöfer and Rosman, 2000, 2001; Nriagu, 1996), and the fact that wildfire events are likely to increase in frequency, intensity and magnitude due to global temperature rises (Hennessy et al., 2006; IPCC, 2007; Liu et al., 2010), we contend that historic industrial lead depositions will be concomitantly re-released during such events. Of particular concern are fires occurring near urban centres or industrial towns where lead and other anthropogenic metal loadings in the environment are higher (Chiaradia et al., 1997; Farrington and Boyd, 1981; Farrington, 1988; Gulson et al., 1981; Laidlaw and Taylor, 2011) and because a greater proportion of the industrial emissions from leaded petrol occurred in these locations. Given the paradigm that there still is no established safe level for lead (NHMRC, 2009; WHO, 2010), it is feasible that young children could be at risk of additional lead exposures from wildfires, especially when they are close to large urban centres.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.03.025.

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Paper Five

Lead and zinc dust depositions from ore trains characterised using lead isotopic compositions

Kristensen, L. J., Taylor, M. P., & Morrison, A. L. (2015). Environmental Science: Processes & Impacts, 17, 631-637.

Supplementary Information in Appendix E

This paper measures the environmental impact of a single aspect of mining operations, the transport of lead and zinc ore products. This study contributes to this thesis as it demonstrates the extensive reach of mining related emissions beyond mining leases and towns. It shows that even small volumes of emissions can be measured in the environment and affect environmental quality. It also reveals that major mining operations emit such large quantities of lead as to obscure the smaller emissions that can be measured elsewhere.

Environmental Science Processes & Impacts



PAPER



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Lead and zinc dust depositions from ore trains characterised using lead isotopic compositions[†]

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This study investigates an unusual source of environmental lead contamination – the emission and deposition of lead and zinc concentrates along train lines into and out of Australia's oldest silver–lead– zinc mine at Broken Hill, Australia. Transport of lead and zinc ore concentrates from the Broken Hill mines has occurred for more than 125 years, during which time the majority was moved in uncovered rail wagons. A significant amount of ore was lost to the adjoining environments, resulting in soil immediately adjacent to train lines elevated with concentrations of lead (695 mg kg⁻¹) and zinc (2230 mg kg⁻¹). Concentrations of lead and zinc decreased away from the train line and also with depth shown in soil profiles. Lead isotopic compositions demonstrated the soil lead contained Broken Hill ore in increasing percentages closer to the train line, with up to 97% apportioned to the mined Broken Hill ore body. SEM examination showed ceiling dusts collected from houses along the train line were composed of unweathered galena particles, characteristic of the concentrate transported in the rail wagons. The loss of ore from the uncovered wagons has significantly extended the environmental footprint of contamination from local mining operations over an area extending hundreds of kilometres along each of the three train lines.

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rsc.li/process-impacts

Environmental impact

This paper examines lead and zinc deposits from a long history of transporting uncovered ore concentrates that have caused contamination along hundreds of kilometres of train lines. These transport corridors pass through pristine environments and local towns resulting in elevated concentrations of the toxic metal lead. Dangerous levels of lead have been found in drinking water supplies in these towns and our study reveals dusts in houses to contain lead and zinc ore. This shows that the impact of mining operations can be detected well beyond acceptable limits. This study has widespread implications to any mining operations or indeed, any operations where hazardous materials are transported and can cause losses into the environment.

Introduction

Mining in Broken Hill, New South Wales (NSW) commenced in 1884 after the discovery of the world's largest lead–zinc–silver ore body in 1883.¹ From 1886 until 1897 smelting of the ore was conducted on site with up to 28 smelters in operation.² Due to a lack of local fuel sources for the smelters, it became necessary to conduct smelting operations outside of Broken Hill. The South Australian Government responded quickly to the opportunity and constructed a train line in 1885 (ref. 3) in order to transport the raw ore to the new Port Pirie smelter. South Australian Railways opened their train line for operation in June 1887 to connect Adelaide and Port Pirie in South Australia (SA) to Cockburn on the NSW/SA border close to Broken Hill.⁴ As the NSW government refused the construct a rail link from Cockburn to Broken Hill,³ the privately owned Silverton Tramway Company (STC) train line was subsequently opened for operation in January 1888 (ref. 1–3) to connect the SA train line at Cockburn to trains coming from Broken Hill, *via* Silverton (Fig. 1). Following completion of the train line connections between Broken Hill and Port Pirie, and the start of smelting operations in Port Pirie in June 1889, ore was transported to Port Pirie for smelting *via* rail on the STC and South Australian Railways narrow gauge (1067 mm) train line in uncovered wagons.⁵ By 1897 all smelting operations were moved to Port Pirie.^{1,2} As of the end of June 1964, the Silverton train line had transported 38 747 602 tonnes of ore concentrate from Broken Hill.²

In 1970, a new standard gauge train line (1435 mm) connecting Broken Hill to Port Pirie *via* Triple Chance (Fig. 1) enabled a greater tonnage of ore to be carried on this route. However, not all ore concentrates were sent to Port Pirie for smelting, as lead and zinc concentrates were also sent eastward *via* rail to either Rozelle in Sydney, NSW, for shipment overseas or Cockle Creek, NSW, for further processing.² The standard gauge Broken Hill to Sydney train line was opened in October

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Fig. 1 Map of train lines into and out of Broken Hill along with the location of sampling transects.

1927 (ref. 1) and 594 498 tonnes of lead and zinc concentrate had been transported *via* this line during the period from 1947 to the end of June 1964,² although these ore wagons were covered with tarpaulins.

Ore was loaded into the wagons wet at Broken Hill, however, it would dry rapidly while in the shunting yards and also during transport (summer temperatures exceed 40 °C (ref. 6)). The result was that, as the uncovered ore was moved between Broken Hill and Port Pirie, it was subjected to dispersal along the train line, either by wind, train movement or through gaps in the wagons.⁵ A survey of the Broken Hill to Port Pirie railway corridor was conducted in 1986 to investigate lead losses from ore trains as part of the Port Pirie Lead Survey.5 Forty-five transects of surface soils (0-5 cm) across the train lines were sampled between Broken Hill and Port Pirie, including both the old narrow gauge (Silverton line) and new standard gauge train lines. The study showed significant elevation of soil lead levels (over 21 000 mg kg^{-1}) immediately adjacent to the train tracks, with lead concentrations decreasing with distance away from the tracks.5 The railway corridor survey also investigated the difference between the old and new train lines where they deviated from each other and found a noticeable increase in lead concentration along the old rail corridor. This was to be expected given that the new standard gauge line had only been subject to 15 years of ore dust deposition at the time of the study in 1986,5 compared to more than 80 years of ore movements along the old narrow gauge line.

In 1996 in a delayed response to the Broken Hill railway corridor survey, the NSW Environment Protection Authority (NSW EPA) required that all ore wagons be covered to prevent ore dust being blown from the wagons into the surrounding environment.⁷ In 1997, fiberglass covers were introduced for ore wagons carrying lead and zinc ores to eliminate product loss and reduce the environmental risk of ore wagon dust emissions.^{8,9}

While the Broken Hill railway corridor survey in 1986 characterised the extent of lead contamination in surface soil along the Broken Hill to Port Pirie train line, there is limited published literature on the loss and impact of heavy metal ore minerals during rail transport. Lead and zinc dust emissions from uncovered ore wagons from the Red Dog Mine in the Yukon Territory, Canada, showed extensive contamination of the city of Skagway, where the trains passed, with elevated levels of lead along the transport routes of up to 28 000 mg kg⁻¹.¹⁰ Emission losses from the haulage of ore has been occurring since ore was first transported, with lead and zinc contamination identified adjacent to Roman roads from as early as the $2^{nd}-4^{th}$ century.¹¹

This study examines the effect of industrial processes on the environment in and around the lead and zinc ore mining town of Broken Hill, Australia. Although the effects of lead exposure on young children in Broken Hill has been well documented for over 20 years,12 the source and cause of childhood blood lead exposures has not been clarified accurately. In 1993 Woodward-Clyde¹³ completed a report on the environmental lead problem in Broken Hill and concluded "the primary source of this lead is the ore body, arising from erosion of the surface due to geological processes, and the mining and mineral processing activities over the past 100 years". This unfounded 'belief' about the natural source and cause of the lead problem has stymied a fully integrated strategy to deal with emissions from the Broken Hill mining operations. Indeed, many residents in Broken Hill still believe that the environmental lead problem is predominantly due to lead occurring naturally in the soils and dusts around the city.14

Therefore, this study examines the role of ore transport as a contributing source of industrial contamination on the environment in and around Broken Hill city, and importantly to the environment outside of mining operations. The impact from ore transport on Broken Hill train lines is evaluated by measurement of lead and zinc concentrations in soils and dusts. Lead isotopic composition and scanning electron microscopy analyses are used to confirm the source and origin of the environmental contamination.

Methods

Field sampling methods

Soils were collected along transects perpendicular to train lines at varying distances up to 150 m from the line and at varying depths (0–2 cm; 2–10 cm; 10–20 cm; 20–30 cm; 30–40 cm; 40–50 cm) using established methods.¹⁵ Soil samples collected at depth were intended to provide local background values (total metal concentrations and lead isotopic composition) compared to the more recently contaminated surface samples. Soil samples (n = 104) were collected along four train line transects in 2009, 2011 and 2012.

Soil samples (n = 36) along the standard gauge Broken Hill to Port Pirie train line were collected 31 km SW of Broken Hill at the turn off to Triple Chance Mine in October 2009 (referred to as Triple Chance). Soil samples (n = 18) along the old narrow gauge train line were collected on the Silverton Tramway Company train line 10 km NW of Broken Hill in September 2011. The Broken Hill to Sydney train line was sampled in two locations, just outside the limits of Broken Hill city (referred to as Broken Hill (n = 18) in September 2011 and at The Gorge 27 km east along the train line (n = 32) in September 2012.

Laboratory analysis

All 104 soil samples were analysed for lead and zinc concentrations and select samples (n = 35) for lead isotopic composition. Samples collected in 2009 (n = 36) and 2012 (n = 32) were analysed at National Measurement Institute (NMI), North Ryde, NSW and samples collected in 2011 (n = 36) were analysed by ChemCentre, Western Australia for lead and zinc concentrations and lead isotopic compositions. Samples were digested in a mix of HCl and HNO₃ and measured for lead and zinc concentrations on a Varian Vista Pro ICP-OES and for lead isotopic compositions on a PerkinElmer Elan DRC II and Agilent 7500ce ICP-MS. Blanks returned less than 0.01 mg kg⁻¹ for both Pb and Zn.

Duplicate analysis returned relative standard deviations (RSD) < 6% for Pb and <7% for Zn. Recovery rates at NMI were measured using reference material AGAL-10 and sample matrix spiking. Recovery rates were 91% for Pb and 100% for Zn for the certified reference material and 90% for Pb and 106% for Zn for the matrix spikes. Lead isotopic compositions were determined for select samples (n = 16) and mass fractionation was corrected using NIST SRM981 (common lead standard). RSDs reported by NMI for ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb were 0.12%, 0.07% and 0.08% respectively. Recovery rates at ChemCentre were measured using NRCC reference material PACS-2 with recovery rates for Pb 102% and 106% for Zn. Lead isotopic compositions were determined for selected samples (n = 16)and mass fractionation was corrected using NIST SRM982 (equal-atom lead isotopic standard). RSDs reported by Chem-Centre for ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb were 0.23%, 0.23% and 0.24% respectively.

Two ceiling dust samples (House#1 and House#2) were sampled and approximately 2 g of each material was subjected to heavy media separation using a sodium polytungstate solution at a density of approximately 3 g cm⁻³ to remove organic components and minerals such as silica with a low density leaving the heavy metal components. The high density component of the ceiling dust samples were mounted into epoxy resin (Araldite) blocks. A section through the mounted material was polished on a diamond lap to a fine finish and examined with a JEOL-JSM-6480LV high-performance scanning electron microscope (SEM) using a resolution of 3.0 nm in combination with an energy dispersive X-ray spectrometer (EDS). In back scatter electron imaging mode, materials of high atomic density (such as lead minerals) appear brightest on the screen and are therefore more easily identified.¹⁶

Results and discussion

Concentrations of lead and zinc along the soil sample transects covered a large range; Pb: 7–695 mg kg⁻¹; Zn: 19–2230 mg kg⁻¹. Lead, zinc along with copper concentrations and lead isotopic composition data for soils sampled along the train line transects can be found in ESI Table S1.[†]

Lead and zinc total soil concentrations

Soil samples collected from the original narrow gauge Silverton train line (in operation 1888–1970) show elevated concentrations of lead and zinc as both a function of distance from the train line and with depth through the soil profiles (Fig. 2). Lead and zinc concentrations decrease in surface soils (0–2 cm) at the sample points moving outwards in both the northerly and southerly directions from the train line. The deepest subsurface soils (40–50 cm) remain consistent in both lead and zinc concentration across the transect and within the range considered to be natural soil concentration levels¹⁷ (Pb: <30 mg kg⁻¹;^{17,18} Zn: <100 mg kg⁻¹ (ref. 17)). Dispersal patterns of lead and zinc are highly correlated (Pearson correlation r = 0.998, p < 0.01) indicating that losses of ore from the train wagons was the only likely source.

The change in concentration through the soil profile expressed as a Surface Enrichment Ratio (SER),¹⁵ shows a consistent pattern at each location along the transect. The SER decreases with distance from both sides of the train line reflecting a decreasing contribution from the external point source. It is also evident from the soil profiles (Fig. 2) that the most dramatic change in lead and zinc concentrations occur between the top two sampled soil layers: 0–2 cm and 2–10 cm. This demonstrates that elevated lead and zinc concentrations are found only in the surface soils must be sourced from recent atmospheric deposition and are not likely to have existed before the operation of the train line.

While the lead concentrations measured in this study are not as high as those found in the Port Pirie Lead Survey,⁵ the pattern of dispersal from the train lines is consistent. Surface soils analysed by in 1986 Body in the first transect along the Silverton train line returned lead concentrations of 139 and 1404 mg kg⁻¹, 10 m north and south of the train line,⁵ which are consistent with the findings of this study.

Lead and zinc concentrations in the soil samples from the new standard gauge line (1970 to present) collected at Triple Chance (Fig. 3) display a similar spatial pattern of lead and zinc concentrations to those along the Silverton train line (Fig. 2).



Fig. 2 Soil lead and zinc soil concentration profiles either side of Silverton train line.



Fig. 3 Soil lead and zinc concentration profiles across Triple Chance transect.

Soil samples were collected at depth intervals along the Triple Chance transect, with the soil profiles (Fig. 3) revealing that surface enrichment generally only occurs in the top (0-2 cm) layer of soils. Below the surface there is a sharp decrease in concentration in the immediate sub-surface layers (2-10 cm), which continues down the soil profile. While the lead and zinc concentrations are also correlated at this train line (Pearson correlation r = 0.998, p < 0.01), lower lead concentrations and higher zinc concentrations are seen by comparison to those from the Silverton train line. The likely cause of these changes in concentration is the increase in zinc ore production and its transport along the new line in recent years. By 1966, 13.2 million tonnes of lead ore and 9.4 million tonnes zinc ore was produced in Broken Hill1 while in 1995-1999 only 896 550 tonnes of lead ore compared to 1 857 406 tonnes zinc ore was produced.19

In contrast to Silverton and Triple Chance transects, the lead and zinc concentrations across the Broken Hill transect, which is close to the city and mining operations, do not decrease to the same extent with distance from the rail line. The SERs along this transect are the highest of this study and also do not correlate to distance from train line. The lead–zinc soil concentration profiles are likely to have been influenced to a greater degree by the nearby Broken Hill mining operations than by ore emissions from trains (ESI Fig. S1[†]).

In order to ascertain the impact of ore wagons on the Broken Hill to Sydney train line without the confounding effect of the Broken Hill mining operations, the train line was resampled, further along the train line at The Gorge in 2012 (Fig. 1), some 19 km from the city (27 km by train). Peak lead and zinc concentrations occur closest to the train line and decline with distance (ESI Fig. S2†), which is characteristic of the effect of ore concentrate losses from the trains. However, it cannot be determined from total lead and zinc concentrations alone whether the losses from the ore wagons are solely from those going east out of Broken Hill. Lead concentrates were also transported west to Broken Hill on route to Port Pirie from 1983 (ref. 20) from the Endeavor mine, which is 405 km east of Broken Hill (~1220 km by train). While the SERs demonstrate clearly the magnitude of surface soil enrichment when compared to background metal concentrations found at depth, they are all lower than those found at the Broken Hill City location, indicating limited deposition from ore wagons. The lower soil concentrations are consistent with the small tonnage of ore coming westwards from the Endeavor mine combined with that the small tonnage of Broken Hill ore going eastwards to the NSW coast for processing, by comparison with that going to the Port Pirie smelter. The effect of mining operation emissions on The Gorge transect can be dismissed by virtue of the spatial pattern of increasing surface lead and zinc concentrations closer to the rail line, indicating the only logical point source for the depositions are emissions from ore wagons.

Across all transects, the highest concentrations of lead and zinc were found consistently in the surface soils (0-2 cm) closest to the train lines. The lowest concentration of lead and zinc were found both at distance and depth with the majority in the deepest sub-surface samples (40-50 cm) at the most distal points of the samples transects (ESI Fig. S2[†]). The lower soil metal concentrations at depth and distance from the rail lines are considered to be characteristic of background lead and zinc concentrations.17 The consistent correlation of lead and zinc concentrations in the soil samples further supports the argument of a single contributing source.15 For the lead and zinc in the soil to be naturally occurring, other metals would also be expected to display a similar spatial pattern, which they do not. Copper soil concentrations for example, remain more or less constant regardless of the distance from the train lines or depth of sampling (ESI Table S1[†]). This consistent pattern of lead and zinc dispersion across the transects is clear evidence that the origin of the elevated metal levels result from emission and dust deposition of ore and concentrate products from the uncovered ore rail wagons. The same soil lead concentration pattern of elevated surface concentration and rapid subsurface concentration decline has been observed around city highways as a result of leaded petrol usage.21

Lead isotopic compositions

Although lead and zinc concentrations in the soil samples show clear spatial patterns of ore wagon dust emissions and subsequent depositions, total soil concentration values do not allow source apportionment or enable percentage contributions from the Broken Hill ore to be established. To address this question, lead isotopic compositions of the sampled soils collected along the four transects were measured. A sample of Broken Hill ore was also measured for its lead isotopic composition with values (ESI Table S1†) shown to be match published literature values.^{22–24} The lead isotope compositions of the Triple Chance transect are shown in Fig. 4, with all other transects in the ESI† (Silverton transect: ESI Fig. S3;† Broken Hill transect: ESI Fig. S4;† The Gorge transect: ESI Fig. S5†).

The lead isotopic compositions of surface soils at all train transects plot directly on a mixing line between local natural soil lead and Broken Hill ore (*e.g.* the Triple Chance transect, Fig. 4). The same, consistent pattern is observed in all train transects not influenced by mining operations, with surface soil Paper



Fig. 4 Soil lead isotopic compositions at either side of the rail line at Triple Chance, benchmarked against Broken Hill ore.

samples (0–2 cm) becoming increasingly similar with respect to the background lead isotopic compositions (40–50 cm; at >100 m from the train line) with increasing distance from train line.

A two end member mixing model^{25,26} was applied to the surface soil samples to quantify the contribution of Broken Hill lead derived from the loss of ore from uncovered wagons. Surface soil samples (0-2 cm) at Triple Chance closest to the train line (\leq 70 m) contained 73–93% Broken Hill ore, while samples at distance (120 m north; 125 m south) only contained 46-63% Broken Hill ore. The surface soils along the Silverton transect have higher proportions of Broken Hill ore with 94-97% closest to the train line. Surface soils furthest from the train line (101 m either side) consist of 77-78% lead from Broken Hill ore. Of all of transects, lead in surface soils at The Gorge transect were closer to those representing background values (40-50 cm, 100 m). Mixing model calculations apportioned 42–73% of the lead in surface soil samples \leq 51 m from the train line and 35-46% of lead in soils 100 m from the train line to the Broken Hill ore body. Nevertheless, the effect of the loss of ore on surface soils is demonstrated clearly by comparison to sub-surface soils (40-50 cm) at the same location, which have a markedly different isotopic composition (Fig. 4; ESI Fig. S1–S3[†]).

The Gorge site was sampled in order to assess the Broken Hill to Sydney train line without the confounding impact of mining in Broken Hill as the proximity of the site to the central and north mine in the city of Broken Hill (<2 km). It is highly likely that the surface lead contaminants at the Broken Hill transect are not sourced entirely from train transport of the ore, but also from wind dispersion of ore from current and historic mining practices within Broken Hill city. The fact that the Broken Hill ore contribution at The Gorge is markedly lower than that measured at the other three locations is likely to be due to two main factors. Firstly, there has been significantly less ore transported along this line compared to that transported *via* the Silverton or the Triple Chance line. Secondly, the ore from the Endeavor mine that was transported to Broken Hill for almost 15 years has a lead isotopic composition not dissimilar to that of the background soils of the Broken Hill region (Endeavor ore ²⁰⁸Pb/²⁰⁷Pb: 2.448; ²⁰⁶Pb/²⁰⁷Pb: 1.152)²⁷ as identified at The Gorge site. From the commencement of mining at Endeavor in 1983, lead concentrates were railed to Port Pirie *via* Broken Hill, with 896 026 tonnes being transported by 2009.²⁰ Endeavor mine to Broken Hill ore wagons were however, not covered until 2000.²⁰ Although lead ore from the Endeavor mine also passed through Broken Hill, it was a fraction of that produced and transported from the Broken Hill mines. For example, 145 576 tonnes of (wet) lead ore concentrates were transported from Endeavor mine to Port Pirie between 1991 and 1994, while by significant contrast, a total of 1 990 157 tonnes of (wet) lead ore concentrates were transported from Broken Hill to Port Pirie in the same time period.²⁸

At the NSW/SA border town of Cockburn, 50 km from Broken Hill, which is located at the junction of the old narrow gauge (Silverton) and the new standard gauge (Triple Chance) train lines (Fig. 1), ceiling dust was collected from a house immediately adjacent to rail corridor. Elevated total concentrations of lead (1400 mg kg⁻¹) and zinc (3300 mg kg⁻¹) and lead isotopic compositions were measured in the ceiling dust, which had the following values: 208 Pb/ 207 Pb: 2.323; 206 Pb/ 204 Pb: 16.12. Given that these values are analogous to those of the Broken Hill ore (ESI Table S1†), there is little doubt that the ceiling dust contaminants were sourced from the uncovered ore concentrates being transported along the train lines.

Overall, the results show conclusively that dust emissions from uncovered ore wagons transporting ore and concentrates to and from Broken Hill left a significant legacy of contamination in surface soils and dusts along the corridor.

SEM examination

As an additional confirmation of the source of the lead being deposited along the Triple Chance rail line to Port Pirie, two samples of internal ceiling dusts from Broken Hill houses immediately adjacent to the rail corridor were examined using SEM and EDS. The houses from which these samples were obtained were to the north and within ~200 metres of the train line in Broken Hill city. The concentrated ore was crushed to fine particle size, which was predominantly less than 200 µm, making wind transport possible. The shunting of wagons broke the surface ore crusts that had dried in the heat of Broken Hill, rending them available for wind erosion.²⁹ The prevailing winds in the area would have contributed to the aeolian transport of concentrate dusts emitted from uncovered rail wagons towards these houses. Subsequent photographic evidence of significant dust losses from the wagons confirms the proposition that significant and visible losses from the wagon occurred (ESI Fig. S6[†]).

Galena (PbS), the principal lead mineral mined and concentrated from Broken Hill ore, is a relatively soft mineral (Mohs hardness 2.5) of high density (7.57 g cm⁻³). The longer the material is exposed to the atmosphere, the more likely that the surface will not only react chemically but the external

structure will be worn and rounded by collisions with other harder materials. The high density of galena ensures that large crystalline particles (~20 μ m and greater) are unlikely to be windblown for significant distances without contacting the ground, thus requiring episodic re-entrainment for large travel distances,³⁰ which would increase the potential for loss of crystallinity and angularity. Therefore, the existence of crystallinity, angularity and lack of surface alteration is indicative of an emission source in the immediate vicinity of deposition, followed by protection (*e.g.* a roof cavity) from the elements such as wind or rain.

EDS spectral output allows accurate elemental identification of individual mineral grains, and in the case of this study, visual observation of grain morphology and elemental determination were adequate to identify the mineral species. Even though heavy media concentration had been carried out on the ceiling dust samples, SEM examination showed that the dusts were extremely heterogeneous and contained many mineral species including galena, marmatite, pyrite and related alteration products.

The SEM examination concentrated on the larger lead bearing particles in the polished samples and typical examples of lead bearing particle types were selected for more detailed examination. From the polished section of the material from House#1, 23 particles were identified visually as potentially lead bearing examples were subjected to 48 separate EDS analyses. From the House#2 sample, 20 particles were visually selected and 28 EDS analyses were undertaken.

Not all particles selected visually proved to contain lead as there were also other high atomic density materials present, including silver, rare earths and residual sodium polytungstate (from the mineral separation process). The samples shown in Fig. 5 contain lead bearing particles with significant similarity to lead concentrates, that is, particles showing crystallinity and lack of surface alteration. However, the sample also contained lead particles that were rounded, with significant surface alteration indicating weathering.



Fig. 5 SEM micrographs of dust samples (scales shown on images) (a) House#1 \sim 40–80 μ m composite crystalline galena and marmatite particle. (b) House#2 \sim 150 \times 75 μ m galena particle. (c) Galena particle from House#2. (d) Galena particle from House#2.

Both the crystallinity, maintenance of angularity and lack of surface alteration in a large proportion of the lead containing particles is indicative of material that was transported short distances before deposition in the roof space of the houses. Examples of crystalline galena of this description are shown in Fig. 5a and b, which both show cubic crystallinity, maintenance of angularity and lack of surface alteration. These features are typical of fresh, recently mined minerals and not those of old weathered long-term deposits being recycled in the environment.

A smaller proportion of the lead containing particles from the ceiling dusts were rounded, with surfaces that had been chemically altered. The EDS analyses showed that the surface layer frequently included high levels of O, Cl, P, Fe as well as Pb and S. The development of this type of morphology would require particles to have been exposed to the environment for extended periods of time, during which they may have been subject to more frequent and longer transport distances than the particles shown in Fig. 5a and b. However, the large size of many of the particles implies that the source of origin is more likely to be close to their final deposition site in the roof spaces of the sampled houses.³⁰ Examples of these types of particles are shown in Fig. 5c and d, which show rounding and surface alteration. In Fig. 5d, the galena particle contains Cl and O in the surface layer encapsulating the galena.

Overall, the SEM examination of the two ceiling dust samples supports strongly the proposition that lead concentrates (and zinc by default) were emitted from uncovered rail wagons and that these emissions were deposited adjacent to the train line and in domestic residences within the city of Broken Hill.

As a result of the uncovered transport of ore concentrates, high levels of lead was shown to be found in house dusts and water tanks along the train lines in 1986 (ref. 5) when ore wagons were uncovered. SEM examination of dust from ceilings along with recent reports of lead levels 10 times the drinking water guidelines (0.01 mg L^{-1}) in water tanks³¹ in towns along the Triple Chance train line reveal a lingering legacy and health risks from mining activities outside of Broken Hill. This legacy of lead and zinc ore concentrates deposition along transport routes is not limited to Broken Hill as similar issues have been shown in Canada and Alaska, where uncovered transport of lead and zinc ore concentrates have resulted in elevated levels of toxic metals in adjoining communities.¹⁰

The environmental and health consequences are not limited to lead and zinc transportation and could be found at any location where materials that pose a health risk, whether known or unknown, have been or are currently being transported in a way that causes losses to the environment to occur (ESI Fig. S6†). This was found to be the case in Russia, where the highest incidence of thyroid cancer occurred along transport routes, both train and road, from Chernobyl.³² Losses of dust from transportation are difficult to quantify, however, experiments of fugitive dusts from uncovered coal trains calculates that 0.0048% of the load is lost during uncovered transportation.^{33,34} Although not directly transferable to this study, this data provides an initial estimate to establishing overall lead and zinc losses from uncovered ore transportation in Broken Hill. Soil lead and zinc concentrations from transects across train lines into and out of Broken Hill reveal the environmental impact from transporting ore concentrates in uncovered wagons. The soil lead isotopic composition from all transects show a clear difference between the surface soil samples and the sub-surface soil samples. Generally, surface soils that are closer to the train line have lead isotopic compositions that are similar to the lead isotopic composition of the ore mined from Broken Hill and transported by rail. SEM examination of deposited ceiling dusts from houses near the train line adds further credence to the chemical and isotopic evidence as to the source of lead. The morphology of particles found in these dusts is indicative of a source close to the point of deposition.

While the ore wagons are now covered by EPA mandate and losses of ore to the environment is no longer occurring as a result of train transport, this is not a resolved issue. This study shows that the contamination along the train lines is still present. Given the aridity of region and the prevalence of dust storms, transport of ore-contaminated dust particulates into nearby houses and water supplies is a current concern. Rehabilitation along the train lines is necessary to prevent further movement of contaminated soils.

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Paper Six

Unravelling a 'miner's myth' that environmental contamination in mining towns is naturally occurring

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Supplementary Information in Appendix F

This paper addresses the multiple arguments that have been used to obsfucate the cause of elevated toxic metals in the environment surrounding industrial activities, particularly mining operations in Broken Hill, NSW. This study confirms the dominance of emissions from lead mining operations in Broken Hill and the environmental footprint that can be measured resulting from those lead emissions. This study contributes to this thesis as it employs a range of measurement methods to confirm that the primary source of lead contamination in Broken Hill city is being caused by the ongoing mining activities.

ORIGINAL PAPER



Unravelling a 'miner's myth' that environmental contamination in mining towns is naturally occurring

Louise Jane Kristensen D · Mark Patrick Taylor

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Abstract Australia has a long history of metal mining and smelting. Extraction and processing have resulted in elevated levels of toxic metals surrounding mining operations, which have adverse health effects, particularly to children. Resource companies, government agencies and employees often construct 'myths' to down play potential exposure risks and responsibility arising from operating emissions. Typical statements include: contaminants are naturally occurring, the wind blows emissions away from residential areas, contaminants are not bioavailable, or the problem is a legacy issue and not related to current operations. Evidence from mining and smelting towns shows that such 'myths' are exactly that. In mining towns, the default and primary defence against contamination is that elevated metals in adjacent urban environments are from the erosion and weathering of the ore bodies over millennia-hence 'naturally occurring'. Not only is this a difficult argument to unravel from an evidence-based perspective, but also it causes confusion and delays remediation work, hindering efforts to reduce harmful exposures to children. An example of

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L. J. Kristensen (⊠) · M. P. Taylor Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, North Ryde, Sydney, NSW 2109, Australia e-mail: louise.kristensen@mq.edu.au this situation is from Broken Hill, New South Wales, home to one of the world's largest lead–zinc–silver ore body, which has been mined continuously for over 130 years. Environmental metal concentration and lead isotopic data from soil samples collected from across Broken Hill are used to establish the nature and timing of lead contamination. We use multiple lines of evidence to unravel a 'miner's myth' by evaluating current soil metal concentrations and lead isotopic compositions, geological data, historical environmental assessments and old photographic evidence to assess the impacts from early smelting along with mining to the surface soils in the city.

Keywords Australia · Broken Hill · Emissions · Lead · Mining

Introduction

Broken Hill city, in the far west of New South Wales (NSW), owes its existence to one of the world's largest lead–zinc–silver ore deposits (Solomon 1988), which after initial discovery in 1883, has been producing ore since 1884 (Jaquet 1894). When the "broken hill" was discovered, it rose approximately 45 m from the surrounding plains and was covered by thick vegetation (mulga) with outcrops of black rock (Sawer 1985). The hill no longer exists and has been replaced by capped mining waste. Broken Hill residents have experienced lead poisoning and toxicity since the

inception of mining with children closest to mining operations exhibiting the most severe symptoms (Thompson et al. 1893; Jaquet 1894). This problem has improved in recent decades, but it has not abated, despite better environmental knowledge and practices. Blood lead testing of children 1-4 years revealed that 21 % of children in 2012 and 2013 had blood lead levels in excess of the previous guideline of 10 μ g/dL (National Health and Medical Research Council (NHMRC) 2009; Lesjak et al. 2013; NSW Government 2014). Although blood lead levels have fallen in Broken Hill since regular childhood screening began in 1991, the 'miner's myth' continues to shape the understanding of the cause of the elevated blood lead levels in the community (Balding and Reddan 1997; Humphries 2015), potentially hindering further interventions to effect declines in blood lead levels. Recent work examining ongoing toxic metal exposure to children (Taylor et al. 2014b) resulted in \$13 million being allocated by the NSW Government to revive the Broken Hill Environment Lead program (Humphries 2015). Although the new funding will rejuvenate awareness of lead risks in the city and implement clean up where significant problems are identified, until the 'miner's myth' is properly debunked, proper intervention strategies are likely to be limited. With the blood lead intervention level lowered to 5 µg/dL in 2015 (National Health and Medical Research Council (NHMRC) 2015) and no safe limit of lead identified (CDC 2012), it is now timely to finally acknowledge the actual primary cause of environmental lead contamination in Broken Hill.

Weathering/erosion

Due to the shape of the main ore body lode, it is believed that it was originally much larger than its current assessed tonnage of 300 million tonnes (Conor and Preiss 2008). Early estimates of the volume of ore lost due to weathering and erosion from the time of formation of the ore body until discovery range from 40 to 60 million tonnes (Plimer 1984; Gulson et al. 1994b). More recent estimates after detailed examination of the ore lenses put the loss from weathering and erosion at less than 4.7 million tonnes, none of which contained significant volumes of lead (Webster 2006). Additionally, the ironstone–coronadite cap of the ore body was highly resistant to erosion and in terms of a geological timescale is believed to have only just begun breaking the surface when it was discovered (Webster 2006).

The conflicting theories about the formation of the ore body and amount of erosion have allowed mining companies (inter alia anyone who had a vested interest in the economic outcome of the mine) to perpetuate the myth that the high levels of lead found around Broken Hill city have come about predominantly from weathering and erosion of the ore body or through natural mineralisation, and are therefore naturally occurring. Mining companies have sought to downplay or ignore the environmental consequences of extracting more than 200 million tonnes of ore from the ore body since mining began (Morland and Webster 1998; Perilya Limited 2015). In comparison with the most recent estimate of lead released from natural weathering processes (<4.7 million tonnes), some 80 million tonnes of ore was mined by 1962 (Lewis et al. 1965). This is a significantly greater tonnage of ore than even the most conservative early estimates of the potential amount of ore lost through weathering. It is more likely that the volume of ore derived from erosion and weathering was matched in initial years of extraction from mining-related emissions alone (Webster 2006).

While there is some limited acknowledgement that mining practices have contributed to lead levels in the city, in nearly all references to the problem, mining operations are considered and listed second to the stated primary cause of natural weathering and erosion. For example, a report to the Environment Protection Agency (EPA) summarises the cause of the environmental lead in Broken Hill as:

The primary source of this lead is the orebody, arising from erosion of the surface due to geological processes, and the mining and mineral processing activities over the past 100 years (Woodward-Clyde 1993).

Despite the recent funding to manage the lead problem in Broken Hill, the comment by the then NSW Minister for the Environment, Dr. Rob Stokes, in announcing the new \$13 million funding to address the persistent problem with elevated childhood blood lead levels, shows the 'miner's myth' persists in the minds of decision-makers:

Natural deposition and lead mining have left a legacy of widespread lead contamination

throughout Broken Hill and this has had a direct impact on the health of children in Broken Hill (Humphries 2015).

Further, it is a scientifically absurd notion to consider that any products of weathering/erosion of the ore body since its formation almost 1700 million years ago (Page et al. 2005) have not been transported beyond the limits of Broken Hill city. Broken Hill lead, which was smelted at Day Dream Mine (20 km north) in 1885 (Blainey 1968), then on site between 1886 and 1897 (Woodward 1965), and also in Port Pirie from 1889, has been identified as responsible for a significant increase in lead concentrations in Antarctica ice cores aged-dated from 1885 (McConnell et al. 2014).

Legacy issue

To further misdirect the focus of liability on current mining operations and companies, another argument associated with the 'miner's myth' is the other commonly stated 'fact' that elevated lead levels are the result of historic operations. These are called 'legacy' issues, to which the current mining companies claim they are not beholden to. Production by one of the two remaining of Broken Hill's mining companies, Perilya, who bought out Pasminco in June 2002, has raised 15 million tonnes of ore to the surface in its first 8 years of operation (Perilya Limited 2015). Estimates of lead and zinc emissions from Perilya's operations 2002-2013 to the National Pollution Inventory (NPI) are 77.4 tonnes for lead and 170.6 tonnes for zinc (NPI 2014). Recent studies in Broken Hill have shown that exposure to high levels of arsenic, cadmium and lead is the result of current mining practices with daily dust depositions close to the operations containing up to 59,900 µg/m2 of lead (Taylor et al. 2014b).

Bioavailability

Another aspect to the 'miner's myth' is that even if the source of the lead is proven to be from the mine and the associated mining activities such as smelting, it is in a form that is not bioavailable (e.g. Steele et al. 1990). The first enquiry into lead poisoning in Broken Hill even noted that insoluble lead (i.e. what is considered to be not bioavailable) was able to be absorbed in the body to cause negative health problems:

bad effects of a serious character are produced upon those who habitually absorb minute portions of these insoluble forms. This result is due to a power possessed by the natural juices to transform the insoluble into soluble compounds, so that they can be taken up by the blood and carried to the farthest recesses of the body (Thompson et al. 1893).

Bioavailability studies specifically relating to Broken Hill indicate high levels of solubility of soils and dust (Gulson et al. 1994a, b). Irrespective of the technical geochemical arguments about the measurement of lead bioavailability in environmental samples, the fact is that 'natural experiments' by way of lead emissions onto and into the community have shown Broken Hill lead is readily absorbed into the body. The exposures over time show quite clearly that elevated blood lead concentrations in children are persistent and pervasive across the whole of the city (Phillips and Hall 1994; Boreland and Lyle 2009; Lesjak et al. 2013).

Other lead sources (anything but the mining) argument

Government environmental regulators, mining companies and their experts often go as far as blaming environmental lead pollution and childhood exposures on other sources of lead including leaded paint, petrol and old batteries (Zheng et al. 2013; Wilson 2015). While some of these sources have contributed to elevated blood lead levels in children (e.g. Gulson et al. 1994b), they cannot reasonably account for levels of environmental lead contamination across the city particularly when elevated concentrations are paralleled by elevated zinc and other metal concentrations measured in Broken Hill (Taylor et al. 2014b; Dong et al. 2015). Despite Broken Hill hosting one of the world's largest lead-zinc-silver ore bodies, the Woodward-Clyde (1993) report to the EPA concluded:

The brief comparative review shows that Broken Hill has few similarities with other mining and even smelting communities. In fact it appears closer to urban communities where intensive traffic movements and/or paint have been identified as prime sources of lead (Woodward-Clyde 1993).

Not only are paint and petrol historic sources, but also they cannot be used to explain current emissions and depositions (Taylor et al. 2014b). Further, lead from paint cannot account for the widespread distribution of soil contamination across Broken Hill. The similarity of lead isotopic compositions in environmental samples to paint and petrol lead sources is not proof in itself that these are the significant and only contributors. Assigned environmental lead sources to paint and petrol in Broken Hill is confounded by the use of Broken Hill lead as the predominant source of lead in petrol and sometimes in paint (Gulson et al. 1994b; Kristensen 2015). However, the volumes of lead emitted from petrol in Broken Hill were too small to be a major source of environmental lead. For example, Australia's smallest capital city, Darwin, with a population approximately four times that of Broken Hill, emitted a maximum of \sim 35 tonnes a year from leaded petrol (Kristensen 2015). By contrast, Broken Hill smelters were emitting 100 tonnes a week in 1893 (Thompson et al. 1893) and the current mining operations continue to emit an estimated 28 tonnes a year (NPI 2014). Furthermore, if the cause of the environmental lead problem was attributable to leaded petrol, an associated striking decrease in blood lead levels following the removal of lead in petrol in 2002 would have occurred, in tandem with Australian capital cities (Kristensen 2015). It is notable that a rise in children's blood lead levels from 4.7 µg/dL (2010), 4.9 µg/dL (2011), 5.4 µg/dL (2012) to 5.6 µg/ dL (2013) (NSW Government 2014) parallels a rise in lead emissions from the Perilya operations from 0.69 tonnes (2009/2010), 11 tonnes (2010/2011), 28 tonnes (2011/2012) to 26 tonnes (2012/2013) (NPI 2014).

Recent research conducted in Broken Hill revealed the contribution of lead and zinc to the environment was also a result of the rail transport of concentrate ore (Kristensen et al. 2015). In addition, significant daily depositions of dust rich in lead and zinc have been attributed to current mineral processing facilities that crush, grind and separate the ore (Taylor et al. 2014b; Dong et al. 2015). A 1991 investigation of risk factors for blood lead levels across Broken Hill returned average soil levels (n = 400) of 661 mg/kg (max 10,875 mg/kg) for lead and 866 mg/kg (max 9502 mg/kg) for zinc (Phillips and Hall 1994). Analysis of ceiling dust from houses returned extremely high metal levels with 8790 mg/kg mean (1200-39,600 mg/kg) for lead and 14,140 mg/kg mean (2500-36,800 mg/kg) for zinc (van Alphen 1991). Another study from the 1990s found an average lead concentration in soil of 1500 mg/kg (max 7270 mg/kg) and measurement of lead isotopic compositions in ceiling dusts matching the Broken Hill ore (Gulson et al. 1994b). The surface of the ore body at the time of discovery consisted of a gossan, characterised by secondary mineralisation including the following lead minerals: cerussite (PbCO₃), coronadite (PbMn₈O₁₆), anglesite (PbSO₄) and pyromorphite $(Pb_5(PO_4)_3Cl)$, but importantly, no galena (PbS)(Plimer 1984; Davis 1993). The primary, unweathered sulphide-rich ore minerals including galena (PbS) were found at an average depth of 75 m below the gossan, but in some cases up to 200 m deep (Andrews 1922; Plimer 1984). Therefore, lead rich dusts found in ceilings, containing galena, can only be from mining activities in Broken Hill, since there were no houses in the city prior to the discovery and extraction of ore in 1883 (Kristensen et al. 2015). High levels of lead in aerosols, dust, soil and human blood are found in towns adjacent to lead mines both in Australia and globally (Meyer et al. 1999; Fontúrbel et al. 2011; Soto-Jiménez and Flegal 2011; Mackay et al. 2013).

Broken Hill is not alone in this scenario of generating myths to obscure the dominant and immediate source and impact of industrial emissions and contamination. Other examples in Australia where aspects of the 'miner's myth' are maintained relate to the Mount Isa mining and smelting operations in Queensland and Port Pirie's smelting operations in South Australia (Taylor et al. 2010, 2014a, 2015). The dismissal of the importance or the influence of mining, smelting or industrial chemical emissions on surrounding communities also takes different forms. For example, smelting operations and elevated emissions from Kalgoorlie Consolidated Gold Mines, Western Australia, were summarily dismissed using the arguments that the arsenic emission breaches did not pose a threat to health because the arsenic in the ore was low compared to other ore bodies and that the wind blows it away (ABC News 2003). Internationally, the owners of the Herculaneum lead smelter in Missouri, USA, have applied similarly distracting arguments for many years in relation to the impact of the their operations on the community (Klose 2001). More recently, environmental mercury measurements associated with a Sydney chemical plant were implied to have been skewed by fish consumption, broken thermometers, power station emissions and dental fillings (Robertson 2013). The point being is that industrial operators concoct 'myths', stories or other arguments to distract the public and the authorities away from understanding and determining the true source and cause of environmental contamination. In untangling the long-held and favoured 'miner's myth', this paper uses multiple scientific lines of evidence, including soil geochemistry, geology, historic photos and reports to establish what the preponderance of evidence shows when considered on its true merits.

Materials and methods

This paper uses multiple lines of evidence to examine and assess the contribution of industrial versus natural lead to contamination in Broken Hill city. In addition to new soil geochemistry data collected by the authors, this study is supported by historical literature detailing the geology of Broken Hill, mining activities, early environmental investigations, photographs and previously published literature on lead contamination in Broken Hill.

Field sampling methods

Thirty-four soil samples were collected around Broken Hill city (Fig. 1; Supplementary Figure S1) at a depth of 0-2 cm in accordance with AS 4874-2000 (Standards Australia 2000). Additional sub-surface soil samples were collected at the same locations using established methods (Taylor et al. 2010) to determine historical and local background soil metal values. Samples were collected during the month of September in 2011 and 2012 and prepared for analysis by sieving to <2 mm. In September 2013, a further 23 surface soil analyses were conducted on site using Olympus Delta Premium 40-kV portable X-ray fluorescence (pXRF) across Broken Hill. Two standard reference materials NIST 2710a (Montana soil I) and 2711a (Montana soil II) were analysed with recovery rates of 109 % for lead and 102 % for zinc. Analysis of a blank (SiO₂) returned <0.5 mg/kg for both lead and zinc. Chemplex 3.6-µm X-ray film was used for each sample to reduce contamination between samples.

Laboratory analysis

Soil samples collected in 2011 (n = 30) were analysed by ChemCentre, Western Australia, and samples collected in 2012 (n = 88) were analysed at National Measurement Institute (NMI), North Ryde, NSW, for total extractable lead and zinc concentrations and lead isotopic compositions. Samples were digested in a mix of HCl and HNO₃ and measured for lead and zinc concentrations on a Varian Vista Pro ICP-OES and for lead isotopic compositions on a PerkinElmer Elan DRC II and Agilent 7500ce ICP-MS. Blanks returned less than 0.01 mg/kg for both Pb and Zn. Duplicate analysis at both laboratories returned relative standard deviations (RSD) <6 % for Pb and <7 % for Zn. Recovery rates at ChemCentre were measured using NRCC reference material PACS-2 (marine sediment) with recovery rates for Pb 102 % and 106 % for Zn. Recovery rates at NMI were measured using in-house reference material AGAL-10 (Hawkesbury River Sediment) and sample matrix spiking. Recovery rates were 91 % for Pb and 100 % for Zn for the reference material and 90 % for Pb and 106 % for Zn for the matrix spikes. Lead concentrations were optimised (20 ppb) for isotopic analysis and were bracketed by NIST SRM981 (common lead standard) to correct for mass fractionation. RSDs reported by NMI for ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb were 0.18, 0.15 and 0.07 %, respectively.

Results and discussion

Geology

The Broken Hill ore body, referred to as the 'line of lode' was formed 1685 ± 3 million years ago and is hosted in the Hores Gneiss in the Broken Hill Group that dates from 1685 to 1693 million years ago (Page et al. 2005) (Figure 1; Supplementary Figure S2). The south of Broken Hill city lies generally over the Thackaringa Group, which was deposited approximately 1704–1710 million years ago (Willis 1989; Parr et al. 2004; Page et al. 2005). The Sundown Group on which the north of Broken Hill is situated is aged-dated to 1670–1680 million years (Willis 1989; Conor and Preiss 2008). Soil samples were collected from these three geological groups represented in Broken Hill (Fig. 1) to evaluate the impact of mining activities



Fig. 1 Location of all soil samples collected around Broken Hill city plotted against basic geological groups [terminology based on Willis (1989)]. Open circle samples were also analysed for lead isotopic composition

in altering the surface soil geochemistry with respect to the corresponding natural basement geology. Elevated lead concentrations are found in surface soils overlying the Sundown Group but not in the subsurface soils (Supplementary Table S1). The geology and location of the ore body and its host rocks are discrete within the vicinity of Broken Hill city (Supplementary Figure S2). A geochemical 'halo' expression producing similar lead isotopic signatures and elevated elemental composition can be found immediately surrounding lead ore bodies due to natural weathering (Gulson 1984; McQueen 2004). However, elevated soil metal concentrations and associated lead isotopic compositions are typically variable and have a limited spatial extent around the target ore [see Butt et al. (2005) and references therein relating to base metal examples of regolith expression]. The argument that natural mineralisation has resulted in high levels of lead in surface soils across the wider Broken Hill city area is not supported by the basement geology. While there is the possibility of a geochemical halo within the Broken Hill Group, the halo hypothesis cannot explain elevated surface metal concentrations in the soils overlying Sundown and Thackaringa Groups up to three kilometres away. The evidence for this is detailed in the *Soil data, Lead isotopes* and *Historical evidence* sections of the discussion.

Soil data

Analyses of surface soil samples show widespread contamination of lead across Broken Hill city (Fig. 2). Mean surface (0–2 cm) soil concentrations measured by ICP-OES across Broken Hill city were 2000 mg/kg for lead and 2700 mg/kg for zinc, representing recent accumulation of lead in the soil. Including the data from the pXRF analysis, which incorporates more samples from the north of Broken Hill and provides a more representative determination of soil metals



Fig. 2 Lead and zinc concentrations of surface (0–2 cm) soil samples. *Circles* analysed by ICP-OES (this paper), *crosses* analysed by pXRF (this paper), *diamonds* analysed by ICP-MS (Taylor et al. 2014b)

across the city, the average surface soil concentrations are 1500 mg/kg for lead and 2100 mg/kg for zinc. Median surface soil concentrations are 1300 mg/kg ($\sigma = 2200$) for lead and 1600 mg/kg ($\sigma = 2900$) for zinc. Soil samples collected at depth (>30 cm), representing background concentrations, returned a median of 100 mg/kg ($\sigma = 560$) for lead and 96 mg/ kg ($\sigma = 445$) for zinc.

Of the surface soils tested by ICP-OES, 24 of 34 (70 %) exceeded the Health Investigation Level (HIL) of 600 mg/kg for public open spaces (Australian Government 1999). Given soil contamination risks do not discriminate between public open spaces and private residences, application of the residential HIL standard of 300 mg/kg reveals that the number over the guideline increases to 28 (82 %) soil samples. Whilst this constitutes the majority of soil samples collected from Broken Hill, the distribution of greatest lead contamination within Broken Hill is focused to the south (Fig. 2). All surface soils collected from Broken Hill city south of the mining operations, had lead levels above the 600 mg/kg guideline.

Elevated soil lead contamination is not restricted to south Broken Hill, with levels in excess of 1000 mg/

kg also measured north of the mining operations (Fig. 2). Elevated surface soil lead levels do not extend generally into the northern most part of Broken Hill city (Fig. 2). However, only five samples exceeded the residential guideline of 7400 mg/kg for zinc and no samples exceeded the public open space guideline of 14,000 mg/kg. However, more conservative soil zinc guidelines of 300 mg/kg for Norway (Norwegian Pollution Control Authority 2009) and 2300 mg/kg for the USA (United States Environmental Protection Agency 2015) are used to depict spatial variations across the city (Fig. 2). The similar spatial distribution between lead and zinc in surface soils is characteristic of a common source, in this case the Broken Hill ore body.

Surface enrichment ratios (SER) measured as the ratio of surface (0–2 cm) to sub-surface (40–50 cm) soils demonstrate the significantly elevated lead concentrations evident in surface soils are not present in corresponding deeper soils. Average SER across Broken Hill is 25 with highest SER found in south Broken Hill and lowest found in north Broken Hill (Fig. 3). Soil depth profiles (Fig. 3; Supplementary Figure S3) show similar trends across Broken Hill with

elevated and enriched surface soils declining rapidly to markedly lower concentrations in the sub-surface soils (2–10 to 40–50 cm). Elevated sub-surface soils in central Broken Hill samples at 40–50 cm (Fig. 3) are due to two sub-surface soils containing mining waste deposits. If natural weathering and erosion were responsible for the elevated concentrations of lead and zinc found in surface soils around Broken Hill as claimed in the 'miner's myth', then levels of lead and zinc in sub-surface soils should correspond to those found at the surface.

Lead isotopes

Lead isotopic compositions were also measured in select surface soil samples (HS1, HS2, HS4, LOLW1, LOLW2, LOLW3, LOLW4 and BHW2; Supplementary Table S1) and compared with lead isotopic compositions from the corresponding sub-surface soils (40–50 cm) and with the Broken Hill ore itself (Fig. 1; Table 1). Soil samples from depth are considered to represent natural, in situ soil concentrations and isotopic compositions (i.e. unaffected by



atmospheric emissions and depositions) and are noticeably different across the different basement geologies. The samples from the Sundown Group have markedly different lead isotopic compositions at depth compared with values in the corresponding surface soils (Table 1). This demonstrates that bedrock composition is an important control on the nature of the lead found at depth, which is counter to the argument that the surrounding city soils are a product of the weathering and erosion of the ore body since formation almost 1700 million years ago.

The two samples collected from the Broken Hill Group, which is host to the Broken Hill ore deposits, have lead isotopic compositions that are largely consistent between the surface and sub-surface soils. This is not unexpected within the mineralised soil of the Broken Hill Group (Gulson 1984). When the isotopic composition data are considered in tandem with the concentration of lead in the soil profiles, the source and cause of the elevated metals is clear. Elevated concentrations of lead (and zinc) are found only in the surface soils around Broken Hill. The concentrations of lead and zinc decline rapidly with depth from the first sub-surface samples (2–10 cm) and more evidently in the deepest sub-surface soils (40–50 cm) (Figs. 3, 4; Table 1; Supplementary Table S1), attesting to role of recent deposition in determining environmental soil metal values.

Historical evidence

A study of soils in Broken Hill was undertaken in 1892 as part of an enquiry into lead poisoning amongst mine workers and residents (Thompson et al. 1893). Samples from these locations were collected in 2012 (HS1-6; Supplementary Table S1; Supplementary Figure S1) to replicate the historic samples that returned 'no lead'. The sites have been undisturbed since at least the 1930s when the area was designated a regeneration reserve (CBH Resources Limited 2010). Although the determination of 'no lead' in the 1890s does not compare to current analytical capabilities, lead levels were reported by Thompson et al. (1893) as low as 0.008 % (80 mg/kg), which is well below the HIL

Table 1 Lead isotopic composition of samples collected in Broken Hill

Geological group	Soil depth (cm)	Pb (mg/kg)	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb
Sundown					
LOLW3	0–2	200	1.051	2.321	16.17
	30–40	13	1.267	2.401	19.97
LOLW4	0–2	46	1.079	2.352	16.69
	40-50	15	1.223	2.428	19.15
Thackaringa					
LOLW1	0–2	815	1.042	2.316	16.04
	40-50	44	1.071	2.349	16.54
BHW2	0–2	1340	1.043	2.317	16.08
	40-50	18	1.077	2.355	16.65
HS1	0–2	2850	1.038	2.314	16.03
	40-50	700	1.044	2.322	16.08
HS2	0–2	1060	1.043	2.323	16.00
	40-50	48	1.072	2.358	16.67
Broken Hill					
LOLW2	0–2	2400	1.040	2.319	16.02
	40-50	77	1.049	2.328	16.11
HS4	0–2	3580	1.042	2.321	16.05
	40-50	290	1.044	2.320	16.03
Broken Hill ore	n = 12		1.041 ± 0.002	2.312 ± 0.006	16.02 ± 0.07



Fig. 4 Soil depth profiles for lead and zinc of historic site samples 1-5

guideline for lead in soil of 300 mg/kg (Australian Government 1999). Thus by inference, 'no lead' is likely to have meant values of no greater than 80 mg/ kg. Of the six surface samples collected to replicate the historic locations, only one (HS6) returned lead concentrations below the guideline of 300 mg/kg with the rest >1000 mg/kg. Nevertheless, the surface soil lead concentration in the HS6 sample was more than double what might have been present in 1892 (<80 mg/kg). The other five historic replica samples collected from the south of the mining operations (HS1-5) returned surface lead levels between 1060 and 2900 mg/kg (Supplementary Table S1). The subsurface soils (40-50 cm) returned concentrations between 48 and 700 mg/kg, with the highest being closest to mining operations. Zinc soil concentrations returned similar down profile metal distributions (Fig. 4). The discrepancy between surface and subsurface soil lead and zinc concentrations at the historic sites and the initial determination in 1892 that no lead was present, makes it inconceivable that the process of long-term weathering and erosion (or even a orebody halo effect) can be ascribed as the cause of the elevated surface soil metal levels. Further, depositions from leaded paint or petrol are also highly improbable as a significant source of lead due to the distal location of the samples in regeneration reserves outside and away from the city's urban environment. Thus, it is implausible that the levels of lead seen in the surface samples were the result of anything other than mining operations.

Photographs

In addition to the soil geochemistry evidence detailed above, the development of Broken Hill city included the massive disturbance of surface soils (Fig. 5). Reworking of the surface soils means that it is



Fig. 5 Broken Hill Proprietary mine in the centre of Broken Hill in 1888 (Broken Hill Municipal Library 2015). Note the disturbance of surface soil around the mine area

impossible to contemplate the use of contemporary surface soil metals (lead or zinc) as an indicator of long-term geological accumulation. The reworking of surface soils may also account for increased lead and zinc concentrations being found at depth in profiles close to the mine operations.

Other additional sources of metals included the multiple uncovered skimp and tailing (mining waste) dumps around town (Supplementary Image S4) that were subject to substantial wind and water erosion before they were re-treated or covered (Gulson et al. 1994b). Due to the limited ability to extract all the lead and any of the zinc in the early days of mining in Broken Hill, these skimp dumps were known to contain up to 18 % lead (Kearns 1974). The arid climate in Broken Hill (precipitation 260 mm/year) is conducive for the transport of fine particles rich in lead and zinc, derived from mining activities, to be distributed across Broken Hill since the advent of mining (Woodward-Clyde 1993).

Conclusion

The preponderance of evidence from soil geochemistry data, geology, historical photographs and current emissions and depositions demonstrates that the 'miner's myth' is tantamount to a 'lode of lies'. Our study data reveals that the dominant and ongoing source of lead in Broken Hill is unequivocally due to mining operations. The evidence does not support the argument that the environmental contamination in Broken Hill (*inter alia* other equivalent locations) is due to naturally occurring mineralisation or additional alternative sources of lead such as paint or petrol. The creation of the 'naturally occurring' myth has acted as a considerable barrier to proper and permanent environmental mitigation strategies and effective remediation not only in Broken Hill, but elsewhere in Australia and internationally. Unravelling the facts from the constructed truth, or myth, is essential for contaminated communities to be able to move forward in addressing exposures in a positive and effective manner.

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Paper Seven

Environmental lead exposure risks associated with children's outdoor playgrounds

Taylor, M. P., Camenzuli, D., **Kristensen, L. J.**, Forbes, M., & Zahran, S. (2013). *Environmental Pollution*, 178, 447-454.

Supplementary Information in Appendix G

This study measured the deposition of toxic metals, including lead, that children are exposed to on playgrounds as a direct results of smelter emissions. Previous studies have established the environmental quality and human health effects in Port Pirie from the smelter emissions. This study contributes to the literature and this thesis by measuring a previously unknown yet contemporary exposure route to children. These measurements provide evidence of the deficiency of regulations to in Port Pirie to reduce lead emissions to the environment to protect children from the toxic effects of lead.

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Environmental lead exposure risks associated with children's outdoor playgrounds

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1. Introduction

This study examines childhood exposure risks associated with environmental lead emissions from the Port Pirie (South Australia) lead smelter at four of the city's outdoor playgrounds. Port Pirie is home to the world's third largest lead—zinc smelter, which was established in 1889. The Nyrstar Port Pirie Pty Ltd smelter site and its emissions are the dominant source of atmospheric lead in Port

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ABSTRACT

This study examines exposure risks associated with lead smelter emissions at children's public playgrounds in Port Pirie, South Australia. Lead and other metal values were measured in air, soil, surface dust and on pre- and post-play hand wipes. Playgrounds closest to the smelter were significantly more lead contaminated compared to those further away (t(27.545) = 3.76; p = .001). Port Pirie post-play hand wipes contained significantly higher lead loadings (maximum hand lead value of 49,432 µg/m²) than pre-play hand wipes (t(27) = 3.57, p = .001). A 1% increase in air lead (µg/m³) was related to a 0.713% increase in lead dust on play surfaces (95% CI, 0.253–1.174), and a 0.612% increase in post-play wipe lead (95% CI, 0.257–0.970). Contaminated dust from smelter emissions is determined as the source and cause of childhood lead poisoning at a rate of approximately one child every third day.

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Pirie, with The National Pollutant Inventory (NPI) reporting 44,000 kg of lead being released in 2010–2011 (NPI, 2012). The smelter also emitted significant amounts of other aerosol pollutants during 2011–2012 including arsenic (1100 kg), cadmium (1200 kg), copper (690 kg), zinc (49,500 kg) (NPI, 2012).

The sources of lead, and their local and regional distribution at Port Pirie have been studied extensively (Baghurst et al., 1992; Body et al., 1991; Calder et al., 1994; Cartwright et al., 1977; Esterman and Maynard, 1998; Maynard et al., 2006, 2003; van Alphen, 1999). Esterman and Maynard's (1998) and van Alphen's (1999) studies were fundamentally important in terms of addressing the environmental lead problem in Port Pirie. Prior to these studies, the prevailing view was that the source of exposure was predominantly due to the 'lead sink'; that is, the contaminated legacy of lead in soils in and around Port Pirie (Body et al., 1991). Esterman and Maynard (1998) and van Alphen's (1999) studies showed that elevated concentrations of atmospheric lead dust (and other metal contaminants) from smelter emissions were the likely dominant source of elevated blood lead levels in Port Pirie children.







Abbreviations: ABS, Australian Bureau of Statistics; ACCLPP, Advisory Committee on Childhood Lead Poisoning & Prevention; As, arsenic; AS, Australian Standard; ASTM, American Society for Testing and Materials; ATSDR, Agency for Toxic Substances and Disease Registry; Cd, cadmium; Cu, copper; EPASA, Environment Protection Authority, South Australia; NEPC, National Environmental Protection Council; NHMRC, National Health Research and Medical Council; NPI, National Pollutant Inventory; NTP, National Toxicology Program; Pb, lead; TA LUFT, Technical Instructions on Air Quality Control; WA Health, Western Australia Health; WHO, World Health Organisation; Zn, zinc.

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The city of Port Pirie has a population of 18,076 of which, approximately 21.0% are <14 years old (ABS, 2010b). The long history of smelting in the city has resulted in generations of children having long-term, elevated blood lead levels (Maynard et al., 2006; Taylor, 2012; Simon et al., 2013). This is in spite of the ongoing efforts to reduce exposure via the city's lead awareness and education programs 'Tenby10' and the more recent 'Ten for Them' initiative (TenforThem, 2012), the aims of which are to reduce blood lead levels in all children below 10 µg/dL. Blood lead levels remain elevated with 24.9% (excluding maternal blood lead as surrogate values) for children less than 5 years of age having a blood level >10 µg/dL in 2012 (Simon et al., 2013). The geometric mean blood level in children aged 24 months in 2012 was 6.3 µg/dL. The percentage of children exceeding 10 μ g/dL, the current Australian goal for blood lead (NHMRC, 2009), is more than double the most recent surveys from Broken Hill (Lesjak, 2011) or Mount Isa (Queensland Health, 2010), Australia's two other primary locations with known blood lead problems in children.

Although several studies have examined the link between blood lead exposures and elevated levels of lead-enriched dust in Port Pirie (Baghurst et al., 1992; Calder et al., 1990; Esterman and Maynard, 1998; Simon et al., 2007), no research has been undertaken to investigate the potential risks associated with lead contaminated dust at Port Pirie's outdoor public playground environments. Outdoor environments such as children's recreational or kindergarten facilities represent a potentially hazardous environment for children in lead contaminated communities because of their potential interaction with contaminated surfaces and soils (Duggan et al., 1985: Gulson et al., 2006: Mielke et al., 2011: Nielsen and Kristiansen, 2004). Thus, the primary purpose of this study is to investigate exposure to lead at children's outdoor playground facilities in the lead and zinc smelting city of Port Pirie following a timed period of play activity. To measure exposures pre- and postplay hand wipes were collected using a standard process after child-simulated play by an adult. Surface soils and dusts were also sampled to provide a better understanding of other potential sources of lead exposure. In addition to lead concentration values, arsenic, cadmium, copper and zinc concentration values were also measured in the samples to provide complementary data on environmental contamination and possible exposure risks.

2. Methods and approach

Exposure risks at the playground sites were determined using surface and subsurface soil samples, dust wipes on outdoor surfaces, and hand wipes before and after a 20 min timed child-simulated play activity by an adult at each playground. Lead-in-air data was provided by the Environment Protection Authority, South Australia (EPASA).

2.1. Field sampling methods

Dust data was collected from four outdoor playground facilities at Port Pirie over a 7-day period between 26 June to 3 July, 2011. The four playgrounds in Port Pirie were all within 3.0 km of the smelter stack: Foreshore Playground (1.0 km); Memorial Park Playground (1.2 km); Sports Park Playground (2.4 km); Woodward Park Playground (3.0 km), Fig. 1. A reference playground site in Port Augusta, situated 85 km NNW of Port Pirie was subject to the same sampling procedures (Fig. 1). Port Augusta was deemed to be a suitable reference site as it has no lead smelting and its population of 14,669 (ABS, 2010a) is similar to Port Pirie, the principal study site.

Surface wipes (n = 72) were collected using a Ghost WipeTM following the methods described in ASTM E1728-03 (ASTM, 2003), with values transformed to $\mu g/m^2$. Surface dust wipe samples were collected daily from the same two flat, unpainted, horizontal surfaces at each playground site (details of the wiped surfaces are provided in the Supplementary Data, Table S1). The sampled sites were not accessible during normal play routines and therefore did not influence the post-play hand wipe measures. The only exceptions were at Sports Park and Woodward Park where one of the surfaces was swapped at each location on day two because they were partially covered by an adjacent structure, and were deemed unsuitable. The original surfaces were also sampled on day two, producing an extra sample at each of those sites, giving a total of 72 samples for the 7-day study period.

For the hand wipe samples, the same person (L. Kristensen) conducted the child-simulated play at each of the playground sample sites for a fixed 20 min timed period each day over the 7-day study period. The objective of the pre- and post-play hand wipes was to measure exposures that were representative of each playground. Given that each of the playgrounds were comprised of different structures (see Supplementary Data, Fig. S2a-e), it was not possible to replicate the same exact play activities at each of the facilities. However, a standard protocol was applied to each location for the child-simulated play activities that meant each structure within the playground e.g. slide, ladder, climbing apparatus was utilized at least twice over the set 20 min timed play period. L. Kristensen simulated the play of a five year old using her four years of childcare work experience involving supervising play equipment and also participating with children during their activities (see Supplementary Data S2a-e for more information). Hand wipe samples were collected from the child-simulated play participant each day before and after the timed play period (n = 70). Playgrounds were selected to be as close as possible to the EPASA lead-in-air monitoring stations to facilitate correlation between atmospheric lead concentrations and those in surface and hand wipes (Fig. 1). A single sample consisted of two wipes (i.e. one wipe per hand). The play participant's anterior surface area of a single hand was calculated as 1% of the total body surface area (BSA) using the DuBois and DuBois (1916) method.

At all playgrounds and EPASA air monitoring stations, three surface soil samples (0-2 cm) were collected to provide average soil arsenic, copper, lead and zinc concentrations. In total, 29 surface soil (0-2 cm) samples (26 in Port Pirie and 3 in Port Augusta) were collected using the Australian Standard AS4874 (Australian Standard AS4874-2000, 2000) method. In order to approximate background concentrations for the Port Pirie area, subsurface soils were also analysed from two pits excavated to a depth of 50 cm at opposite ends of Port Pirie ity (Fig. 1). Samples were collected at 0-2; 2-10; 10-20; 20-30; 30-40; 40-50 cm (total for both pits: n = 12). Soil samples were analysed for metal concentrations in the <2 mm fraction, which is the recommended Australian method (NEPC, 1999). Soil and dust lead measures were benchmarked against relevant Australian guidelines and standards. Arsenic and cadmium dust concentrations were compared to the German TA Luft (TA Luft (Technical Instructions on Air Quality Control), 2002) dust guideline values to provide environmental quality benchmarks.

2.2. Laboratory analyses

A total of 39 soil samples, 70 hand wipes and 72 surface dust wipe samples were analysed using a Varian Vista-Pro Inductively Coupled Plasma Optical Emission Spectrometer for arsenic, cadmium, copper, lead and zinc concentrations. Dust wipes were digested using the National Institute for Occupational Safety and Health Method 7303 (NIOSH, 2003). Six procedural wipe blanks returned average concentrations of 0.78 µg/wipe for arsenic, 1.45 µg/wipe for copper and 66 µg/wipe for zinc. Cadmium and lead blanks were <0.5 µg/wipe. Field blank wipes were collected during sampling. Lead concentration was significantly higher in field blanks (1.25 μ g/wipe on average), compared to laboratory blanks (<0.5 μ g for all wipes); t(6) = 4.43, p = .004. No significant differences were observed for arsenic, cadmium, copper and zinc. Soil samples were digested using a modified procedure based upon United States Environmental Protection Agency Method 3050 for sediments, sludges and soil (Edgell, 1989). Duplicate analyses for soils (n = 4) and wipes (n = 16)returned relative percent deviations (RPD) for all elements of <11%. Recovery rates were measured using matrix spikes. Spike recovery rates for soil (n = 2) were 79– 110% and those for the wipes (n = 8) were 84–107%.

3. Results

3.1. Soil lead concentrations

The summary statistics for soil metals are provided in the Supplementary Data, Table S3. A one-way analysis of variance (ANOVA) showed that there were no significant differences in soil lead levels across all Port Pirie playgrounds (F(24, 1) = 159.952, p = .062). Soil metal results show that 69% (n = 18) of the Port Pirie playground surface soil (0–2 cm) samples were greater than or equal to the Australian 300 mg/kg guideline health investigation level (HIL-A) for residential soil lead (NEPC, 1999). The mean concentration of lead in Port Pirie surface soils (0–2 cm) was 1443 mg/kg (n = 26). No soil samples (n = 3) from the Port Augusta reference site exceeded the NEPC residential soil lead guidelines (NEPC, 1999). Independent samples *t*-tests on soils demonstrated that there were significant differences between Port Pirie and Port Augusta for lead levels in surface soil (t(25.002) = 3.630, p = .001). Other soil metal concentration values displayed similar patterns of



Fig. 1. Map of Port Pirie showing the four South Australian EPA high volume lead-in-air sample sites and the four playgrounds sampled for surface and hand wipe lead dust values. The Port Pirie smelter is located at the north of the town. The Boat Ramp lead-in-air sample site that forms part of Nyrstar's licence conditions is also shown. Image taken from Google maps.

being markedly higher in Port Pirie compared to the Port Augusta reference site (Table S3, Supplementary Data).

Lead levels from the two soil pits displayed a trend of decreasing concentrations with depth; lead concentrations averaged 235 mg/kg at the surface (0-2 cm) and 37.5 mg/kg at depth (40-50 cm). The mean surface soil lead concentration from the Port Augusta reference site was 7.5 mg/kg.

3.2. Surface dust wipe results

Table 1 shows the descriptive statistics for lead loadings on surface dust wipes. Seventy-one percent (n = 41) of all of the surface dust wipe samples collected in Port Pirie exceeded the Western Australian Health clean-up goal of 400 µg/m² (lead) for

surfaces accessible to children (WA Health, 2007). Fourteen percent (n = 9) were greater than or equal to the Australian acceptable lead dust limit of 8000 µg/m² for exterior surfaces (Australian Standard AS4361.2-1998, 1998). At Foreshore Play-ground, 29% (n = 4/14) of surface dust wipe samples exceeded 8000 µg/m². Seventy-one per cent (n = 10/14) of Foreshore Playground samples exceeded the 400 µg/m² clean up goal for lead (WA Health, 2007). Memorial Park Playground was similar, with 36% (n = 5/14) of surface dust wipe samples greater than or equal to 8000 µg/m² (Australian Standard AS4361.2-1998, 1998); 93% (n = 13/14) were above the WA Health (WA Health, 2007) lead clean up goal of 400 µg/m² for surfaces accessible to children. The two playgrounds furthest from the smelter, Sports Park and Woodward Park (Fig. 1), were less contaminated, with no surface

Table 1

Surface dust wipe metal loadings (arsenic – As, copper – Cu, cadmium – Cd, lead – Pb and zinc – Zn) recorded over the 7 day study period at Port Pirie and the Port Augusta reference site. Some samples returned cadmium values below the instrument detection limit of 0.5 µg/wipe were estimated at zero to enable descriptive statistics to be calculated.

	Element	Foreshore Playground	Memorial park playground	Sports park playground	Woodward park playground	Port Augusta reference site playground
Surface dus	t samples (µg/m ²)					
Mean ^a	As	112.48 ± 156.93	91.75 ± 74.96	20.87 ± 10.82	17.56 ± 7.94	8.64 ± 4.32
	Cd	23.57 ± 33.25	24.99 ± 22.46	0.49 ± 1.89	1.92 ± 3.37	0.61 ± 2.29
	Cu	502.92 ± 655.57	277.49 ± 223.94	62.34 ± 35.69	55.77 ± 35.21	26.03 ± 9.24
	Pb	5057.83 ± 7351.71	6956.41 ± 7571.74	721.33 ± 782.22	750.48 ± 780.14	19.35 ± 19.39
	Zn	7296.19 ± 7864.94	6094.26 ± 4790.19	1471.54 ± 646.43	1525.93 ± 854.06	1127.78 ± 427.51
Median	As	31.65	86.11	18.75	16.97	8.72
	Cd	0	22.78	0	0	0
	Cu	220.86	216.67	48.75	46.38	23.89
	Pb	660.04	4611.11	567.31	475.11	14.44
	Zn	2441.23	5277.78	1375	1222.22	1030
Range	As	13-589	16-256	9–53 ^b	6-35	0-15
	Cd	0-96	0-78	0-7 ^b	0-8	$0-9^{b}$
	Cu	34-2222	57-789	28-154 ^b	15-124	18-54
	Pb	141-24222	323-22444	58-3365 ^b	9-2149	6-83
	Zn	783–23778	1222-15222	695–3000 ^b	565-3394	589-1867
n		14	14	15	15	14

^a Mean \pm SD.

^b Locations where surface wipe metal or metalloid values recorded on day one of the sampling period were the maximum recorded for that site (including sites that were swapped after day one – see text). These higher values indicate the effect of historical atmospheric deposition of contaminated dust on surfaces (i.e. surfaces were not precleaned prior to the first sample at that location). Removing these elevated first surface wipe values for Sport Park results in lower mean values: As – 19.29 μ g/m²; Cd – 0.0 μ g/m² (values below detection at 0.5 μ g/wipe); Cu – 57.97 μ g/m²; Pb – 530.58 μ g/m²; Zn – 1405 μ g/m². At Port Augusta all of the surface wipe values for Cd other than day 1 were below detection at 0.5 μ g/wipe.

dust wipe samples exceeding 8000 μ g/m² (Australian Standard AS4361.2-1998, 1998). However, 67% (n = 10/15) of dust wipe samples at Sports Park playground exceeded 400 μ g/m² of lead for surfaces accessible to children, and 53% (n = 8/15) of Woodward Park samples exceeded the same WA Health (WA Health, 2007) clean up goal.

In contrast, no surface dust wipe samples from the Port Augusta control site exceeded any of the aforementioned standards or guideline values. An independent samples *t*-test showed that surface lead dust wipes were significantly higher at the Port Pirie playgrounds (M = 3280.63, SD = 5762.35) compared to the Port Augusta reference site surface wipes (M = 19.35, SD = 19.39); t(57.005) = 4.310, p < .001. Within Port Pirie, playgrounds close to the smelter (Foreshore Playground and Memorial Park Playground) had significantly higher lead concentrations on surface dust wipes than playgrounds further from the smelter (Woodward Park and Sports Park playground); t(27.545) = 3.76, p = .001.

In terms of the other elements measured, the German TA Luft emission standards provide maximum acceptable dust loading values for lead at 100 $\mu g/m^2/day$, arsenic at 4 $\mu g/m^2/day$ and cadmium at 2 μ g/m²/day but none for copper or zinc. Although cadmium measurements at Port Pirie were frequently below detection levels (0.5 μ g/wipe), all sites with the exception of the Sports Park playground and the Port Augusta reference site returned some values in excess of the German benchmark. Similar to lead levels, Foreshore and Memorial Park had the most elevated cadmium surface dust values with between 0–96 and 0–78 $\mu g/m^2/day$, respectively (Table 1). Arsenic was detected at all sites, including the control site, in excess of the German 4 $\mu g/m^2/day$ standard. Consistent with the other dust metals data presented here, Foreshore and Memorial playgrounds had the highest levels of arsenic, with surface dust wipes containing between 13-589 and 16-256 μ g/ m^2/day , respectively (Table 1).

3.3. Hand wipe results

All hand wipe samples collected after the timed child-simulated play activity from Foreshore, Memorial Park and the Sports Park playgrounds exceeded the WA Health clean up goal of 400 μ g/m² of

lead for surfaces accessible to children. At Woodward Park, 86% of post-play hand wipes exceeded the 400 μ g/m² lead clean up goal. Eighty-six percent of hand wipe samples from Foreshore Play-ground, 71% of the hand wipes samples collected at Memorial Park Playground, 14% of the Sports Park samples and 29% of the Woodward Park exceeded the WA Health clean up goal of 4000 μ g/m² for surfaces not accessible to children (WA Health, 2007).

Hand wipe samples collected from Port Pirie playgrounds after 20-min of timed play had significantly higher lead loadings, compared to hand wipe samples collected prior to playtime; t(27) = 3.57, p = .001. Foreshore Playground and Memorial Park Playground demonstrated the highest mean lead loadings on hands after play (Table 2), with a maximum value of 49,432 µg/m² being recorded at Memorial Park. Hand wipes collected at Memorial Park Playground displayed a mean increase of approximately 18,158 µg/m² (i.e. lead increased by a factor of 63) after the 20-min play activity. At Foreshore Park, post-play activity returned a mean value of 11,733 µg/m², 72 times greater than mean pre-play hand wipe values. Lead hand wipe values from Sports and Woodward parks were lower but were elevated after the timed play activity, with mean values of 2123 µg/m² (23 times increased) and 2269 µg/m² (11 times increased), respectively.

Post-play Port Pirie hand wipe lead concentrations were significantly greater than those from the reference site (t(27.008) = 3.513, p = .002). The maximum hand wipe lead value recorded at Port Augusta was $455 \,\mu\text{g/m}^2$ on a pre-play hand wipe. It is possible that hands were inadvertently contaminated due to the transfer of lead dust from clothing to hands, given the Port Augusta reference site was sampled last on each day of the study. Contamination from clothing is also evidenced by the fact that pre-play hand wipes were on average higher than post-play hand wipes (Table 2).

With respect to the other elements measured, hand wipes followed a similar pattern to dust wipes, with arsenic, cadmium, copper and zinc being greatest at the sample sites closest to the smelter - Foreshore and Memorial Parks. In particular, arsenic and cadmium recorded post-play mean values of 255 μ g/m² and 53 μ g/m² at Foreshore Park and 302 and 64 μ g/m² at Memorial Park (Table 2). In each case, the measured values are markedly above the

Table 2

Metal loadings (arsenic – As, copper – Cu, cadmium – Cd, lead – Pb and zinc – Zn) on pre- and post-play hand wipes collected from Port Pirie and the Port Augusta reference site over the 7 day study period. The mean daily difference in metal loadings between pre- and post-play values at each location are also provided. Some samples returned cadmium values below the instrument detection limit of $0.5 \ \mu g/wipe$ were estimated at zero to enable descriptive statistics to be calculated.

	Element	Foreshore	Memorial Park	Sports Park	Woodward Park	Port Augusta
		Playground	Playground	Playground	Playground	reference site
Due also handestra annales (al	2					
^a Moop pro play motal loadings	m-)	71.02 + 15.12	6404 + 1267	61.60 ± 11.01	C0 99 10 25	57.50 + 21.45
Mean - pre-play metai loadings	AS Cd	71.02 ± 15.12	04.94 ± 13.07	01.09 ± 11.91	0.80 ± 10.55	57.59 ± 21.45
	Cu	0 ± 0	0 ± 0	0 ± 0 120.20 + 12.22	0 ± 0 120 20 + 22 01	0 ± 0 155.02 + 56.15
	Db Cu	101.93 ± 39.91 052 72 + 667 64	146.15 ± 24.55	130.20 ± 12.32 01 72 + 49 19	136.35 ± 23.01 200.01 \pm 104.20	133.03 ± 30.13 204.29 \pm 166.69
	ru Zn	533.73 ± 007.04 6209.42 ± 1443.27	293.43 ± 103.09 5025 32 ± 1346.85	51.72 ± 40.10 5104.81 ± 1518.53	209.01 ± 104.39 5065.01 ± 1538.64	504.58 ± 100.08 5235 30 ± 0.0018
Median	Δs	71.02	5325.52 ± 1540.85	5134.01 ± 1510.55	65 3 <i>1</i>	5255.55 ± 540.18
Wiedian	Cd	0	0	0	0	0
	Cu	147 73	142.05	130.68	139.20	13636
	Ph	937 50	267.05	73.86	167.61	369.32
	7n	5965.91	5113 64	4545.46	5113.64	4829 55
Range	As	40-88	45-88	40-71	40-68	20-82
Runge	Cd	0	0	0	0	0
	Cu	114-230	108-182	108-148	102-170	80-261
	Pb	313-2216	139-597	43-170	122-426	68-455
	Zn	4830-9091	4830-7955	3977-7670	4545-8523	4261-6818
n		7	7	7	7	7
Post-play hand wipe samples (μg	$/m^{2})$					
^a Mean post-play metal loadings	As	255.28 ± 145.81	302.35 ± 202.56	122.16 ± 19.34	97.40 ± 32.79	59.66 ± 15.30
	Cd	52.52 ± 50.46	63.64 ± 43.31	7.39 ± 9.41	14.94 ± 16.13	10.02 ± 13.61
	Cu	868.51 ± 549.86	767.05 ± 438.89	321.83 ± 64.30	257.31 ± 109.20	189.94 ± 51.85
	Pb	$11,\!732.95 \pm 11,\!930.79$	$18,\!453.73 \pm 18,\!604.84$	2122.57 ± 1040.55	2268.67 ± 2476.62	269.07 ± 74.66
	Zn	$20{,}211.04 \pm 9328.15$	$24{,}512{.}99 \pm 9557{.}90$	$16{,}274{.}35 \pm 3979{.}69$	10917.21 ± 3238.54	5844.16 ± 834.04
Median	As	221.59	241.48	133.52	82.39	65.34
	Cd	45.45	53.98	0	15.91	0
	Cu	653.41	625.00	340.91	201.70	167.61
	Pb	8806.82	10,227.27	2073.86	994.32	252.84
	Zn	18,465.91	22,443.18	15,340.91	9943.18	5681.82
Range	As	114–511	105–682	94–139	71–162	31–71
	Cd	0-159	16–122	0-21	0-40	0-34
	Cu	284-1761	313–1420	222-426	179–455	128-278
	Pb	1449-37784	1903-49432	966-4261	369-6818	159-369
	Zn	7386–38636	14,205–38352	13,068–24432	7955–16193	4830-7386
n		7	7	7	7	7
Mean daily increase in metal loadings on hands (µg/m²)						
	As	184.25	237.42	60.47	36.53	2.07
	Cd	52.52	63.64	/.39	14.94	10.02
	Cu	/06.57	618.91	191.56	118.91	34.90
	PD	10,779.22	18,158.28	2030.84	2059.66	-35.31
	Zn	14,001.62	18,587.66	11,079.55	4951.30	608.//

^a Mean \pm SD.

German TA Luft standard for surfaces for arsenic at $4 \mu g/m^2/day$ and cadmium at $2 \mu g/m^2/day$.

Post-play hand wipe metal loadings were analysed (y) using a fixed effects model by way of a least squares dummy variable (LSDV) regression procedure. Allowing i to denote our play participant, j to denote the playground of observation, and y_{ij} to denote the post-play hand wipe metal loadings of subject i in playground j, our regression model is:

$$y_{ij} = \beta_0 + \beta_1 P_{ij} + \beta_2 S_j + \Gamma_1 D_j + e_{ij}$$

Where, β_0 is the average post-play hand wipe metal loadings in our reference playground, Port Augusta, P_{ij} is the pre-play hand wipe metal loadings of subject *i* in the playground *j*, S_j is the mean metal dust loadings on surfaces of playground *j*, D_j represents a set of dummy variables corresponding to each playground in Port Pirie, and e_{ij} is the random disturbance term.

The regression procedure seeks to predict metal loadings on the hands of the experimental subject after timed play as a function of settled dust on playground surfaces, adjusting for metal loadings on the hands of our subject prior to play, and unobserved characteristics specific to each playground (represented via the use of dummy variables).

3.4. Dust and air modelling results

Graphical presentation of the association between post-play hand wipe metal loadings (Y-axis) and the mean dust metal loadings on play surfaces across all playgrounds (X-axis) illustrates the exposure relationship (Fig. 2). For ease of interpretation, observed values across metals are standardized (z-scored). Fig. 2 shows clearly that metal loadings on the hands of our subject after timed play increase monotonically as the quantities of settled metal dust increase on playground surfaces. The calculated correlation (r_{xy}) between hand and surface dust is strongly positive for all metals: where arsenic (As) is r = .866 (p < .001), copper (Cu) is r = .812(p < .001), lead (Pb) is r = .948 (p < .001), and zinc is r = .837(p < .001). The calculated correlations for arsenic, copper, and lead exclude a single outlier measurement of settled dust on playground surfaces taken for the Foreshore Playground in Port Pirie on Day 2 of the experiment. The outlier sample measured four standard deviations above the mean for each metal.

Table 3 reports fixed effects regression analyses for each metal measured. Cadmium was not analysed as the majority of samples (48/72) were below detection (0.5 μ g/wipe). Column 1 (Table 3) shows that after adjusting for pre-play hand wipe metal loadings and unobserved playground characteristics, a 1% change in the


Fig. 2. Scatterplot of mean metal loadings on playground surfaces vs. mean metals loadings on hand wipes after timed play (summarized data is in Tables 1 and 2).

quantity of arsenic dust on play surfaces increases hand arsenic loadings by 0.374% (95% CI, 0.155–0.592). A 1% increase in play surface copper loadings raises post-play hand wipe copper loadings by 0.42% (95% CI, 0.186–0.656). For lead and zinc we observe a similar effect of increased play surface loadings on hand wipes; lead - 0.402% (95% CI, 0.202–0.602) and zinc - 0.263% (95% CI 0.108–0.418). Between 77.6% (arsenic) and 89.3% (lead) of variation in post-play hand wipe metal loadings across all sites is explained by our suite of variables.

Given the emphasis on lead exposure in this study, Table 4 reports the marginal effects from regression analyses where surface dust lead, pre-play hand wipe lead, and post-play hand wipe lead loadings are regressed independently against the available lead-in-air data (Table S4, Supplementary Data) derived from monitoring stations corresponding to the Foreshore and Memorial Park locations. The reported constant is Foreshore Playground. Results show that a 1% increase in air lead (μ g/m³) increases the loading of lead dust on play surfaces by 0.713% (95% CI, 0.253–1.174), and increases the measured quantity of lead on post-play wipes by 0.612% (95% CI, 0.257–0.970). The results demonstrate that lead-in-air depositions are the primary source of risk encountered by children using the playgrounds.

4. Discussion

This study reveals conclusively that significantly elevated environmentally sourced metal contamination is present in dust wipes, hand wipes and surface soils across the four playground sites examined at Port Pirie. The contamination of surfaces with lead rich dust is related predominantly to ongoing emissions from the

Table 4

Regression results of relationships between air station lead, surface dust lead, and hand wipe lead loadings.

	Surface dust (lead)	Pre-play wipe (lead)	Post-play wipe (lead)
Air station	0.713*** (0.209)	0.205* (0.112)	0.614*** (0.162)
Foreshore Park	1.707* (0.811)	-0.664* (0.364)	1.567** (0.591)
playground			
Constant	6.623***	6.242***	7.777***
f	(0.770)	(0.322)	(0.513)
n	14	14	14
F-test	6.44	6.54	7.19
R^2	0.488	0.555	0.519

Robust errors in parentheses ***p < .01, **p < .05, *p < .1.

Nyrstar lead smelter (Esterman and Maynard, 1998; van Alphen, 1999). While the legacy of emissions over the last 120 years has rendered the city's surface soils heavily contaminated (Table S3, Supplementary Data; Baghurst et al., 1992; Calder et al., 1990, 1994; Cartwright et al., 1977), further increased contamination of soil continues due to ongoing smelter emissions, which amounted to 44000 kg of lead during 2011 (NPI, 2012).

Risks associated with metal rich airborne dusts deposited on playground facilities have received little attention compared to lead exposures in home environments (Dixon et al., 2009; Lanphear et al., 2002, 1998). In one of the only Australian studies of its kind, Gulson et al. (2006) measured lead exposure on children's hands after outdoor play in Sydney and found maximum mean hand wipe lead values on males of 14 μ g/hand. Simon et al. (2007) measured hand lead on Port Pirie infants < 15 months old who were restricted primarily to indoor environments and recorded median values on males between 94 and 672 $\mu g/m^2$, depending on their age. In both cases, the hand lead exposures were markedly lower than those identified in this study of outdoor play facilities at Port Pirie. In addition to the well-established effects of lead exposure, the elevated arsenic and cadmium dust values are concerning because of their known neurotoxic effects and impact on cognition and behaviour (Ciesielski et al., 2012; Rosado et al., 2007; Roy et al., 2011).

Although the risk of exposure in home environments is greater due to the length of exposure times, this study shows that outdoor playgrounds at Port Pirie host a suite of neurotoxic contaminants that pose a significant risk to health. While the synergistic human health exposure effects from multiple metals are not well understood (ADSTR, 2004a,b), the hazards of binary exposure to arsenic, cadmium or lead are well established, particularly with respect to lead (NTP, 2012). The lead dust values recorded in both surface and hand wipes in this study shows that there needs to be clean up of play areas, and significant and immediate reductions in emissions to the environment from the smelter. On December 3rd 2012, Nyrstar Australia Pty Ltd announced that they would commit to an

Table 3

Least square dummy variable regression results of post-play hand wipe metal loadings. The constant reported in our model reflects the average post hand wipe level in the Port Augusta playground.

	Arsenic	Copper	Lead	Zinc
Pre-play wipe	0.253 (0.287)	-0.0914 (0.294)	0.434** (0.191)	0.246 (0.196)
Surface dust	0.374*** (0.106)	0.421*** (0.115)	0.402*** (0.097)	0.263*** (0.076)
Foreshore Playground	0.663** (0.283)	0.613* (0.313)	1.443** (0.525)	0.869*** (0.157)
Memorial Park Playground	0.655** (0.281)	0.487* (0.285)	1.808*** (0.556)	0.966*** (0.154)
Sports Park Playground	0.309 (0.218)	0.267 (0.205)	1.289** (0.521)	0.952*** (0.117)
Woodward Park Playground	0.218 (0.201)	0.072 (0.194)	0.691 (0.420)	0.514*** (0.117)
Constant	2.226* (1.234)	4.202*** (1.394)	1.743* (1.021)	4.710*** (1.522)
n	33	34	34	34
F-test	15.00	18.63	37.71	35.80
R ²	0.776	0.805	0.893	0.888

Standard errors in parentheses ***p < .01, **p < .05, *p < .1.

in principle transformation and replacement of the smelter with assistance from the South Australian Government and the Australian Federal Government at a cost of (Australian) \$350 million (Nyrstar, 2012). Thirty-five million Australian dollars was also allocated for environmental clean up and abatement of contamination over the next decade. If a permanent solution cannot be found, as a temporary measure, all the playgrounds should be covered to minimize atmospheric deposition and washed (hosed) at least daily. While this approach will reduce potential surface contamination and exposure, it will, unfortunately, only have the effect of transferring the metals to the already contaminated adjoining soil, grass (where present) or other surfaces, which also pose a risk to health given their elevated metal concentrations.

At the time of this study (July 2011) cleaning of the playgrounds was limited to the Foreshore Playground being cleaned (hosed) twice weekly. We were able to obtain an indication of the cleaning effects via our data, which showed that there were some, but not statistically significant, daily variations in hand wipe lead values after play activity at Foreshore Playground. The initial findings from our study were provided to the Environmental Health Centre at Port Pirie in January 2012. As a result there has been an increase in the playground cleaning regimes under partnership between Nyrstar and the Port Pirie local government (Port Pirie Regional Council, 2013). The Foreshore playground (also known as Flinders View) is now being cleaned 7 days a week, Memorial Park 5 days a week with other playgrounds being cleaned less frequently. The efficacy of the intervention has not been tested but the authors have recommended to the Environmental Health Centre at Port Pirie that this is essential because significant reductions/elimination of lead-in-air emissions have not yet been initiated and it is these emissions that are contaminating playgrounds.

It now accepted by several national and international organizations (ACCLPP, 2012; Health Canada, 2013; NHMRC, 2009; NTP, 2012; WHO, 2010; Wilhelm et al., 2010) that there is no safe level of lead exposure and that all exposures should be eliminated. Indeed, the WHO rescinded its previously promulgated safe daily intake of lead for both adults and children (WHO (World Health Organisation), 2010). These shifts in understanding of the risks associated with lead exposure, particularly in children, are somewhat at odds with the current prevalence (24.9%) of elevated blood lead values in children below 5 years old (Simon et al., 2013) and the existing monitoring and licence regime imposed upon the Nyrstar smelter at Port Pirie (EPASA, 2012). While mandated maximum lead-in-air values are set at the national standard of $0.5 \ \mu g/m^3$ averaged over a year as measured at Oliver Street and Pirie West Primary School (Fig. 1), the evidence is that this is clearly too high and fails to take into account short-term emission events that blanket the city with lead contaminated dust (Esterman and Maynard, 1998; van Alphen, 1999). These short-term elevated emission events are evident in the data from all four of the EPA's monitoring sites at Port Pirie (Table S4, Supplementary Data). The other sites listed in the smelter licence, Ellen Street and the Boat Ramp site (Fig. 1), have non-enforceable targets of lead-in-air maximums of 1.6 μ g/m³ and 0.6 μ g/m³, respectively.

The EPASA's two most distal air monitoring sites at Frank Green Park and Oliver Street are used to report values to Australia's National Environment Protection Council as part of the nation's measurement and monitoring of air quality (Hunt and Mitchell, 2012). These sites correspond to the two most distal playgrounds examined in this study (Woodward Park and the Sports Park, Fig. 1), which were subject to markedly lower lead dust depositions and lead-in-air values (Table 1; Fig. S5, Supplementary Data). Thus, the effect of selecting these sites for use in the licence or national reporting arrangements is twofold: First, the monitoring sites do not encompass the full range of exposures across the city. Second, as demonstrated in this study, reliance on data from these two most distal sites does not describe adequately the blanketing effect of emissions across the whole city nor does the use of an annual average value for lead-in-air portray accurately the exposure risks faced by the city's residents. Given that Port Pirie has the highest lead-in-air concentrations of any Australian city (as evidenced via the various Australian air quality reports (NEPM, 2012)), significantly elevated dust and soil metals (Table S1, Fig. S5, Supplementary Data), it is not surprising that on average, approximately one child every three days presents with lead poisoning in Port Pirie (Simon et al., 2013).

5. Conclusion

The evidence shows that atmospheric emissions from the Port Pirie smelter are causing seriously elevated dust metal levels in all playgrounds, which are easily transferred to hands during play activity. The data suggest that Nyrstar Port Pirie Pty Ltd smelter licence arrangements are not adequate and need to be reconstructed so that the whole of the city is protected by much lower enforceable lead-in-air limits such as the 0.15 μ g/m³ concentration maximum applied by the United States EPA (USEPA, 2012). In addition, averaging periods need to be much shorter so as to prevent episodic elevated concentrations of lead and other metal depositions across the urban area. Without such changes, chronic exposures from metal rich dusts will continue to create a hazardous environment for children and older residents in Port Pirie. The solution to the lead exposure problem at Port Pirie is clear: smelter emissions must be eliminated or significantly reduced and city-wide and domestic garden soils need to be evaluated and remediated where necessary.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.03.054.

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Paper Eight

Environmental arsenic, cadmium and lead dust emissions from metal mine operations: Implications for environmental management, monitoring and human health

Taylor, M.P., Mould, S.A., Kristensen, L.J. & Rouillon, M. (2014). *Environmental Research*, 135, 296-303.

Supplementary Information in Appendix H

This study measured the contemporary exposure from toxic metals in dust depositions due to current mining activities on playgrounds across Broken Hill. This study demonstrated the extensiveness of lead emissions produced by the mining operations and measured the rate of contemporary exposures solely to children. This study contributes to the literature and this thesis by measuring the contemporary exposure from current emissions in a location where vast historical emissions have also occurred. Contents lists available at ScienceDirect





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Environmental arsenic, cadmium and lead dust emissions from metal mine operations: Implications for environmental management, monitoring and human health



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ABSTRACT

Although blood lead values in children are predominantly falling globally, there are locations where lead exposure remains a persistent problem. One such location is Broken Hill, Australia, where the percentage of blood lead values $> 10 \ \mu g/dL$ in children aged 1–4 years has risen from 12.6% (2010), to 13% (2011) to 21% (2012). The purpose of this study was to determine the extent of metal contamination in places accessible to children. This study examines contemporary exposure risks from arsenic, cadmium, lead, silver and zinc in surface soil and dust, and in pre- and post-play hand wipes at six playgrounds across Broken Hill over a 5-day period in September 2013. Soil lead (mean 2,450 mg/kg) and zinc (mean 3,710 mg/kg) were the most elevated metals in playgrounds. Surface dust lead concentrations were consistently elevated (mean 27,500 $\mu g/m^2$) recorded close to existing mining operations. Surface and post-play hand wipes (60,900 $\mu g/m^2$) recorded close to existing mining operations. Surface dust wipes from the playgrounds across from the playgrounds revealed the source of lead contamination to be indistinct from the local Broken Hill ore body. The data suggest frequent, cumulative and ongoing mine-derived dust metal contamination place as a serious risk of harm to children.

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1. Introduction

This study examines metal and metalloid concentrations (arsenic (As), cadmium (Cd), lead (Pb), silver (Ag) and zinc (Zn)) in contemporary soils and dusts in Australia's oldest lead-zinc mining city of Broken Hill. The adverse health risks to humans from metal and metalloid exposure are serious and well known. Childhood Pb exposure causes irreversible damage to neurological functions due to its toxicity (National Toxicology Program (NTP) 2012; Needleman, 2004; Taylor et al., 2012; 2014b). Children are at higher risk of environmental metal poisoning than adults due to their small body size, earlier stage of development, and because of their tendency to engage in hand-to-mouth behaviour (Kranz et al., 2004; Simon et al., 2007; Viverette et al., 1996). Environmental sources and pathways of exposure are important areas of study for risk mitigation. Research focused on household exposures has identified sources of Pb in metal mining and smelting communities as being dominated by ore body and smelted metals

along with lesser contributions from a combination of lead-based paints and leaded petrol residues. Lead dust in houses and surrounding soils are important exposure pathways (Gulson et al., 1994, 1995, 1996; Mackay et al., 2013; Soto-Jiménez and Flegal, 2011; Taylor et al., 2010). Recent research in the smelting community of Port Pirie, South Australia, identified playground use as a potential source of metal exposure (Taylor et al., 2013). Similarly, Viverette et al. (1996) found in their day care centre hand Pb study that outdoor sources of contamination can be more important for childhood Pb exposure than indoor sources.

Broken Hill in far western New South Wales (NSW; Fig. 1) was established around one of the world's largest silver-lead-zinc deposits, which has been mined continuously since its discovery in 1883 (Solomon, 1988). Smelting was also carried out in the city during the early years of ore extraction, but ceased in 1898 (Woodward, 1965), with the majority of the ore being transferred to Port Pirie for smelting until recently when the bulk has been sent to overseas for processing. The waste from 130 years of mining dominates the city's landscape, with the old gossan extrusion being replaced by covered slagheaps in the centre of the city. Mining operations in the city of Broken Hill continue

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Fig. 1. Map of Broken Hill showing playground sites sampled, locations of contemporary mining activity, and pollution monitoring sites referred to herein.

underground in the central area of the line of lode (CBH, Rasp Mine, Fig. 1) and also to the south (Perilya mining leases, Fig. 1). Although mineral extraction at both sites is now entirely underground, processing and transport of the ore occurs at the surface. Industry monitoring data from CBH Resources Ltd. (2014) and Perilya Broken Hill Ltd. (2014) show that Pb-rich dust emissions and deposition continue to impact the surrounding environment, although the full impact of operations on the urban environment are difficult to ascertain as there are limited dust deposition monitoring sites in the city (measuring total dust or Pb in dust as $\mu g/m^2$). There are no NSW Environmental Protection Authority monitoring sites for dust, dust Pb or lead-in-air or other metals in Broken Hill, despite other similar mining and smelting impacted locations such as Mount Isa and Port Pirie having independent monitoring in their city environments (Taylor et al., 2014a). National Pollutant Inventory (NPI) data show that Perilya Broken Hill mines (North and South) emitted an estimated 26,000 kg Pb, 58,000 kg Zn, 670 kg As and 240 kg Cd to the atmosphere during 2012-2013 (National Pollutant Inventory (NPI) 2014b). CBH Resources (Broken Hill Operations Pty. Ltd.), emitted an estimated 97 kg Pb and 150 kg Zn to the atmosphere over the same period (National Pollutant Inventory (NPI) 2014a) in 2012-2013.

Unlike most locations in Australia, blood Pb levels have been rising in recent years in Broken Hill (Taylor et al., 2014b). For example, the geometric mean blood Pb of children aged 1-4 years has risen from 4.8 μ g/dL in 2011 to 5.4 μ g/dL in 2012 (Lesjak et al., 2013). Further, the proportion of children over the current national goal of 10 μ g/dL (which is currently under review, (Taylor et al., 2014b)) has also increased in recent years from 12.6% (2010), to 13% (2011) to 21% (2012) (Lesjak et al., 2013). Therefore in the context of rising blood lead levels, the purpose of this study is to evaluate contemporary metal exposure risks in soils and dusts across Broken Hill city and to determine the likely sources as well as possible mitigation strategies, where necessary.

2. Methods

2.1. Field sampling

Six playgrounds distributed across Broken Hill (Fig. 1) were sampled daily over a 5-day period between 16th to 20th September 2013. Playgrounds 1 (Duff St. Park; PG1), 2 (Patton Park; PG2) and 3 (Zinc Lakes; PG3) were located south of the ore body. Playgrounds 4 (Sturt Park; PG4), 5 (Queen Elizabeth Park; PG5) and 6 (Broken Hill Regional Aquatic Centre; PG6) were located north of the ore body. A minimum of two surface soil samples were taken from each of the six playgrounds (n=14) at a depth of 0–2 cm in accordance with AS 4874-2000 (Standards Australia, 2000). Soil samples were collected using a plastic trowel that was wiped clean each time prior to sampling using KimWipesTM and deionised water. Before sampling commenced, the trowel was passed through soils immediately adjacent to the

sample site to remove any possible effects associated with the previous sample site (c.f. Taylor and Hudson-Edwards, 2008). Bulk soil samples were collected in sealed polyethylene ziplock bags and sent for analysis at the National Measurement Institute (NMI), Sydney.

Dust wipes were used to measure the daily deposition of dust on horizontal surfaces in playgrounds. A single horizontal surface was chosen for each playground and re-sampled once per day for five days (n=30). Sample areas were marked out and measured, allowing all results to be standardised to a concentration expressed in μ g/m². The wiped surface areas are provided in Supplementary Table S1. The surfaces selected for sampling were free from paint and exposed to the atmosphere but were in discrete locations such that they were unlikely to be disturbed by playground users. The dust wipes used were the Lead WipeTM and were collected using the method described in ASTM E 1728-03 (American Society for Testing and Materials, 2003). Dust wipes were collected at approximately the same time (9am) each sample day.

Playground sampling involved 'simulated play' to measure metal loadings that children might be exposed to during interaction with the playgrounds (see the approach used in Taylor et al., 2013). Each day, the same researcher 'played' on the play equipment at the allocated site for 10 min (1 researcher for each of the 6 playgrounds sampled over the five days), mimicking the exploratory behaviour of a child. Adult researchers undertook the child-simulated play rather than actual children to provide reliability and consistency of method. The researchers' hands were cleaned thoroughly with dust wipes prior to play and following play (n=30 paired samples) using the method employed by Taylor et al. (2013). Pre- and postplay wipes were analysed separately for metals and compared to measure the effect of contact with the play equipment. Hand surface area was calculated for each play participant using DuBois and DuBois (1916) and then converted to $\mu g/m^2$ to allow comparison between each of the playgrounds over the 5-day period.

2.2. Laboratory analysis

Soil samples and dust wipes were analysed by NMI for As, Ag, Cd, Pb and Zn. Soil samples were sieved to < 2 mm prior to digestion. Soil samples (0.5 g) were digested in a 1:1 ratio of nitric acid and hydrochloric acid (Evans, 2012). Dust wipes were digested in a 3:1 ratio of aqua regia (Evans, 2013). Soil samples and dust wipes were measured for their metal concentrations using a Varian 730-ES ICP-OES and Perkin Elmer Elan DRC II ICP-MS. Reagent blanks, dust wipe blanks, duplicates, matrix spike and reference material AGAL-10 (Hawkesbury River Sediment) were also analysed to verify sample data quality.

Lead isotopic compositions of selected samples (n=11) were determined using a PerkinElmer Elan DRC IIS ICP-MS after optimising sample concentrations. Analyses were conducted with concentration-matched measurements of NIST SRM 981 bracketing each sample, which were used to correct for isotopic mass fractionation.

2.3. Laboratory Quality Assurance / Quality Control

Soil blanks returned < 0.5 mg/kg for all metals. Duplicate analysis returned relative percent differences (RPD) < 13% for all elements. Recovery rates were measured using certified reference material AGAL-10 and sample matrix spiking. Recovery rates were 98–120% for the certified reference material and 93–99% for the matrix spikes. Dust wipe blanks returned < 0.1 µg/wipe for As and Zn and < 0.05 µg/wipe for Cd, Pb and Ag, all of which were below the laboratory limit of reporting. Recovery rates were 94–98% for AGAL-10 and 85–103% for matrix spikes. Analytical precision (RSD) for lead isotopic compositions was 0.14%, 0.10% and 0.20% for 206 Pb/ 207 Pb and 206 Pb/ 204 Pb respectively.

2.4. Statistical analysis

Wilcoxon signed-rank tests for hand wipe data were performed using the VassarStats web-based application developed by Lowry (2014). Regression analysis was used to assess the relationship between surface Pb loadings and those recovered on post-play hand wipes. Values were calculated using the Minitab

version 16.2.4 software package. Data were Log-transformed to satisfy normality assumptions.

3. Results

3.1. Surface dust metal

Daily data measured from the playground surface dust wipes show that deposition of fine Pb-rich particles across Broken Hill was a daily occurrence over the 5-day study period. Playground 3 showed consistently higher dust Pb loadings than all other playgrounds (Table 1). Australian Standard AS 4361.2-1998 (Standards Australia, 1998) provides an outdoor dust Pb limit of $8,000 \,\mu\text{g/m}^2$, which was exceeded at Playground 3 on all days and at Playground 5 on two days. We also applied the Government of Western Australia (2007) clean up goal of 400 μ g/m² for surfaces accessible to children to our data as a benchmark because of its specific reference to children. Table 1 shows the specific days and corresponding locations where the Government of Western Australia cleanup goal was exceeded. The cleanup goal was exceeded on all days at Playgrounds 3 and 5, and at Playground 1 on 4 of the 5 sample days. Supplementary Table S1 shows metal loadings on surfaces for each playground on Day 1 as an indication of 'typical' loadings on surfaces not regularly cleaned, with subsequent sample days 2-4 showing the daily (24-hour) rate of deposition. There is no Australian standard for dust As, Cd or Pb deposition rates. However, the German TA Luft (2002) standard sets maximum acceptable daily dust loading values for As $(4 \,\mu\text{g/m}^2/\text{day})$, Cd $(2 \,\mu\text{g/m}^2/\text{day})$ and Pb $(100 \,\mu\text{g/m}^2/\text{day})$. The same standards are used as trigger values with respect to the environmental monitoring and assessment of the Mount Isa Mines operations (Taylor et al., 2014a; Supplementary Table 1). Playgrounds 2 and 3 exceeded this limit for As and Playgrounds 1, 2 and 3 exceeded the Cd benchmark. All playgrounds except Playground 6 exceeded the TA Luft (2002) value for dust Pb deposition. Rainfall of 1.2 mm very early on Day 1 of sampling (Bureau of Meteorology, 2014a) could have contributed to reducing the metal loading measured on this day. Rainfall of 6.8 mm was also recorded on 13th September, three days prior to Day 1 (Bureau of Meteorology, 2014a). We note also that sampling was undertaken at a particularly windy time of year, with mean 3 pm wind speeds being typically higher in September compared to the rest of the year at Patton Street (51-year record) (Bureau of Meteorology, 2014b).

3.2. Soil metal

Soil Pb concentrations in three playgrounds (Playgrounds 1–3) exceeded the National Environmental Protection Measure (NEPM, 2013) Health Investigation Level (HIL) soil Pb guidelines (600 mg/kg) for land categorised as Recreational C, public open space. Mean concentrations of all metals in the <2 mm fraction were highest at Playground 3 (Fig. 2). Playgrounds 1–4 exceeded the HIL soil Pb value (300 mg/kg) for land categorised as Residential A (including

Table 1

Summary of daily surface dust Pb loadings for each playground to three significant figures. Values in bold exceed the Government of Western Australia (2007) cleanup goal of 400 µg/m².

Playground	Day 1 ($\mu g/m^2$)	Day 2 $(\mu g/m^2)$	Day 3 $(\mu g/m^2)$	Day 4 $(\mu g/m^2)$	Day 5 $(\mu g/m^2)$
1	942	628	507	411	362
2	333	467	389	767	267
3	59,900	35,600	15,500	16,400	9,960
4	633	733	211	167	100
5	8,440	6,560	4,220	8,780	6,890
6	418	102	173	84.4	37.8



Fig. 2. Mean metal concentrations in soils at each playground. Playgrounds 1, 2 and 3 exceeded Pb concentrations for recreational zones according to NEPM (2013) soil guidelines. The NEPM (2013) soil guideline is shown only for Pb because playground soils did not exceed the guideline values for As, Cd, Ag or Zn.

childcare centres, kindergartens, preschools and primary schools and their integral playgrounds), which is considered to be more appropriate standard for our study given that young children use these facilities.

No other soil metals exceeded the NEPM (2013) guidelines. Total extractable metal concentrations of As, Ag, Cd, Pb and Zn, for all soil samples can be found in Supplementary Table S2. Other international organisations provide more conservative guidelines for metals in soil than Australia. California, Canada and the US EPA set soil Pb guidelines at 80 mg/kg, 140 mg/kg and 400 mg/kg respectively, while soil As guidelines are 0.07 mg/kg, 12 mg/kg and 0.61 mg/kg, respectively (California Environmental Protection Agency (CEPA), 2005; Canadian Conference of Medical Education (CCME), 2013; United States Environmental Protection Agency (EPA), 2013). The Norwegian soil guidelines specifically refer to soil used in children's playgrounds for As, Cd, Pb and Zn of 8 mg/kg, 1.5 mg/kg, 60 mg/kg and 200 mg/kg, respectively (Norwegian Pollution Control Authority (NPCA), 2009). The data in Fig. 2 show clearly that these playground-specific values were exceeded in nearly all of the playgrounds in the south part of Broken Hill (PG1 – PG3) compared to the playgrounds in the north of the city (PG4 – PG6), which have much lower soil metal concentrations.

3.3. Pre- and post-play hand wipe metal loadings

Pb loadings on hands increased significantly on post-play wipes at all playgrounds (Fig. 3; Supplementary Table S3), indicating the availability of contaminated dust to children using play equipment. The mean increase in Pb on post-play hand wipes across all playgrounds was 72 times higher than pre-play loadings. The maximum post-play loading measured was 60,900 μ g/m² (more than 150 times the Government of Western Australia cleanup goal of 400 μ g/m²). A Wilcoxon signed-rank test showed that the increase in metal loading on hands after play was significant (95% confidence) for As (p=0.001), Cd (p=< 0.0001), Pb (p=< 0.0001),



Fig. 3. Lead loadings on hands pre- and post-play for each of the six playgrounds sampled. Post-play hand wipes had significantly higher loadings than pre-play for As, Cd, Pb and Zn (see Supplementary Table S3).

and Zn (p = < 0.0001). No significant increase was found for Ag (p = 0.221).

Pearson correlation analysis showed a significant, positive relationship between surface dust metals and those recovered in post-play hand wipes (As -p = < 0.0001; Ag -p = < 0.0001; Cd -p = < 0.0001; Pb -p = < 0.0001; Zn -p = 0.007), demonstrating the importance of atmospheric deposition of fine metal rich dusts in contributing to the total playground exposure risks.

3.4. Lead isotopic analysis

Lead isotopic compositions (²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁷Pb) for dust samples from Playgrounds 3–5 (Supplementary Table S4) were compared to those of the Broken Hill ore body values published previously (Chiaradia et al., 1997; Cooper et al., 1969; Gulson and Mizon 1979; Townsend et al., 1998). Dust wipes from Playground 3 are indistinguishable, within analytical precisions, from the ore body isotopic composition (Fig. 4). Lead isotopic compositions from Playgrounds 4 and 5 dust wipes are similar to Broken Hill ore, and although there is minor scatter in the dust wipe sample data, the ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb values of all the dust wipe samples have no more than 1% relative difference (RPD) to published isotopic composition values of the Broken Hill ore (Chiaradia et al., 1997; Cooper et al., 1969; Gulson and Mizon 1979; Townsend et al., 1998). The lead isotopic data demonstrate that the Pb in dust at Playground 3 originates from the Broken Hill ore body. Although the Pb isotopic values from the remaining play-grounds are dominated by Broken Hill ore, it is evident that the dust contains Pb from other sources. These might include other natural sources such as dust and soil not from the ore body and industrial sources such as paint and petrol (Gulson et al., 1996).

4. Discussion

Elevated surface dust metal concentrations found in Broken Hill playgrounds, particularly with respect to Pb, demonstrate a



Fig. 4. Stable lead isotope ratios for playground dust Pb were similar to values published for Broken Hill ore body Pb (Chiaradia et al., 1997; Cooper et al., 1969; Gulson and Mizon, 1979; Townsend et al., 1998).

potential risk to the health of children living in the city. Data from the pre- and post-play hand wipes provide a direct measure of the dust metal exposure hazard available to children during the use of the play facilities. Although this study did not specifically measure blood Pb values and their isotopic composition in playground participants, the environmental data presented here are cause for concern, particularly with respect to the most metal-impacted playgrounds (Playgrounds 1-3). Blood Pb measured annually by NSW Health in Broken Hill children aged 1-4 years reveals the persistent risk of exposure in the community over the last 30 years, with 21% of children still having a blood Pb lead level above 10 µg/dL in 2012 (Lesjak et al., 2013). Susceptibility to environmental metal exposure is greatest in children under three years of age who are more prone to hand to mouth behaviours, which are known to result in the ingestion of contaminated dusts (Simon et al., 2007).

Playground 3 not only had the highest concentrations of metals in soils, the wipe samples had the highest loadings of metal-rich dust consistently on surfaces and on post-play wipes (see Supplementary Image 1). The proximity of this playground to the Perilya Southern operations facility ($\sim 400 \text{ m}$) is unlikely to be coincidental as it lies within the downwind direction of the city's prevailing winds. Playground 6 in Broken Hill North, furthest from the ore body, had post-play dust Pb levels of $300 \,\mu g/m^2$ on Day 4 of sampling. Prevailing winds on Day 4 were from the northwest (Bureau of Meteorology, 2014a), which indicate that even when the winds are not flowing across current mining operations and transporting contaminated dusts, elevated metals can still be found on playgrounds. Given the 130-year history of ore processing and extraction at Broken Hill, it is very likely that the contamination identified is sourced from historic metal deposition that is re-entrained and then re-deposited on surfaces. By contrast, on Day 2, dust Pb loadings at Playground 6 reached $> 400 \,\mu g/m^2$ when the wind flow at the time of sampling was 31 km/h from the west-south-west (Bureau of Meteorology, 2014a). The airflow patterns at this time would have been moving approximately across the ore body and the current mining operations, and would have had the capacity to transport contemporary emissions across the urban environment. Playground 5 surface dust levels returned elevated Pb concentrations (Table 1), which were inconsistent with the lower post-play wipe results (Fig. 3). This suggests the surface samples contained an additional source of Pb that is not attributable to daily dust depositions.

The Pb isotopic compositions ²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁷Pb from the hand-wipes at Playground 3 show that the dust is indistinguishable from the Broken Hill ore body. During September 2013 the nearest Pb-in-air monitoring site (Licence Point 12, LP12, Fig. 1) to Playground 3 returned an average value of 0.248 µg/m³ (Perilya Broken Hill Ltd., 2013). Monthly dust deposition Pb values were elevated during September 2013 with the dust deposition licence point closest to Playground 3 (LP6, Fig. 1; Perilya Broken Hill Ltd., 2013) returning a Pb dust value of 7,000 µg/m²/month. Licence point 3, proximal to the CBH Resources lease and the centre of the town (Fig. 1), returned a Pb dust value of 12.000 µg/m²/month in September 2013 (Perilva Broken Hill Ltd., 2013). Although the EPA licence sets no specific limit for Pb dust deposition, its measurement is required as part of the facility licence environmental monitoring programme (Environmental Protection Authority, 2012). Lead dust loadings at monitoring site LP3 exceed the Australian Standard value for outdoor Pb dust of 8,000 µg/m² frequently (Standards Australia, 1998). The industry licence monitoring data show clearly that there is significant contemporary deposition of Pb rich dust, which is contributing to exposures in playgrounds and elsewhere in the city. Although the data presented herein show elevated As and Cd dust values, the existing licence arrangements do not require their measurement. The data show a strong statistical relationship between surface and post-play hand wipes for all metals, suggesting that they have a common source. Consequently, As and Cd should be monitored along with Pb. It would also be prudent to include trigger values for these contaminants, which could mirror those used for environmental monitoring of the Mount Isa Mines operations in north-west Queensland (Taylor et al., 2014a).

Elevated Pb in Broken Hill playgrounds may be compared with other locations reported in the literature that are frequented by children. Mean surface dust Pb loadings at Playground 3, the most heavily impacted site sampled in Broken Hill (27,500 μ g/m²), are almost four times higher than the highest mean surface loadings measured at Foreshore Park Playground (6,960 μ g/m²) in the smelting city of Port Pirie, South Australia (Taylor et al., 2013). Post-play hand wipe mean Pb loadings at Playground 3 $(32,700 \,\mu g/m^2)$ were 1.8 times higher than those recorded at Memorial Park (18,500 μ g/m²), Port Pirie's most impacted playground in terms of post-play Pb hand wipe values (Taylor et al., 2013). The range of soil Pb concentrations across all Broken Hill (24–3,340 mg/kg) is also within the range reported by Glorennec et al. (2012) for playgrounds across France (2-3,400 mg/kg) and is similar to Port Pirie playground soil Pb values 22-2,600 mg/kg (Taylor et al., 2013). In New Orleans, USA, Viverette et al. (1996) reported on elevated soil and dust Pb in day care centres, the most impacted returning a median soil Pb concentration of 498 mg/kg (range 287–1,880 mg/kg). Playground 3 at Broken Hill returned a median soil Pb concentration of 2,540 mg/kg (range 1,390-3,340 mg/kg), which is more than five times the most impacted New Orleans day care centre.

Given the potential serious risk to children's health identified in the present study, it would be prudent to consider mitigation strategies. Mielke et al. (2011) demonstrated that soil remediation using geotextile and clean topsoil can reduce concentrations of Pb in soil significantly. Mielke et al. (2011) reported a decrease in median soil Pb from 558 mg/kg (range of 14–3,690 mg/kg) and not dissimilar to Broken Hill playgrounds soil Pb levels (Supplementary Table S2) to 4.1 mg/kg (range 2.2–26.1 mg/kg) using these methods. However, the contemporary data suggest strongly that subsequent recontamination due to ongoing emission, deposition and remobilisation of metal-rich dust sourced from mines in Broken Hill may render this kind of intervention ineffective. Taylor et al.'s (2013) research at Port Pirie prompted a frequent and widespread cleaning programme for the city's playgrounds (Port Pirie Regional Council, 2013), but an evaluation of its effectiveness is still in review. Surface dust data from Broken Hill playgrounds showed that significant recontamination of playground surfaces occurred within 24 h of sampling. Despite the fact that sampling for the present study was carried out at a particularly windy time of year (Bureau of Meteorology, 2014b), a seasonal increase in hazard severity still presents a potential risk of harm. Notwithstanding the outcome of the evaluation of the Port Pirie cleaning regime, washing is unlikely to offer a long-term solution to the problem of daily dust contamination in the city of Broken Hill. The ongoing mine emissions and associated deposition of contaminants will also be affecting neighbouring residences, schools and kindergartens simultaneously, and needs to be addressed. Therefore, a more a sustainable and effective mitigation strategy in the longer term is required. Any such strategy will need to identify and then mitigate all source(s) of contamination and should include enclosure and containment of remaining surface ore processing operations.

5. Conclusions

Elevated As, Cd and Pb mining-related dust deposition continues to contaminate surfaces and contribute to blood Pb exposure risks in the city of Broken Hill.

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.envres.2014.08. 036.

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CHAPTER 4: Impacts and consequences of lead emissions

Chapter Four presents the following four papers:

- Paper Nine: Omissions about the sources of contaminant emissions and depositions

 A reply to comments on "Taylor, M.P., Davies, P.J., Kristensen, L.J., Csavina, J., 2014. Licenced to pollute not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations. *Aeolian Research*, 14, 35-52." Taylor, M.P., Kristensen, L.J., Davies, P.J., Csavina, J.L., Mackay, A.K., Munksgaard, N.C., & Hudson-Edwards, K.A. (2015). *Aeolian Research*, 17, 205-213.
- Paper Ten: Evaluating the efficacy of playground washing to reduce environmental metal exposures. Taylor, M.P., Zahran, S., Kristensen, L.J., & Rouillon, M. (2015). *Environmental Pollution*, 202, 112-119.
- Paper Eleven: Lead exposure risk in a former lead smelting community: assessment of a lead abatement strategy. Harvey, P.J., Taylor, M.P., Kristensen, L.J., Grant-Vest, S., Rouillon, M., Wu, L., & Handley, H.K. (2015). *Environmental Geochemistry and Health*, DOI: 10.1007/s10653-015-9779-8.
- Paper Twelve: The potential for environmental arsenic, cadmium and lead exposures to influence early childhood health and behavioural outcomes in an Australian mining community. Dong, C., Taylor, M.P., & Kristensen, L.J., & Zahran, S. (2015). *Environmental Pollution, 207*, 345-356.

In the interconnected and overall cycle relating to lead emissions, the ensuing effects of lead occur in the form of environmental impacts and human health consequences. The four papers in Chapter Four examine those aspects relating to the end results of lead emissions. By examining the widespread and serious effects of lead emissions, the appropriate changes can be made to the way lead emissions are monitored and assessed in Australia. This will then connect back to regulations on the sources and volumes of lead emissions, with the goal of eliminating sources and reducing volumes of lead released into the atmosphere.

The impacts and consequences of lead emissions presented in Chapter Four include levels of contamination in residential areas, remediation of contamination, limitations to regulations and the effect on children. These papers include only a select few in regards to the impacts and consequences of lead emissions to demonstrate the severity to environmental impacts and human health consequences that occur at the end of the lead emissions cycle.

Paper Nine

Omissions about the sources of contaminant emissions and depositions - A reply to comments on "Taylor, M.P., Davies, P.J., Kristensen, L.J., Csavina, J., 2014. Licenced to pollute not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations

Taylor, M.P., **Kristensen, L.J.**, Davies, P. J., Csavina, J. L., Mackay, A.K., Munksgaard, N.C., & Hudson-Edwards, K.A. (2015). *Aeolian Research*, *17*, 205-213.

This paper is in response to comments made in regard to 'Licenced to pollute but not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations' (Paper Two, page 24). This paper contributes to this thesis by demonstrating the resistance faced in Australia to proper regulation regarding emissions of toxic substances. This hindrance delays effective pollution prevention and remediation to mitigate ongoing lead emissions which lead to severe impacts and consequences including elevated blood lead levels.

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We would like to thank Dr Wilson for increasing the interest in our 2014 Aeolian Research study along with our other articles that he referred to in his letter to the journal. Before we tackle the specifics of his letter, we would like to inform the readers that our response is inclusive of several other authors whose Mount Isa research was referred to in Dr Wilson's letter.

In our Mount Isa manuscripts we have documented our relevant interests, unlike recent research on Mount Isa by others, see Taylor et al. (2015). In this regard, we believe it is relevant to report Dr Wilson's former role as Director of the Queensland Environmental Protection Agency (EPA) from 1999 to 2009 and then Senior Director of the Queensland Department of Environment and Resource Management from 2009 to 2011 (Wilson, 2015). M.P. Taylor telephoned Dr Wilson in early January 2015 to clarify his role in the Queensland Government Mount Isa Lead Management Report (Queensland Environmental Protection Agency, 2008) because we were aware that he was a Queensland Government spokesperson for matters at Mount Isa for some years (Australian Broadcasting Corporation, 2008a,b). Dr Wilson confirmed that although he was not the primary author of the Mount Isa Lead Management Report (no author is listed in the document) (Queensland Environmental Protection Agency, 2008), he was involved with reviewing and editing the report prior to its publication. Dr Wilson also confirmed he had reviewed and edited earlier versions of this report, of which we have obtained copies. These earlier reports are significant because they contain statements and data that reveal the Queensland Government had a well-developed knowledge of the source of the environmental lead problem in Mount Isa. In this reply to his letter, we detail some relevant statements from two draft versions of the Mount Isa Lead Management Report (Queensland Environmental Protection Agency, 2007a,b). In light of the aforementioned information, it is surprising Dr Wilson did not consider his previous role as a Director of the Environment Protection Authority for Queensland as a possible conflict of interest.

Following our review of the comments made by Dr Wilson, we highlight three important facts:

- (1) Dr Wilson does not adduce any new or independently reviewed or verified data to support his primary contention that the environmental lead exposures and its presence in soils and dust in the urban area of Mount Isa is due to "natural lead mineralisation".
- (2) Our studies (21 to date including this article) have been subject to multiple peer reviews, which amounts to >40 independent assessments of our work on environmental metals covering a wide range of sample media from Mount Isa: aerosols, biota, dust, sediments, soils, and water. In addition to these publications, two post-graduate theses support the degradation of environmental quality by mining activities in Mount Isa (Kuypers, 2009; Mackay, 2011), which were subject to 2 and 3 independent peer reviews, respectively.
- (3) All of the data published in Aeolian Research was collected predominantly by government authorities from Queensland or South Australia, with some supplementation from reports from Mount Isa Mines. The data is not 'ours' *per se*, but we mined and compiled disparate sources of data covering atmospheric emissions at Mount Isa and Port Pirie along with environmental health data. While this was not an easy task, the readership can validate our findings of the source of environmental contamination using the data and the links provided, which is included in the extensive supplementary section.

In Dr Wilson's opening paragraph he implies we do not understand how lead is managed in Australia. We draw the reader's attention to the detailed explanation of the legislation, licence arrangements and air quality measures provided in the paper for Australia as a whole and for the state managed jurisdictions of Port Pirie and Mount Isa. Additionally, Dr Wilson is incorrect to imply we mis-referenced the setting up of the National Environment Protection Council as our cited reference of the National Environmental Protection Measure (1998) clearly states the accomplishment of creating air quality standards: "On 26 June 1998, the National Environment Protection Council made Australia's first national ambient air quality standards as part of the National Environment Protection Measure for Ambient Air Quality (the 'Air NEPM)".

Dr Wilson's statement about the measurement of lead: "*The protocol requires one monitoring station for regions with a population of between 25,000 and 333,333 (and more stations for larger cities)*" implies Mount Isa is fortunate to have any such monitoring. Further, a formulated and rigid approach to the reporting of the data in our paper is disingenuous to our underlying message: atmospheric emissions of lead, arsenic and other contaminants are too high in Mount Isa, particularly over the short-term when benchmarked against current Australian or international standards. Irrespective of the requirements of the protocol, the

 $0.5 \,\mu g/m^3$ lead-in-air standard (averaged over a year) has been used and applied almost universally across Australia. It may also be considered outdated when compared to the revised 2008 USA lead-in-air standard of $0.15 \,\mu g/m^3$, averaged over 90 days.

The over-riding message in Dr Wilson's letter is that he promotes significant down-playing of the impact of smelter and mining emissions on the adjoining community. There is not one global example that shows smelting does not contaminate the surrounding environment in all directions. Assessment of the National Pollutant Inventory (2015) for atmospheric emissions shows for all the years that reports are available, 1998/99–2012/13, Mount Isa Mine's atmospheric emissions of contaminants were massive; arsenic: 970,240 kg; cadmium: 150,108 kg; lead: 3,601,200 kg; sulfur dioxide: 3,780,005,000 kg and zinc: 2,943,000 kg. The argument that airflow blows emissions away from the town most of the year and that the mining operations do not influence significantly atmospheric and environmental quality around the city including human health outcomes is absurd (Taylor et al., 2010).

Below, we provide some brief examples of the attempts to downplay the significance of the smelter and the mining operations on the urban environment in Mount Isa, particularly in relation to the Queensland EPA's Mount Isa Lead Management Report (Queensland Environmental Protection Agency, 2008). The following statement in Dr Wilson's letter makes his position clear:

"The sporadic distribution of the homes of the few children with elevated blood lead levels raises doubt that air emissions are the main cause of these anomalies. While emissions are contributing to lead exposure, the air quality limits set by government are intended to restrict the exposure to acceptable levels. This appears to be working in Mount Isa as >95% of the children showed levels <10 μ g/dL."

This statement demonstrates Dr Wilson's arguments are flawed and informed poorly. First, there is an admission that air emissions are a source of exposure (*inter alia*). Any reference to the relationship between lead-in-air and associated childhood blood lead will reveal that the two are inextricably linked. For example, Annest et al.'s (1983) study correlates falling blood lead concentrations with the removal of leaded gasoline as a source of exposure in the USA (see also Schwartz et al., 1985). Kristensen (2015) has shown a very similar relationship between the total petrol combustion emissions of lead and blood lead in Australian children, r = 0.970. There is no physical, chemical or biological reason why it would be any different in Mount Isa.

Second, children with blood lead anomalies are scattered sporadically across the town (Queensland Health, 2008, 2011) indicating the findings cannot be related to geology, which would present a more systematic pattern of exposure according to where bedrock strata is enriched in lead. A comparison of the geological map in the Mount Isa Lead Management Report (Queensland Environmental Protection Agency, 2008) and the pattern of children with elevated blood levels in the most recent blood lead studies (Queensland Health, 2008, 2011), shows the two variables are not related.

Third, reliance by Dr Wilson on the smaller blood lead survey from 2010 (n = 167) (Queensland Health, 2011) is inconsistent with previous comments from Queensland Health that 400 children were required for a representative sample (Queensland Health, 2008). Also, careful review of Fig. 1 in the report shows that 15/167 had a blood lead level $\geq 10 \,\mu g/dL$ (Queensland Health, 2011). However, Queensland Health stated in the media following questions about the 2011 study that there was a formatting issue with the graph because the department had changed graphic designers and that according to Brad McCulloch (Queensland Health): "It's simply a badly drawn graph" (Anonymous, 2011). Therefore, the data should be interpreted as 15/167 or 8.9% with a blood lead level $\ge 9 \,\mu g/dL$. In either case, this level of exposure significantly exceeds childhood blood lead levels in the USA, where the National Health and Nutrition Examination Survey undertake population assessments annually. The last large study for blood lead exposures in Australia took place in 1995 (Donovan, 1996). In 2012, only 0.56% of USA children exceeded 10 µg/dL (Centers for Disease Control and Prevention, 2014).

Fourth, Dr Wilson's comment that "the air quality limits set by government are intended to restrict the exposure to acceptable levels" ignores the fact that only some of the emissions from Mount Isa Mines and the Port Pirie smelter are held to state or federal



standards that are applied elsewhere. For example, maximum 1-h sulfur dioxide concentrations in Mount Isa are permissible up to nearly 5 times (0.9995 ppm) the Queensland and Australian Government value of 0.2 ppm (Table 2, Taylor et al., 2014a).

Dr Wilson's comment that "Concerns about blood lead levels below 10 μ g/dL did not arise until after 2005 and are still subject to debate", is factually and materially incorrect. First, it is not clear why 2005 is chosen as a year of significance, and in any case, there was significant research about the deleterious effects of low level exposures (i.e.<10 μ g/dL) well before this date (e.g. Bellinger and Needleman, 2003; Canfield et al., 2003; Schwartz, 1993). Second, concerns about elevated blood lead levels in Mount Isa children above the National Health and Medical Research Council's goal for Australians of 10 μ g/dL were identified in the early 1990s (Neville, 1994).

The debate about the absence of concern associated with blood lead levels below 10 µg/dL seems to rest only with those who wish to defend and promote the mining industry and is not consistent with current practice or knowledge. There have been multiple major international health bodies that have either lowered the intervention/reference level for blood lead or have made it clear that $10 \,\mu g/dL$ is not a safe level of exposure (see Taylor et al. (2014b) and references therein). More recently, in July 2014, Australia's premier health authority, the NHMRC (National Health and Medical Research Council, 2014), completed its review (July 15th 2014) of blood lead levels and exposure effects below the current goal of 10 µg/dL. The systematic review concluded, like others, there were significant associations arising from exposure below $10 \,\mu g/dL$ to a range of negative outcomes, including adverse behavioral effects (attention, impulsivity and hyperactivity) among children. Queensland Health (Queensland Government, 2014b) responded to the review of blood lead levels (National Health and Medical Research Council, 2014) by recommending on July 17th 2014 the blood lead notification level for Queensland be lowered to $5 \mu g/dL$

Dr Wilson refers to our 2010 Mount Isa Applied Geochemistry study in his letter (Taylor et al., 2010) but not does tackle the substance of the evidence therein, upon which Mackav et al. (2013) builds. In our 2010 article about Mount Isa soil contamination (Taylor et al., 2010), we compile a range of environmental and geological evidence to establish the source using a weight of evidence approach. This included surface and sub-surface soil metal concentrations and inter element relationships; the location, depth and footprint of the principal lead and copper ore bodies, as published by Mount Isa Mines' geologists (Conaghan et al., 2003), air modeling and lead dust deposition data from across the city. The collective environmental and geological data provides compelling evidence of the source of environmental lead contamination. In addition, the individual surface soil metal data results were published in the Supplementary Information, which Dr Wilson could subject to GIS analysis independently. In regard to the GIS analysis, we made it explicitly clear of our method, including our removal of a single outlier from the spatial modeling of soil lead concentrations (Section 3.4, Taylor et al., 2010).

Dr Wilson also criticizes our AUSPLUME air modeling in Taylor et al. (2010) suggesting we predict concentrations above the then standard of 1.5 mg[sic]/m³. The AUSPLUME model does not show concentrations of 1.5 mg[sic]/m³ over the majority of urban area; it shows maximum values of $1 \mu g/m^3$ or less. The output from our AUSPLUME model is broadly consistent with the modeling presented in the Mount Isa Mines Environmental Management Plan (Mount Isa Mines, 2011). Modeling presented in this report shows that mining and smelting emissions (involving a range of related contaminants) clearly impact the city (Fig. 2), even if to a lesser extent than those modeled in Taylor et al. (2010). Perhaps more pertinently, actual air quality data in the report collected by Mount Isa Mines show a maximum lead-in-air level of $12.8 \,\mu g/m^3$ in the urban environment close to the mine. Consequently, it is impossible to discount the material impact of the Mines' emissions on the city, its children and its consequent contribution to blood lead exposures.

In the study by Mackay et al. (2013), a new round of soil sampling was undertaken at co-located sites and was subject to separate and slightly different, but broadly comparable, acid extractable analysis. As per Taylor et al. (2010), the raw data are presented in the Supplementary Information and are available for re-analysis by Dr Wilson. For the Mackay et al. (2013) study, we had retained and re-used some of our original soil profile samples from Taylor et al. (2010) for lead isotopic composition analysis. Dr Wilson questioned why we did not use samples from site 1 of that study. We had previously deduced that the land at this site was disturbed (cf. Section 3.1, Taylor et al., 2010): "the surrounding area did not have the appearance of 'virgin ground'" and was unreliable compared to other sites detailed in the study.

Dr Wilson's letter contains no alternative or new peer reviewed data; indeed, there was no other published raw data on environmental lead in relation to this issue in Mount Isa other than that produced by our team, until late 2013 (University of Queensland, 2015; Zheng et al., 2013). However, there remains ongoing obfuscation and denial of the key contaminant sources by other parties intimately involved with the Mount Isa lead contamination problem. The authors of the Lead Pathways Study (University of Queensland, 2015), a project funded by Mount Isa Mines to examine emissions and impacts in Mount Isa, failed to reveal in their recent study that it was funded by Mount Isa Mines (Zheng et al., 2013). Further, the Zheng et al. (2013) study did not adequately address the source and cause of urban environmental contamination (mine emissions) or even identify the location of the study town, Mount Isa; see Taylor et al. (2015). What is perhaps more concerning is that the Lead Pathways Study that Mount Isa Mines initiated in 2006 (Mount Isa Mines, 2015) is still not complete, with the critical air pathway report still not available some 9 years later. The Lead Pathways Study was intended to provide all of the answers on sources and contributions of contaminants to the urban area in Mount Isa. The delay raises questions about the ability and willingness of the company, its paid experts and the Queensland Government, Dr Wilson's former employer, to publish the vital atmospheric aspect of the Lead Pathways Study program. This is a pattern of behavior that is remarkably consistent amongst those seeking to minimize, defend or deny the source of environmental contamination (Lanphear et al., 2008; Port of Townsville, 2015; Taylor and Schniering, 2010). In lieu of the void of information from the government and Mount Isa Mines, we have filled it with our research, which has been subject to rigorous peer review.

The Queensland Environmental Protection Agency (2008) Lead Management Report to which Dr Wilson refers, and relies upon in his letter, was heavily edited before publication. We have reviewed two draft versions of that report (Queensland Environmental Protection Agency, 2007a,b) and have identified several statements which were removed from the final version (Queensland Environmental Protection Agency, 2008) that revealed the Queensland Government had extensive and concrete understanding of the nature of Mount Isa Mine emissions on the city. Below we list some relevant extracts to emphasize our point that there has been purposeful omissions about the sources of contaminant emissions and depositions. Dr Wilson would have been aware of these omissions given he read and edited the draft and final reports.

"Mass emission rate (kg/y).

Location	Particulates	Pb
270 m Stack	77,000	44,000
HMA Baghouse	73,000	35,000
TP4	23,000	5200
Converters	1,700,000	390,000
Copper Isamelt	4,000,000	9000

Mount Isa Mines Limited Mining Plan 2005–2010 [sic] Results from the February to April 2004 round of stack testing."

(Queensland Environmental Protection Agency, 2007b)

These actual mass emission measurements for lead are markedly greater than the values reported in the National Pollutant Inventory (2015) for the overlapping years of 2003/ 04 (210,000 kg of lead) or 2004/05 (300,000 kg of lead), suggesting that the data in the publicly accessible National Pollutant Inventory downplays the true extent of emissions. Further, the above information was not presented in the final Lead Management Report (Queensland Environmental Protection Agency, 2008), providing further barriers to accessing accurate and reliable information on the impact of the operations. However, these interpretations were 'downgraded' in the final report to:

"The air pathway, particularly through deposition of lead impacted dust, is commonly attributed as a potential pathway, based on experience at similar lead mining and smelter communities. The actual significance of this pathway in Mount Isa is somewhat unclear, given the apparent lack of relationship the incidence of blood lead levels above 10 μ g/dL with distance from the smelter. Nonetheless this pathway warrants further assessment and reduction strategies."

[Queensland Environmental Protection Agency, 2008]

In the final report there are several statements that make it clear the Queensland Government had a well-developed knowledge of the nature, cause and extent of the problem at Mount Isa (Queensland Environmental Protection Agency, 2008):

"The Air Sciences Unit has reviewed the data and reported a relationship between wind direction and lead concentration in air. 2005 data shows higher lead concentrations in air during the periods, during the summer months for example, when there are higher proportions of winds blowing in the direction from the Xstrata operations to the city. A similar pattern was observed for 2006 where air concentrations of lead in the city are less than for 2005, as there were less frequent winds from the west." (p. 5)

"Xstrata dust deposition data selected sites average 2002-2007.

Site	Particulate matter (g/m²/28day)	Pb (mg/m²/28day)	Particulate matter (mg/m²/28day)	Pb (µg/m²/day)	Pb (mg/kg)*
Kruttschnitt Oval	2.58	24.34	92.1	870	9400
Sewage Treatment Plant	1.66	3.61	59.3	130	2200
Healy	1.88	4.24	67.1	150	2300
MIM Exploration Shed	1.42	6.75	50.7	240	4800
Racecourse	3.6	6.77	128.6	240	1900
RSL	1.09	20.9	38.9	750	19,000

* Calculated

Lead in dust deposition decreases with distance from the MIM [Mount Isa Mines] facility. Particulate matter does not show the same decrease. It is noted that the Racecourse dust deposition gauge may have been affected by major redevelopment works occurring at the course."

(Queensland Environmental Protection Agency, 2007b)

The final published Lead Management Report (Queensland Environmental Protection Agency, 2008) only showed the lead data in the fourth column above (daily deposition rates for lead, $\mu g/m^2/day$), which is presented in text and graphic form. These data show that deposition levels are elevated across much of the city, especially when benchmarked against the existing lead dust deposition trigger value of $100 \,\mu g/m^2/day$ as detailed in the Mine's environmental authority (Taylor et al., 2014a).

In the second draft Lead Management Report (dated 12/12/ 2007) the role of air emissions on blood were evaluated (Queensland Environmental Protection Agency, 2007a):

"The air pathway, particularly through deposition of lead impacted dust, would appear to be likely to be a significant contributor to blood lead in children." (p. 37).

The report goes on to state:

"The lead dust deposition data for Mount Isa indicates the need for reduced lead emissions from the Xstrata smelters." (p. 39).

[Queensland Environmental Protection Agency, 2007a]

Human activity has caused some contamination in various parts of the city through use of mineralised rock from the mine as fill and use of contaminated sand from the river in sand pits. Other sources of lead contamination have included inappropriate disposal of car batteries and the previous use of paint containing lead-based pigments. (p. 22)

"It is notable that contaminated sites in the middle to east of the city were most often associated with occupational transport of lead, through vehicles or machinery brought home from the mine. This material was removed and disposed to the mine." (p. 24)

It is clear that at least some of the contamination in the urban environment cannot be explained as having its origins from "*natural lead mineralisation*" and any such argument is an over-simplification, at best.

Our image of pollution blowing across town on February 22nd 2012 (Fig. 8, Taylor et al., 2014a) shows emissions are clearly over the city and residential areas, which are also to the north, where the plume appears to be dispersing. The assumption in Dr



Fig. 2. Current Mount Isa Mine operations plus background annual lead concentrations (Fig. C.77 in Mount Isa Mines (2011) Environmental Management Plan, not publicly available).

Wilson's letter is that the plume is contaminant free and that no contaminants ever reach the ground. All of the data and atmospheric modeling demonstrate that this is a fanciful notion in regard to smelter emissions and depositions here and elsewhere (Csavina et al., 2012, 2011, 2014; Sorooshian et al., 2012; Soto-Jiménez and Flegal, 2011). The fact that atmospheric concentrations of contaminants are not consistent over the year demonstrates the city receives substantive emissions from the Mount Isa Mine operations. There are no natural sources for concentrations of arsenic, cadmium, lead and sulfur dioxide found at the levels reported in Taylor et al. (2014a).

It is disappointing to say the least that Dr Wilson simply sidesteps the clear issue identified in our article of the Queensland Government's seemingly deliberate mis-representation of the air quality in Mount Isa via their on-line monitoring network (Section 8.1, Taylor et al., 2014a). The Queensland Government's reporting of air quality via its online system (Department of Environment and Heritage Protection, 2014) continues to be incorrect and misleading because the index does not use the maximum allowable annual lead-in-air $(0.5 \ \mu g/m^3)$ and arsenic-in-air $(6 \ ng/m^3)$ concentration values as it purports. Instead air quality is benchmarked against nominal 24-h concentration values (lead – $2 \ \mu g/m^3$ and arsenic – $300 \ ng/m^3$), which are not part of any statutory system in Queensland or the Australia Federal Government. The consequences of using higher values to calculate air quality indices over Mount Isa are patently obvious – it lowers the apparent pollution and obfuscates public understanding of the extent of emissions. In regard to the issue of short-term emission spikes, we draw Dr Wilson's attention the recommendations prepared for the National Environment Protection Council by Streeton (2000) in his review of the health data and its relationship to the Australian lead-in-air standard:

"ambient lead levels should be held in the range of $0.3-0.5 \ \mu g/m^3$ on a mean moving monthly (or as an annual) standard, but NOT to exceed $0.5 \ \mu g/m^3$ at any time". There is a significant body of historical data supporting the argument that emissions from the operations have long been significant in terms of environmental quality and human health. The company has also known the source and effect of lead poisoning since the start of operations (Watson and Duhig, 1933). Occupational lead poisoning did not start until smelting was initiated in 1931 and lead dust emissions close to the stack were up to 37 mgs/5 m³ or ~7400 μ g/m³ (Watson and Duhig, 1933).

In regard to the emissions from the smelting operations, the Chief Medical Officer for Mount Isa Mines reported (von der Borch, 1934):

"It is unfortunately true that no provision was made for or thought given to, the control of lead poisoning when the plant was designed and built. The fault here lies in the non-cooperation of the engineering and industrial media aspects, a matter which urgently requires world-wide recognition and adoption."

Dr von der Borch goes on to state:

"A peculiar set of circumstances of an industrial and medical nature alone prevented the full realization of the ideals long held by the management, who were completely cognizant of the problem, and the urgency and completeness of the measures necessary for its solution."

It would be preposterous to suggest that none of the emissions during this time, which were at a low height due to the absence of a large smelter stack, did not impact the city. The effect of the winds blowing contaminants from the mine site towards the city was noted by Duhig (1949) in his investigation and report from his visit to Mount Isa in January 1949:

"Railway Quarters: ...They are situated under a huge slag heap, and in the course of time, the quarters will be either submerged by the slag or completely surrounded by it. The quarters are so situated that fumed [sic] containing sulphur are blown in when the wind is in the east or south-east as was the case during my stay in Mount Isa." Dr Duhig collected samples for analysis by the Government Analyst, one of which was from dust adjacent to a small dam near the railway quarters that contained 15.6% total lead, and 4.6% soluble lead. Thus it is clear dusts from the mining and smelting operations were physically mobile, were being actively transported, and lead concentrations were elevated and soluble.

The management of dusts and emissions is not an issue belonging to the early days of mining (Fig. 3). The improper maintenance of the lead smelter gas cooling tower had two main consequences (Queensland Government, 2014a): first, the death of David Anthony Kelly in 1991, and second, more relevant to the issue of atmospheric contamination discussed here, was the reduced ability of the stack to disperse smelter gases due to the accretion and irregular clean out of lead dust accumulated on the walls of the tower. The Mining Warden, Mr. F.W. Windridge, concluded in 1992 (Queensland Government, 2014a):

"It appears that records about these clean-outs are incomplete, but we are reasonably satisfied such clean-outs seemed to decrease over the past few years. Between clean-outs there was a constant build up of accretion possibly from 2.5 to 10 tonnes per day, and from time to time, there were falls of accretion, ranging from minor to major."

Poor maintenance and accretion inside the boiler would have reduced the smelter gas efflux speed, volume and efficiency, causing the plume to be less well dispersed in the atmosphere, increasing the concentration and deposition of atmospheric contaminants close to the stack (Peter Anderson, former lead stack installation and maintenance engineer, pers. comm.).

Dr Wilson further criticizes our Aeolian Research paper by implying that we interpret wrongly the way the data is compiled from South Australia's blood lead sampling of Port Pirie children. He contends "inclusion of multiple results would exaggerate the proportion of affected children in the cohort" but misses our point



Fig. 3. View looking - west across the city towards the Mount Isa Mining lease. Dusts emissions on the Mount Isa Mine site are clearly evident.

that exclusion of the first blood test occludes the real, higher percentage of children above the Australian goal of 10 µg/dL in any one year. Further, the approach at Port Pirie is not reflected in practices elsewhere in Australia. At Broken Hill, New South Wales (Boreland et al., 2008) and Boolaroo, NSW (Dalton and Bates, 2005), analysis of blood samples for determining population exposures is based on the first or highest test. At Port Pirie, the approach is to use the last test on a child in any year. Therefore, if a child presents with a blood lead level of 20 μ g/dL in March of any one year, SA Health would likely intervene and provide advice and awareness training for parents in order to lower the exposure. This is normally followed by repeated blood tests, the most likely outcome of which would be lower blood lead values. The data we have complied shows the effect of using the last value measured on a child – it reduces the apparent percentage of children who have in any one year presented with a blood lead level >10 µg/dLby 5.8–13.6%. In addition, the preference for SA Health to rely on the mother's blood lead as a surrogate in the absence of measures on children <9 months of age is not appropriate because exposures rise markedly after the first 35 days of a child's life (Simon et al., 2007). Again, the effect of using a mother's blood lead value as a surrogate for a child would be to lower the apparent average, which is why we prefer to use only values actually collected from children. These are real measures on children, free from surrogate/substitute values.

In terms of health impacts from the massive sulfur dioxide emissions at Mount Isa from 1998 to present, which amount to an estimated 3,780,005,000 kg (National Pollutant Inventory, 2015) Dr Wilson retorts simply: "The available hospital admission data indicated that sulfur dioxide was not causing significant health effects." His point is totally and wholly unsubstantiated and we direct the readers to our article and the related references. The unsubstantiated statement looks like a further denial of the obvious, which is that the massive sulfur dioxide emissions have affected respiratory health in a material way.

Donoghue and Thomas's (1999) study of peak sulfur dioxide and hospital presentations for asthma in Mount Isa argued they were not related. The lead author of the article was the medical officer at the Mount Isa Mines Medical Centre at the time of publication. Donoghue and Thomas's (1999) study conclusions contrast those complied recently by Queensland Health (2009), which showed Mount Isa hospitalization rates (2002/02 to 2005/ 06) were higher (80%) compared to the rest of Queensland State. Asthma mortality for the same time period was also significantly higher than the rest of Queensland (322%).

Finally, we make the following minor points on our published manuscript (Taylor et al., 2014a). The *y*-axis text in Fig. 10 appears to have been corrupted when inserted into the final journal article and should be $(\mu g/m^3)$ not $(!g/m^3)$. We concur with Dr Wilson's comment that the *y*-axis text for Figs. 3 and 4 could have been clearer. The text should have been the same as for Figs. 5–7 but in any case the figure captions describe nature of the data, which are the monthly maximum 24-h average values for lead- and arsenic-in-air.

Dr Wilson criticizes the use of the <180 μ m soil grain size in our previous Mount Isa study (Taylor et al., 2010) because he claims it results in "Further exaggeration of the potential risk resulted from comparing lead concentrations in the <180 μ m fraction of samples to a Health Investigation Level (HIL) based on <2 mm samples and from using the residential HIL when one quarter of the properties were commercial or industrial."

In regards to the soil particle size to be used to assess metal concentrations against the Australian Health Investigation Level, we note the relevant NEPM (Australian Government, 1999) was amended in 2013, and includes the following information about particle size:

"4.2.4.3. Sieving

Unless impracticable or not recommended for a specific method, the sample portion for analysis should be of a size to pass a 2.0 mm aperture sieve."

Our 2010 soil metal study (Taylor et al., 2010) used the finer fractions for two reasons: first, smelter emissions are in the fine to ultra-fine size fraction and are unlikely to be adequately represented in coarser particle sample analysis; and second, finer fractions are more likely to adhere to hands of young children and be subsequently ingested.

With respect to the location of our samples, it is incorrect to state that a quarter of our samples were from commercial or industrial sites. The locations can be seen in Fig. 2 in Taylor et al. (2010).

Dr Wilson misinterprets our comments on the real time air quality system in Mount Isa; we think this is an excellent way to provide data to the public. Our criticism relates to the use of the wrong guidelines for benchmarking air quality and its subsequent interpretation, as noted above.

Summary and conclusions

The evidence outlined here, as well as in previous studies (Mackay et al., 2013; Munksgaard et al., 2010; Taylor et al., 2014a, 2010), reveal the extent of contamination and the health consequences to the residents of Mount Isa from the mining and smelting operations. Dr Wilson's concluding paragraph reads like an advert for the lead industry in Mount Isa and does not seem fitting for a former EPA director in charge of regulating that same company. Further, his comment that if the Mount Isa smelter closed, the lead smelted elsewhere would "cause far worse problems" demonstrates that he is aware yet in denial of the fact that the mining operations at Mount Isa are significant contributing factors to community environmental health. Emissions to the environment are a matter of public concern particularly when they contain toxic pollutants. Environmental Protection Authorities are publicly funded organisations that are charged with regulating and protecting the public and the environment from adverse impacts. It would be a reasonable societal expectation of EPA officers to give primacy to human health and the environment over the needs of industry who seek a licence to pollute in order to remain profitable (Australian Broadcasting Corporation, 2015).

Given the weight of environmental evidence relating to emissions from over 90 years of Mount Isa Mines operation, it is inconceivable, if not rather fanciful, to imagine these have not resulted in elevated soil and dust lead concentrations in and around the city and have had limited effect on the community (Munksgaard et al., 2010).

Consequently, we take the opposite view to Dr Wilson's argument that "natural mineralisation remains a plausible explanation for anomalously high blood lead levels in Mount Isa". Instead, we rely on the preponderance of evidence that supports an evidence-based and logical proposition that emissions and activities associated with the mining and smelting operations are the dominant cause of lead exposure in children in Mount Isa. To suggest this is not the case is to infer that the operations have had minimal impact on the environment and the community, an argument that is not supported by the evidence or common sense.

Competing interests

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Paper Ten

Evaluating the efficacy of playground washing to reduce environmental metal exposures

Taylor, M.P., Zahran, S., **Kristensen, L.J.**, & Rouillon, M. (2015). *Environmental Pollution*, 202, 112-119.

Supplementary Information in Appendix I

This study was conducted as a follow up to 'Environmental lead exposure risks associated with children's outdoor playgrounds' (Paper Eight, page 100) that measured and revealed the depositions from the lead smelter at Port Pirie was increasing children's exposure through playground use. This study demonstrates that despite efforts to reduce lead exposure from significant lead emissions by washing the playgrounds, the implemented washing regime was ineffective at mitigating the impacts of significant volume of lead being released. The study contributes to this thesis by highlighting the severe impacts from large volumes of lead emissions which cannot be eliminated through basic cleaning and that impacts and consequences are ongoing in Port Pirie.

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Evaluating the efficacy of playground washing to reduce environmental metal exposures



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ABSTRACT

Washing and wet mopping is often advocated as a remedial treatment to limit exposure to lead dust. Here, surface and pre- and post-play wipes were measured to ascertain dust metal exposures (arsenic, cadmium, copper, lead and zinc) following play routines at four playgrounds in the smelter city of Port Pirie, South Australia, which are washed regularly. Although post-play hand wipe metals were 55.9% (95% CI: -0.78, -0.34) lower on wash days, loadings increased ~5.1% (95% CI: 1.2, 11.7) per hour after washing. Despite washing, post-play hand lead exceeded a conservative value of 800 µg/m² within 24 h or sooner, with loadings increasing in proximity to the smelter. Post-play lead loadings were always >1000 µg/m² at the playground closest to smelter. Playground washing results in short-lived exposure reduction and effective treatment requires elimination of smelter emissions.

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1. Introduction

The problem of childhood lead exposure remains a persistent problem in Australia's primary smelting and mining cities of Broken Hill, Mount Isa and Port Pirie, with the latest figures showing that 21%, 4.8% and 22.7%, respectively, of children under 5 years of age having a blood lead level above 10 μ g/dL, the current (under review) Australian goal (Taylor et al., 2014b). However, the extent of exposures amongst the wider Australian population is unknown because of a lack of available population data. Nevertheless, estimates derived from USA exposure data have indicated that ~100,000 children <5 years of age may have exposures above 5 μ g/dL (Taylor et al., 2012, 2014c), which corresponds to the most recent study on Australian urban children that reported 7.5% (8/107) of the cohort had a blood lead >10 μ g/dL (Gulson et al., 2008).

Where exposures are well documented and the sources known, interventions, screening and advice programs are usually provided. One such case is in the city of Port Pirie in South Australia, where lead smelting has been ongoing since 1889. The effects of the smelter operations has resulted in widespread contamination of the natural and urban environment, which has been associated

* Corresponding author. E-mail address: mark.taylor@mq.edu.au (M.P. Taylor). with persistent, but declining blood lead exposures in children over the last two decades (Maynard et al., 2006; Simon et al., 2007; Taylor, 2012; Taylor et al., 2013). Strategic interventions, lead awareness programs in the city of Port Pirie (Maynard et al., 2006; Thumbs Up for Low Levels 2015), and emission reduction efforts from the city's smelter site (Environment Protection Authority South Australia (EPASA) 2009) have contributed to the fall in blood lead levels. However, the most recent annual data show that exposures have stabilised or even by some measures increased (Taylor et al., 2014c). For example, the geometric blood lead mean for all children under 5 years of age increased from 4.5 μ g/dL in 2012 to 5.0 μ g/dL in 2013. The primary source of the exposures is caused by the ongoing and contemporaneous lead-in-air emissions from the smelter (Simon et al., 2007; Taylor, 2012; Taylor et al., 2014a), which result in elevated concentrations of contaminated metal rich dust being deposited on surfaces (van Alphen, 1999; Taylor et al., 2013, 2014a; Csavina et al., 2014). In addition, there is a substantial reservoir of lead-contaminated soil from accumulated emissions in Port Pirie that has the potential for re-suspension (SA Health, 2013).

The spatial extent of metal- and metalloid-rich dust (hereafter referred to as metals), including lead, was detailed in a study of playgrounds across the city of Port Pirie in 2011 (Taylor et al., 2013). This study showed that atmospheric emissions from the





ENVIRONMENTAL POLLUTION smelter were related directly to surface dust and hand metal exposures following the use of playground equipment (Taylor et al., 2013). Following this study, the Port Pirie Council and the smelter company, Nyrstar Port Pirie Limited Pty Ltd, agreed to a joint program of playground washing. Before these results were published, the playground washing intervention program was limited only to the Foreshore Playground (also known as Flinders View), which was washed twice a week on Mondav and Fridav mornings, with no other playgrounds washed regularly (D. Farguhar, Port Pirie Council, personal communication, 7th July 2011). Given the elevated metal loadings identified across the studied playgrounds (Taylor et al., 2013), we released the environmental data to SA Health and the Port Pirie Council ahead of publication to assist with their management of the problem. The authorities responded on August 1st, 2012 by increasing the frequency of playground cleaning to 22 washes per week across a range of different playgrounds in the city. The program was revised to include 9 playgrounds and 1 kindergarten (Supplementary Fig. S1). Following the online publication of the research on May 1st 2013 (Taylor et al., 2013), the Council and Nyrstar issued a further revision to the cleaning program on May 7th 2013. The new program increased the total number of playground wash events across the city to 49 per week covering 9 playgrounds (a total of 31 washes) and 9 child care centres, primary schools and kindergartens (a total of 18 washes) (Supplementary Fig. S2). Although the specifics of the washing techniques used on the play equipment are not provided in the cleaning schedules (Supplementary Figs. S1, S2), washing was observed at the Sports Park playground and involved scrubbing and hosing down of equipment. However, the effectiveness of the intervention strategy has not been evaluated but it warrants assessment given that other similarly impacted locations such as Broken Hill are considering equivalent regimes in response metalrich dust contamination problems (Taylor et al., 2014b).

Intervention programs in lead contaminated environments typically involve advice to wet wipe and mop in order to reduce the hazard associated with the build-up of lead dusts (and other metals) in domestic environments (e.g. Living Safely with Lead, 2014; New South Wales Government 2014; Thumbs Up for Low Levels 2015). However, a Cochrane review of household interventions for preventing domestic lead exposure in children, including the removal of dust, demonstrated such approaches were not effective in reducing blood lead levels in children (Yeoh et al., 2012).

Lead in dust on surfaces in home environments at levels much lower than the typical intervention levels pose a measurable risk factor for elevated blood lead levels in children (Dixon et al., 2009). Data modelling predicted floor dust lead at concentrations as low as $12 \mu g/ft^2 (129 \mu g/m^2)$ would result in 4.6% of children living in USA homes constructed before 1978 (the era when the use of lead in paint was prevalent) to have a blood lead $\geq 10 \mu g/dL$, with 27% to have a blood lead $\geq 5 \mu g/dL$ (geometric mean 3.9 $\mu g/dL$) (Dixon et al., 2009). Given that the US Centers for Disease Control and Prevention have moved to using $\geq 5 \mu g/dL$ as the reference level for children's blood lead and Australia appears to be moving to the same value for investigating environmental sources of exposure (NHMRC, 2014a,b), it is imperative that effective and evidencebased abatement and risk reduction strategies are promulgated (Taylor et al., 2014c).

Therefore, the purpose of this study was to evaluate the efficacy of the Port Pirie playground cleaning regime to reduce environmental metal exposure risks to children. Such information is useful for other similarly impacted locations where substantial regulatory effort and cost is invested in reducing potential exposures from contemporary metal-rich dust depositions.

2. Methods and approach

2.1. Field sampling

Field sampling was carried out in accordance with established methods (Taylor et al., 2013). The four Port Pirie playgrounds sampled in the previous study, Foreshore playground, Memorial Park playground, Sports Park playground and Woodward Park playground were sampled again each morning for a 5-day period between 20th July and 24th July 2013 (Fig. 1). The distances of the playgrounds from the smelter are: Foreshore Playground (1.0 km); Memorial Park Playground (1.2 km); Sports Park Playground (2.4 km); Woodward Park Playground (3.0 km) (Fig. 1). Images of each of the playgrounds showing the playground equipment and surrounds are provided in Fig. S2a–d of the Supplementary in Taylor et al. (2013).

Given that we wanted to evaluate the efficacy of washing as a remedial treatment, playgrounds that were subject to a morning wash according to the published schedule (Supplementary Fig. S2), were re-sampled in the afternoon approximately 6 h after the initial morning sample. These data were also used to investigate the dimension of washing for reducing playground surface contamination (Table 1).

Two playground surface dust wipe samples were also collected following the methods described in ASTM E1728-10 (ASTM, 2010) at each playground at the time of hand wipe sampling (n = 58). The playground surface wipe sampling approach detailed in ASTM (2010) is, for all intents and purposes, identical to that detailed in Australia's guide to lead paint management, AS 4361.2-1998 (Standards Australia, 1998). The areas wiped were measured to enable surface wipe metal values to be transformed to $\mu g/m^2$. As in the previous study, sites were selected to be close to, but away from the playgrounds, and unlikely to be interfered with during normal play routines or affected by the washing routines undertaken by Council or Nyrstar. The same researcher (L. Kristensen, as per Taylor et al., 2013) undertook the 20 min of child simulated play on the facilities from which we were able to obtain 29 paired samples of pre- and post-play hand wipes over the five-day study period. Hand contact was limited to the equipment and deliberately excluded contact with the ground surface around the playgrounds. The anterior (palmar) hand surface area of the play participant was calculated using the DuBois and DuBois (1916) method and metal concentrations transformed to $\mu g/m^2$ for pre- and post-play wipes.

2.2. Laboratory analyses

All wipe samples were tested for arsenic, cadmium, copper, lead and zinc at the National Measurement Institute, Sydney. Samples were digested in sterile polypropylene tubes using a mixture of 3 mL concentrated nitric acid and 1 mL hydrochloric acid (analytical reagent grade) on a digestion block at 110 °C for 90 min. A further 10 mL of Milli-Q was added to the samples prior to an additional 30 min digestion at 110 °C (Evans, 2013). Element concentrations were determined using a Varian Vista Pro ICP-OES and PerkinElmer Elan DRC II ICP-MS. Reagent blanks, dust wipe blanks, matrix spiking and reference materials AGAL-10 (Hawkesbury River Sediment) and AGAL-12 (Biosoil) were analysed concurrently for quality assurance. Reagent blanks were all below laboratory limit of reporting (LOR) as were the wipe blanks for arsenic (0.2 μ g/wipe) and cadmium (0.05 μ g/wipe). The wipe blanks returned an average copper concentration of 0.67 µg/wipe, lead concentration of 0.03 µg/wipe and zinc concentration of 20.85 µg/wipe. Field blanks collected at each playground were below LOR for arsenic and cadmium and with average values of 0.84 µg/wipe for copper, 25.44 μ g/wipe for zinc and 0.11 μ g/wipe for lead (0.07 μ g/wipe for Memorial Park, Sports Park and Woodward Park and 0.23 µg/wipe



Fig. 1. Site location map - the four playgrounds sampled and the Nyrstar Port Pirie Smelter, in Port Pirie, South Australia.

for Foreshore Playground). Recovery rates for matrix spikes and certified materials were 96–102% and 92–98% for arsenic, 97–100% and 81–95% for cadmium, 96–101% and 88–89% for copper, 95–101% and 94–98% for lead and 95–103% and 87–88% for zinc.

3. Results and discussion

3.1. Playground surface dust wipe results

The surface dust metal data derived from this study shows that

in nearly all cases the metals were markedly lower than those reported previously (Taylor et al., 2013). These differences are highlighted by examining the results from the two playgrounds closest to the smelter, Foreshore and Memorial Park. At Foreshore playground, mean playground surface metal loadings were reported previously as follows (values to 3 significant figures): arsenic – 112, cadmium – 23.6 and lead – $5060 \ \mu g/m^2$ (Taylor et al., 2013). These previous values compare to the lower mean values reported in the current study (Supplementary Table S3) as follows: arsenic – 30.8, cadmium – 4.30 and lead – $850 \ \mu g/m^2$. At Memorial Park, the mean

Table 1

	Saturday 20th July 2013	Sunday 21st July 2013	Monday 22nd July 2013	Tuesday 23rd July 2013	Wednesday 24th July 2013
Rainfall ^a	9.2 mm	5.2 mm	$\begin{array}{c} 1.2 \text{ mm} \\ \checkmark (1130) (1630) \\ \checkmark (1030) (1600) \\ \checkmark (0905) (1500) \\ \checkmark (1000) (1500) \end{array}$	0.8 mm	0.1 mm
Foreshore playground	✓ (1030)	✓ (1030) (1530		✓ (1040) (1620)	✓ (1110)
Memorial Park playground	✓ (1000)	✓ (1000) (1500		✓ (1010) (1545)	✓ (1035)
Sports Park playground	(0900)	(0900)		(0900)	✓ (0930)
Woodward Park playground	(0930)	(0930)		✓ (0930) (1500)	✓ (1000)

^a Total rainfall over previous 24 h measured at 9 am. Rainfall data is from Bureau of Meteorology, Port Pirie Aerodrome station, which is 7 km south of the city (Bureau of Meteorology (2014a)).

playground surface metal values reported previously were: arsenic – 91.8, cadmium – 25.0; lead – 6960 μ g/m² (Taylor et al. (2013). The playground surface mean metal values recorded in this study were: arsenic – 18.8, cadmium – 3.50; lead – 2380 μ g/m².

The differences in playground surface metals between the two studies may be attributable to rainfall that occurred during the July 2013 sampling campaign. No rain was recorded shortly before or during the sampling that took place in 2011 (Taylor et al., 2013). Average wind direction in Port Pirie during the months of June and July were from a north to north-east direction (Bureau of Meteorology (BoM) 2014b), indicating no variance in wind direction between the 2011 and 2013 sampling periods. In terms of atmospheric lead emissions, the Environment Protection Authority South Australia data shows that from ~ mid 2013, atmospheric emissions of lead were actually rising (Taylor and Isley, 2014; EPASA, 2014). Therefore, in the absence of rainfall, these emissions should have been associated with dust deposition levels on playground surfaces that were at least equivalent if not higher than that measured in the 2011 data (Taylor et al., 2013). Notwithstanding the differences between the two studies, this study shows clearly that mean playground surface dust metal loadings were in most cases, considerably in excess of international standards (annual average values, TA Luft, 2002) for arsenic $-4 \mu g/m^2/day$; cadmium $- 2 \mu g/m^2/day$ and lead $- 100 \mu g/m^2/day$. Although surface dust metal deposition is not regulated within the existing licence arrangements at Port Pirie, the TA Luft (2002) dust deposition standards are used in the Mount Isa Mines. Oueensland Environmental Authority to regulate mining and smelting operations (Taylor et al., 2014). Consequently, these values are considered reasonable acceptable benchmarks to compare the results reported herein.

3.2. Hand wipe results

Overall, the values derived from the hand wipe assessments in this study (Supplementary Table S4) reflect the playground surface dust metals in that they are lower than those reported previously from the 2011 study (Taylor et al., 2013). Notable exceptions to this are cadmium post-play hand wipe loadings, which were elevated at Woodward Park playground compared to 2011 wipe data: Woodward Park 2013 cadmium mean 21.9 \pm 15.9 μ g/m² versus 2011 cadmium mean: $14.9 \pm 16.1 \ \mu g/m^2$. Nevertheless, it is notable that the overall mean dust metal loadings for arsenic, cadmium and lead are lower than what they were in 2011. These lower dust metal loadings are likely to have been influenced by rainfall that occurred during the sample period. The lower values at Foreshore may also have been influenced by the addition of a shade cloth over the playground area following publication of the 2011 data. Notwithstanding these lower levels, the data show the mean values on hands following play at all sites remain considerably elevated with respect to international values (TA Luft, 2002). As shown in Table 2 below, average post-play hand wipes exceed the 400 μ g/m² of lead

Table 2

Paired t-tests comparing the mean metal loading of pre-versus post-play hand wipes at all playground.

Metal	Pre-play (µg/m ²)	Post-play (µg/m ²)	Difference (µg/m ²)	t	р
Arsenic	3.21 (0.66)	32.40 (5.17)	29.20	5.68	<0.0001
Cadmium	4.73 (1.20)	14.97 (1.97)	10.24	4.69	<0.0001
Copper	91.50 (5.91)	191.90 (20.77)	100.40	4.73	<0.0001
Lead	279.01 (58.87)	2088.46 (333.75)	1809.44	5.90	<0.0001
Zinc	2782.13 (168.14)	6158.81 (575.96)	3376.13	5.72	<0.0001

Note: Standard errors in parentheses.

on surfaces as applied by the Government of Western Australia (2011) as part of the lead-spill clean up in the town of Esperance (Gulson et al., 2009). These post-play levels demonstrate the persistence of environmental contamination despite the fact that all of the playgrounds were washed on at least two occasions during the sampling campaign (Supplementary Figure S2).

3.3. Playground surface and hand wipe dust metal modelling results and analysis

To understand the efficacy of playground cleaning as a suitable remedy for reducing exposure risks, particularly with respect to time-incremental accumulation of metal-rich dust, we applied a suite of statistical analyses and modelling techniques to the data.

Table 2 details paired t-tests comparing the mean metal loading of pre-versus post-play hand wipes across all sampled playgrounds. This shows that post-play hand wipes had significantly higher levels of arsenic (3.21 µg/m² vs 32.4 µg/m²), cadmium (4.73 µg/m² vs 15.0 µg/m²), copper (91.5 µg/m² vs 192 µg/m²), lead (279 µg/m² vs 2090 µg/m²), and zinc (2780 µg/m² vs 6160 µg/m²), with all values at *p* < 0.0001. With respect to lead and arsenic, even with the increased playground washing regime, post-play levels were ~7 and 10 times higher than pre-play levels, respectively.

Fig. 2 depicts the mean pre- versus post-play hand wipe lead loadings ($\mu g/m^2$) across each playground. The height of each bar corresponds to the average lead loading over sample days at each playground, with the range markers depicting the 95% confidence intervals around the mean values. With the exception of the Woodward playground, hand wipe lead loadings increased significantly (where p < 0.01) after the timed 20 min play events. For example, at the Foreshore playground, average post-play hand wipe lead loadings are 4410 μ g/m² (95% CI: 3633, 5186), compared to the pre-play average of 568 μ g/m² (95% CI: 173, 962), representing more than a seven-fold increase in lead exposure. It is worth noting that Foreshore playground was the last playground sampled each day and that the pre-play wipes contain measurable lead loadings, despite hands having being wiped after play at the previous site. This indicates that the dust metals are pervasive and are being transferred readily between playgrounds to hands from the interior of vehicles, clothing and other surfaces despite efforts to limit any such contact during the sampling process.

As indicated in earlier studies (van Alphen, 1999; Maynard et al., 2006; Simon et al., 2007; Taylor et al., 2013), the data confirm the notion that residing in Port Pirie is akin to "*living in a sea of lead*" (Simon et al., 2007), *inter alia* other metal contaminants, from which there is virtually no escape. Indeed, washing playgrounds only deals with a very limited geographical area of exposure and the data show quite clearly that contamination not only blankets the city daily, it is pervasive and persistent (Taylor, 2011; Taylor et al., 2014a,c). In short the contamination does not 'go away', and even for vigilant persons, let alone young children, or their mothers vested with the responsibility of stopping innate handmouth behaviours. Thus, it is clear exposure cannot be avoided.

The effects of the new and extended 2013 Port Pirie playground washing regime (Supplementary Figure S2) was modelled (Table 3). In modelling the effect of washing, we also treated Woodward and Sport Park playgrounds as having been washed as a result of the prevailing 24-h rainfall of 9.2 mm (Table 1). Specifically, the purpose of the modelling was to evaluate the City's remedial response to metal exposure risks in public spaces frequented by children.

Evaluation of environmental health remedial treatments designed to protect children should be a requirement before they are promulgated as a solution in mining and smelting towns. Indeed, education remedies are often promoted as being an



Fig. 2. Pre- versus post-play hand wipe lead loadings (µg/m²) by playground.

Table 3

Regression coefficients estimating the effect of playground wash on metal exposure risk ($\mu g/m^2$) from timed play.

	Post-play (<i>ln</i>)
Playground wash	-0.559*** (0.114)
Pre-play wipes (ln)	0.008 (0.012)
Surface wipes (ln)	0.015 (0.010)
Reference = Arsenic	
Cadmium	-0.632^{***} (0.177)
Copper	1.901*** (0.191)
Lead	3.932*** (0.199)
Zinc	5.349*** (0.217)
Reference = Woodward Park	
Foreshore	1.446*** (0.152)
Memorial Park	0.579*** (0.151)
Sport Park	0.442*** (0.178)
Weekend	$-0.256^{**}(0.113)$
Constant	2.877*** (0.170)
Observations	145
F-Test	187.61
R ²	0.934

Note: Standard errors in parentheses $^{***}p < 0.01$, $^{**}p < 0.05$, $^*p < 0.1$. *ln* –data was normalised using natural log transformation (*ln*).

acceptable response (Mount Isa – Living with Lead Alliance (2014), NSW Government (2014), Port Pirie – Thumbs Up for Low Levels (2015), Trail, Canada – Trail Area Health and Environment Program (2014)) as a way of mitigating unsafe exposures. However, their efficacy is unproven (Yeoh et al., 2012). Physical intervention measures in New Orleans child care centres involving covering contaminated soil with geotex fabric and overlaying it with clean soil have been shown to be affordable and highly effective (Mielke et al., 2011).

To assess whether washing a playground reduces the metal risk exposure, post-play hand wipe metal loadings were analysed (y) using a semi-log least squares regression procedure. Letting y_{ij} to denote the post-play hand wipe metal loadings of subject *i* in playground *j*, our regression model is:

$$\ln(y_{ij}) = \alpha + \beta_1 W_j + \beta_2 \ln(P_{ij}) + \beta_3 \ln(S_j) + \gamma_1 M_{ij} + \gamma_2 G_j + \gamma_3 D_{ij} + \varepsilon_{ij}$$
(1)

where, α is our model constant (representing the natural log of the average post-play hand wipe metal loadings in our reference grouping), W_j is our wash indicator = 1 if the experiment occurred on a day where playground *j* underwent a wash, P_{ij} is the pre-play hand wipe metal loadings of subject *i* in the playground *j*, S_j is the mean metal dust loadings on surfaces of playground *j*, M_{ij} represents a set of dummy variables corresponding to metal type (with arsenic as our reference metal), G_j is a set of dummy variables corresponding to each playground (with Woodward Park as our reference playground), D_{ij} is an indicator variable = 1 if the playground experiment occurred on a weekend day, and ε_{ij} is the random disturbance term of the model.

The objective of equation (1) is to estimate the parameter β_1 , corresponding to the impact of a playground wash, controlling for pre-play wipe metal loadings, levels of metal accumulation on playground surfaces, and fixed effects for metal type, playground location, and whether the play experiment occurred on a weekend day. If washing a playground reduces the risk of metal exposure, then β_1 ought to be negative and statistically significant. Our dependent variable – post-play hand wipe metal loadings – was normalized by natural log transformation. Because our dependent variable is natural logged, the coefficient corresponding to play-ground wash in Table 3 is interpretable in percentage terms. As shown in Table 3, we find that post-play hand wipe metal loadings were 55.9% (95% CI: -0.78, -0.34) lower on wash-days as compared to non-wash days, demonstrating the effect of washing a playground in lower exposure risk (Table 3).

Despite the clear reductions in metal loading due to washing (natural or as part of the cleaning regime), the salient question is whether washing should be promulgated as an effective strategy to counteract metal-rich dust hazards. To elucidate this pivotal question, Fig. 3 graphs the effect of a playground wash on lead exposure risk at each playground. Predicted values (and intervals of



Fig. 3. Effect of playground washing on hand lead exposure risk ($\mu g/m^2$). Note: point estimates and intervals of confidence derived with delta-method standard errors, and by fixing covariates at sample means (Supplementary Table S4).

confidence) are derived from the regression equation (1) for Table 3. Pre-play and playground surface wipe variables are fixed at their sample means. Post-play hand wipe lead levels on wash days are manifestly lower than non-wash days. At Woodward Park, for instance, post-play lead exposure is 42.8% lower on wash days versus non-wash days (502 versus 877 μ g/m²). While washing a playground clearly suppresses the quantity of lead on hand wipes after timed play, the salient issue is whether observed reductions are sufficient to protect children from potential exposures. Across all metals examined (Supplementary Table S4), post-play hand wipe values remain high relative to international and national dustmetal loading values (based on annual average values). Although the detailed results focus on lead deposition, the washing effect is reflected similarly in all the metals analysed in this study. This is not surprising given that metal emission and deposition are correlated strongly (van Alphen, 1999; Taylor et al., 2013).

Next, we addressed the question of how long the observed reduction in metal exposure risk lasts following a playground wash. To pursue this question, we estimate the following:

$$\ln(y_{ij}) = \alpha + \beta_1 \sqrt{W_j} + \beta_2 \ln(P_{ij}) + \beta_3 \ln(S_j) + \gamma_1 M_{ij} + \gamma_2 G_j + \gamma_3 D_{ij} + \varepsilon_{ij}$$
(2)

where the meaning of all terms carry from equation (1), with the exception of W_{j} , that now denotes the elapsed time (in hours) from the last playground wash. Elapsed time is measured in square root hours to capture the diminishing returns to metal exposure risk in time. By squaring the observed coefficient (b = 0.226) with respect to elapsed time reported in Table 4, we find that post-play hand wipe metal loadings increase ~5.1% (95% CI: 1.2, 11.7) for every hour from the last playground wash. This shows clearly that the benefit of a playground wash in terms of minimizing risk of metal exposure is short-lived.

In Fig. 4, we depict the predicted post-play hand wipe lead loadings at hours of elapsed time since the last playground wash. Predicted values are derived from the regression equation in

Table 4. Again, other covariates are fixed to their sample means. To be conservative, we graph the lower bound estimate of the 95% confidence interval for each playground. Results show that the average time it takes for post-play hand wipes to exceed 800 μ g/m² after a playground wash is ~24 h at Woodward, ~9 h at Sports Park, and ~5 h at Memorial after playground washing. At Foreshore, post-play lead loadings are always >1000 μ g/m² on hands regardless of when the playground is washed. A lead dust value of 800 μ g/m² is a conservative estimate of risk, constituting twice the value used by the Western Australian Government (Government of Western Australia (2011)) for surfaces accessible to children during the Esperance lead-spill clean-up (see also Gulson et al., 2009). To stay under a conservative threshold of 800 μ g/m², our results indicate that Woodward Park must be washed daily, Sports Park twice daily, and Memorial Park three times a day.

Table 4

Regression coefficients estimating hourly change in metal exposure risk from timed play following a playground wash.

	Post-play (ln)
Hours ^{0.5}	0.226*** (0.033)
Pre-play wipes (ln)	0.012 (0.012)
Surface wipes (<i>ln</i>)	0.016 (0.010)
Reference = Arsenic	
Cadmium	-0.639^{***} (0.183)
Copper	1.873*** (0.197)
Lead	3.900*** (0.206)
Zinc	5.307*** (0.224)
Reference = Woodward Park	
Foreshore	1.258*** (0.157)
Memorial Park	0.479*** (0.157)
Sport Park	0.283*** (0.192)
Weekend	-0.215*** (0.117)
Constant	2.177*** (0.191)
Observations	145
F-Test	175.31
R-squared	0.930

Standard errors in parentheses *** p<0.01, ** p<0.05, * p<0.1.



Fig. 4. Predicted hourly lead exposure risk (µg/m²) from timed play following aplayground wash. Note: we graph the lower bound estimate of the 95 % interval of confidence derived with delta-method standard errors.

4. Conclusions

The results from this study are clear. Although washing reduces metal loading on playgrounds and hands after play, it does not resolve the problem of contemporary emissions and their deposition and accumulation on playground surfaces. Until the smelter reduces its emissions to the atmosphere, which is purported to occur following the completion of the \$514 million smelter transformation project (COOE Pty Ltd, 2013; Government of South Australia (2014)) washing of playgrounds can provide only limited protection from toxic dust deposition exposures. Other locations experiencing ongoing atmospheric emissions and subsequent depositions are likely to face similar limitations from washing regimes that are designed to limit the hazard from metal environmental exposures.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.envpol.2015.02.029.

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Paper Eleven

Evaluation and Assessment of the Efficacy of an Abatement Strategy in a Former Lead Smelter Community, Boolaroo, Australia.

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Supplementary Information in Appendix J

The aim of this study was to assess the effectiveness of remediation to improve environmental and human health quality following the closure of a long operating lead smelter. This study provided the opportunity to consider the future environmental impacts that the communities of Port Pirie and Mount Isa may face in the event their lead smelters are shut down. This is in light of the significant ongoing emissions from these smelters and exemption to Australian regulations demonstrated in 'Licenced to pollute but not to poison: The ineffectiveness of regulatory authorities at protecting public health from atmospheric arsenic, lead and other contaminants resulting from mining and smelting operations' (Paper Two, page 24). This study demonstrated the pervasive nature of lead and the ongoing environmental impacts resulting from long term, yet historic, lead smelter emissions. ORIGINAL PAPER



Evaluation and assessment of the efficacy of an abatement strategy in a former lead smelter community, Boolaroo, Australia

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Abstract This study examines the recent soil Lead Abatement Strategy (LAS) in Boolaroo, New South Wales, Australia, that was designed to "achieve a reduction in human exposure to lead dust contamination in surface soils". The abatement programme addressed legacy contamination of residential areas following closure of lead smelting operations in 2003 at the Pasminco Cockle Creek Smelter (PCCS). The principal objective of the LAS was to "cap and cover" lead-contaminated soils within the urban environment surrounding the PCCS. Soil lead concentrations of 2500-5000 mg/kg were scheduled for removal and replacement, while concentrations between 1500 and 2500 mg/kg were replaced only under limited circumstances. To date, there has been no industry, government or independent assessment of the clean-up programme that involved >2000 homes in the

Electronic supplementary material The online version of this article (doi:10.1007/s10653-015-9779-8) contains supplementary material, which is available to authorized users.

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M. P. Taylor · L. J. Kristensen · S. Grant-Vest · M. Rouillon · L. Wu Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, Sydney, NSW 2159, Australia township of Boolaroo. Thus, by measuring postabatement soil lead concentrations in Boolaroo, this study addresses this knowledge gap and evaluates the effectiveness of the LAS for reducing the potential for lead exposure. Soil lead concentrations above the Australian residential soil health investigation level value for residential soils (300 mg/kg) were identified at all but one of the residential properties examined (n = 19). Vacuum dust samples (n = 17) from the same homes had a mean lead concentration of 495 mg/ kg (median 380 mg/kg). Bio-accessibility testing revealed that lead in household vacuum dust was readily accessible (% bio-accessible) (mean = 92 %, median = 90 %), demonstrating that the risk of exposure via this pathway remains. Assessment of a limited number of properties (n = 8) where preabatement soil lead levels were available for comparison showed they were not statistically different to post-abatement. Although the LAS did not include treatment of non-residential properties, sampling of community areas including public sports fields, playgrounds and schools (n = 32) was undertaken to determine the contamination legacy in these areas. Elevated mean soil lead concentrations were found across public lands: sports fields = 5130 mg/kg (median = 1275 mg/kg, playgrounds and schools = 812 mg/kg (median = 920 mg/kg) and open space =778 mg/kg (median = 620 mg/kg). Overall, the study results show that the LAS programme that was dominated by a "cap and cover" approach to address widespread lead contamination was inadequate for mitigating current and future risk of lead exposures.

Keywords Boolaroo · Lead exposure · Lead Abatement Strategy · Remediation evaluation · Smelter

Introduction

Lead mining and smelting operations have been linked to widespread environmental contamination and elevated blood lead levels in children in Australia (Cartwright et al. 1977; Gulson et al. 2004; Martley et al. 2004; McMichael et al. 1985; Morrison 2003; Taylor et al. 2014a). Dispersal of toxic metals from smelter stack and fugitive emissions across urban environments and subsequent accumulation in home environments presents a major potential exposure pathway which is a significant contributor to elevated blood lead concentrations (Boreland and Lyle 2006; Csavina et al. 2014; Graziano et al. 1990; Landrigan et al. 1976; Mielke et al. 2011; Taylor et al. 2013; Yankel et al. 1977; Zahran et al. 2014). The harmful human health impacts of environmental lead exposure are well documented and include severe neurological deficits in young children, even at low levels of exposure (Canfield et al. 2003, Lanphear et al. 2000, 2005; Mielke et al. 2013).

Internationally, the research literature is replete with techniques aimed at reducing the concentration of lead in soils without the need to excavate large quantities of contaminated land. These techniques range from the application of ethylenediaminetetraacetic acid (EDTA) to surface soils as an immobilisation agent to the addition of animal and vegetable by-products including mussel shells, wineprocessing sludge and bio-char (Ahmad et al. 2012; Bolan et al. 2014; Jez and Lestan 2015). These techniques result in variable success, depending on a range of physical and environmental conditions including soil matrix, soil infiltration capacity and the spatial extent of the technique application (Bolan et al. 2014). In contrast to topical applications, the complete removal of contaminated soils is a strategy that has occurred predominantly in locations affected by smelter lead emissions (e.g. US EPA 2012). While comprehensive removal of soil is often effective at eliminating the contaminated soil from the environment, this approach requires a significantly greater cost outlay and is more disruptive to the environment than other methods. With the increasing global acknowledgement of environmental lead contamination, including significant issues in China, Europe, Nigeria and the USA (e.g. Aschengrau et al. 1994; Blacksmith Institute 2011; Farrell et al. 1998; Li et al. 2015, Lillo et al. 2015; Mielke et al. 2011), there is a need to develop successful cost-effective strategies for remediating lead-contaminated environments. Despite the widespread nature of environmental lead contamination in Australia, examples of successful largescale schemes to clean up such contamination are surprisingly rare. In the light of this knowledge gap, this study examines the efficacy of an approach approved by the NSW Environment Protection Authority (inter alia other government departments) for reducing the risk associated with significant atmospheric lead deposition in soils.

Lead Abatement Strategy (LAS) for Pasminco Cockle Creek Smelter

Work to reduce the human exposure hazard from leadcontaminated soils surrounding the former Pasminco Cockle Creek Smelter (PCCS) commenced in 2007, following closure of the smelter in 2003, with work completed in 2013. The Pasminco Cockle Creek Smelter (PCCS) was situated within the urban area of Boolaroo on the New South Wales (NSW), Central Coast, approximately 140 km north from Sydney and 20 km from the regional city of Newcastle, Australia (Fig. 1). The PCCS operated on the Boolaroo site from 1897 as Sulphide Corporation Ltd, with intermittent operation during 1922-1961 and then full-scale operation until the closure of Pasminco Cockle Creek Smelter Pty Ltd in 2003 (Dames and Moore 1994a, b). In 1994, the smelter was producing approximately 80,000 t of zinc, 32,000 t of lead, 500 t of cadmium and 180,000 t of sulphuric acid, generated from gases captured during smelting of the Broken Hill galena (PbS) ore (Dames and Moore 1994b).

The PCCS has a long history of environmental contamination with studies in the 1980s revealing metal contamination of northern Lake Macquarie and surrounding suburbs (Batley 1987; Galvin 1992; Roy and Crawford 1984). Combined with atmospheric emissions resulting in soil lead contamination (Fig. 2),

Fig. 1 Soil lead concentrations from Boolaroo, NSW, Australia, in the <180-μm fraction superimposed on the 1992 point survey grid soil lead data. Contemporary soil lead concentrations are greatest proximal to the PCCS



a significant other source of environmental lead exposure arose from the highly bio-accessible (54 % bio-accessible) smelter slag that was distributed widely as backyard fill throughout the suburbs surrounding the PCCS (Morrison and Gulson 2007). Batley (1992) concluded that "most of the heavy metals present in the slag are in readily bio-available forms. It is likely that ingested slag reaching the gut

would readily release lead, zinc, cadmium and copper, and this could have toxic consequences" (p. 5).

Environmental lead contamination resulting from PCCS emissions in Boolaroo contributed to elevated blood lead levels in children living in the town (Galvin 1992). Multiple studies of soil lead-blood lead relationships show clearly that higher soil lead values are associated with elevated blood lead levels in young


Fig. 2 Average annual atmospheric lead concentrations—First Street, Boolaroo, NSW

children (Bickel 2010; Zahran et al. 2009). Various historical studies have shown that children exposed to the lead emissions of the PCCS had elevated blood lead concentrations above accepted guidelines, the most recent of which was 10 µg/dL but which has now been reduced to 5 μ g/dL with the ultimate aim to have no detectable blood lead concentration (Dalton and Bates 2005; Galvin 1992; Morrison 2003; Ouw and Bisby 1976). Following multiple attempts to "clean up" the suburbs surrounding the smelter, including a property buy-back scheme in 1992 where homes were cleaned and then leased, 37 % of tested children 0-5 years of age presented a blood lead concentration exceeding 10 µg/dL in 2002 (Gulson et al. 2004; Hunter Health 2003; Morrison 2003). Dalton and Bates (2005) demonstrated a decline in population blood lead concentrations post-closure of the PCCS (17 % of children 0–5 years >10 μ g/dL) with a further reduction in 2006 to 7 % of children (n = 171)(Hunter New England Population Health 2006). In mid-2015, 12 % of children and pregnant women tested (n = 72) returned a blood lead concentration above what the NSW Health, Hunter New England Local Health District deemed a low reading (3.3 µg/ dL), with no samples above 5 µg/dL (NSW Health Health 2015a).

The LAS was initiated with the intention of finding "a suitable and workable solution to managing the lead fallout levels from soils in the community surrounding the former PCCS smelter" (Pasminco 2007). The explicit goal of the LAS was "to reduce the current potential exposure for residents of the nominated properties that could arise from previous lead dust deposition such that the exposure levels from lead dust deposition after the LAS has been completed are within acceptable limits during everyday living" (Zines 2007, p. 5). It is unfortunate that this goal was never tested following completion of the urban abatement programme in 2013.

Nominated properties were set out in the 1995 conditions of consent for the upgrade of the PCCS and included "those being likely to be affected by lead dust from the smelter operations" (Zines 2007, p. 5). Nominated properties fell within the LAS grid constructed by incorporating soil data from the 1992 soil lead survey, blood lead data and contour mapping (Supplementary Data 1; Fig. 1). Participation of nominated properties in the LAS scheme was "optin"; landowners were offered participation via written communication over a one-month period. Properties were abated according to the thresholds set out by LAS (Table 1, Zines 2007). Those who did not respond to or declined this invitation received no abatement (Zines 2007). Parkland, open space, schools and other high-use community areas were not included in the LAS because it was deemed as per similar work conducted in Port Pirie that "older children, adolescents and non-occupationally exposed adults exhibit near normal blood levels unless significantly exposed during early life" (Maynard et al. 2006). It is unclear how many properties were actually involved in the LAS as participant numbers are inconsistent in different official documents (Ferrier Hodgson 2013, 2015; Lake Macquarie City Council 2013). According to the document issued by Lake Macquarie City Council (2013), approximately 750 properties recorded soil lead concentrations above 300 mg/kg and were therefore eligible for abatement. This figure of impacted residences, however, is confused by a 2014 communication from the NSW Environmental Protection Authority to MP Taylor in which Ferrier Hodgson confirmed that "437 participants received results above 300 ppm [mg/kg] and were advised of the recommended abatement works" (pers. comm. Coffey, EPA, 2014). It is worth noting that of the 1238 properties that the Administrator Ferrier Hodgson identified as elected participants, 783 (63 %) received only education materials. These properties were deemed to have soil less than 300 ppm [mg/kg] (341 properties—category 1, Table 1) or sufficient grass/mulch covering with soils between 300 and 1000 ppm [mg/kg] (282 properties, category 2, Table 1) or a mixture of category 1 and category 2 (Table 1) with sufficient grass/mulch covering (160 properties).

Measured lead concentration	Abatement strategy action				
<300 mg/kg	No lead abatement action				
300-1000 mg/kg	Option a: if grass covered, then barrier exists and no further action necessary				
	Option b: if not covered by grass but can be, then till and apply turf maintaining practical ground levels for particular site				
	Option c: when in shady spot with low grass cover, add 25 mm topsoil and mulch cover				
1000-1500 mg/kg	Option a: for already grassed areas, add additional 25 mm of topsoil				
	Option b: if not covered by grass but can be, add 25 mm of topsoil and apply turf maintaining practical ground levels for particular site				
	Option c: when in shady spot with low grass cover add 40 mm topsoil and mulch cover				
1500-2500 mg/kg	Option a: for already grassed areas, add additional 50 mm of topsoil as barrier				
	Option b: if not covered by grass but can be, then add 50 mm of topsoil and apply turf				
	Option c: when in shady spot with low grass cover, excavate 50 mm of topsoil and mulch cover				
2500-5000 mg/kg	Option a: for already grassed areas, excavate 50 mm of topsoil and replace with 50 mm of new topsoil a barrier—replace grass cover (if suitable lead content) or otherwise apply new turf				
	Option b: if not covered by grass but can be, then excavate 50 mm of topsoil and then replace with 50 mm of new topsoil and apply new turf				
	Option c: when in shady spot with low grass cover, excavate 50 mm of topsoil and then replace with 50 mm of new topsoil and mulch cover				
>5000 mg/kg	Investigate soil profile vertically to determine level of excavation required (expect 100 mm maximum) and then excavate, reinstate with new topsoil and apply new turf, maintaining practical levels for particular site or mulch as above				

 Table 1
 Lead abatement protocol utilised by Ferrier Hodgson for the Boolaroo abatement following environmental lead contamination by smelting at the Pasminco Cockle Creek smelter

Methods and materials

Field methods

Soil and vacuum dust samples were collected from abated and non-abated residential properties within and outside of the LAS grid in August 2014. The abatement status of each property was withheld from the researchers until after the results had been obtained. Soils were also collected from open spaces and parklands (community areas). Surface soil samples were taken from a depth 0–2 cm following the protocols in the Australian Standard for sampling soils that are potentially lead contaminated (Australian Standard AS4874-2000, 2000).

Each residential property was sampled in three locations, front yard soils, back yard soils and a vacuum dust sample (Supplementary Data S2 and S3). Vacuum dust was sampled to characterise the contemporary exposure within the home and was collected where available directly from the household's vacuum bag or canister. Domestic vacuum samples are a suitable means of sampling lead dust and are comparable to a range of other methods including high-volume sampling (Colt et al. 2008; Deziel et al. 2014: Gulson et al. 1995). In order to characterise soil lead concentrations in front and back yards as a whole, an aggregate of five samples were collected each from the front and back of the property. Soils collected from open spaces and parklands were similarly averaged across the site by collecting up to five samples at each location. In addition, a Government Information (Public Access) Act 2009 (NSW) (GIPA) application was submitted by Newcastle Herald (Fairfax Media Ltd) to the Lake Macquarie Council to access the Pasminco soil assessment data that were used to determine the abatement actions on individual property titles. This yielded data from 8 properties that we had sampled as part of our study, enabling assessment of pre- and post-abatement soil lead levels.

Laboratory methods

Soil samples were oven dried at 60 °C and then sieved to $<180 \ \mu m$. The $<180 \ \mu m$ fraction was selected as

the PCCS's primary environmental contamination was from fine particulate emissions from smelter stacks, making finer soil and dust fractions the most significant health exposure pathway. In order to understand the effect of sieving to <180 µm on soil metal concentrations compared to the more conventional <2 mm fraction, a subset (n = 6) of soil samples was subdivided into the two fractions and analysed (Supplementary Data S4). Dust samples were sieved to <2 mm to remove large particulate debris. Sieving to <180 µm was not possible because of insufficient sample volume once all the coarse and non-particulate matter had been removed (hair, paper, etc.). These protocols are consistent with those defined in the Australian National Environment Protection (Assessment of Site Contamination) Measure 1999 (NEPM 2013), which states at s 4.2.4.3: "Unless impracticable or not recommended for a specific method, the sample portion for analysis should be of a size to pass a 2.0 mm aperture sieve".

Soil (n = 75; front yards, back yards, open spaces, sports fields, playgrounds, schools and 2 mm fractions) and dust (n = 17) samples were analysed at the National Measurement Institute (NMI), Sydney. Approximately 0.5 g of dust or soil was digested in 3 mL concentrated, trace metal grade HNO₃ and 3 mL HCl. Elements commonly detected in smelting environments, antimony, arsenic, cadmium, lead and zinc concentrations were determined using a Perkin Elmer Elan DRC II Inductively Couple Plasma Mass Spectrometer (ICP-MS). Three procedural laboratory blanks returned concentrations below limit of reporting (LOR) of <0.5 mg/kg for all elements. Recovery rates of two NMI standard reference materials, AGAL-10 (river sediment) and AGAL-12 (bio-soil), for all elements were between 92 and 114 %. Duplicate analyses for the samples returned relative per cent difference (RPD) of <20 %.

Vacuum dust samples (n = 17) were also analysed to estimate their bio-accessible lead concentration by digesting 2 g of sample in 50 mL 1 M HCl and tumbling for 1 h. This procedure was selected due to its simplicity and effectiveness in mimicking the internal environment of the human intestinal tract. Procedural laboratory blanks returned average concentrations < 0.5 mg/kg for bio-accessible lead. Spike recovery rates for dusts were 103 %. Duplicate analyses for bio-accessibility in dust returned a RPD of 11 %. Statistical analysis on the various sample media was performed using the Web-based statistical application developed by Stangroom (2014).

Results and discussion

All analysed concentrations are presented in the Supplementary Data (S2–S5). Data were divided into properties that received physical treatment in terms of soil removal or the addition of clean soils over existing contaminated soils and those properties that received no treatment (under the LAS). Due to privacy restrictions, the specific properties are not noted in the Supplementary Data. Mann–Whitney U tests showed that for all metals, the combined soil (<180 μ m) and vacuum bag samples (<2 mm) were not statistically different between the treatments (calculated p values >0.05). Similarly, comparison of front yard and back yard soil samples between the treatment types showed no statistical difference for any of the metals, indicating abatement had not resulted in any material difference in soil metal values. Comparison of the six paired <180-µm and <2 mm soil fractions show a mean RPD of 27 % (Supplementary Data S4), indicating that lead concentrations are similar throughout the two size fractions.

It is worth noting that there are procedural differences in the sampling analysis protocols undertaken by Ferrier Hodgson (Zines 2007) versus those used in our study. The Ferrier Hodgson approach collected five soils from across the property and used the average value to determine the category for abatement (Table 1). In addition, Ferrier Hodgson collected soils from the top 5 cm of soil as opposed to the approach relied upon here (top 0–2 cm of soil), which parallels the recommended method for sampling potentially lead-contaminated soils (Australian Standard AS4874-2000, 2000).

Residential properties

All residential sites, with the exception of site 17, exceeded the NEPM 1999 (2013) health investigation level for domestic residences (HIL-A) of 300 mg/kg for at least one location on the property (Fig. 1, Supplementary Data S2). Antimony, arsenic, cadmium and zinc also exceeded their respective NEPM 1999 (2013) HIL-A guideline values thrice, once,

eight times and once, respectively. As these elements do not appear as dominant contaminants in this environment, they have been included for completeness of the data set and have not been further extensively analysed. A Mann–Whitney U test for lead of all individual soil samples from front and back yards showed there was no significant difference in front yard soils compared to back yard soils ($z \operatorname{score} = -0.10$, $p \operatorname{value} = 0.96$). Soil lead concentrations in the back yards (mean = 1180 mg/kg, max = 3410 mg/kg) do not statistically differ from soil lead concentrations in front yards (mean = 1310 mg/kg, max = 4230 mg/kg) (Fig. 3).

Residential surface soil lead presents a significant health exposure risk to children (Filippelli et al. 2005; Zahran et al. 2014). Exterior soil can continually contribute lead to the internal home environment when seasonally driven decreased moisture content and increased re-suspension causes the re-distributing of finer soil fraction into the home (Hunt et al. 2006). Outdoor playtime is often restricted by parents to the "safe" backyard environment (Holt et al. 2009; Veitch et al. 2006) where children are often free to dig and play in or around soil, resulting in the ingestion of soil and dust, especially for children under 5 who display frequent hand-to-mouth behaviours (Mielke et al. 2011). The soils in the Boolaroo residential environment still contain lead levels that have the potential to pose a significant risk of harm; therefore, it is difficult to conclude that objective of the LAS to reduce human exposure to environmental lead contamination has been achieved (Zines 2007, p. 5).



Fig. 3 Distribution of lead concentrations in soils and dust collected from front yards, back yards and household vacuum cleaner dust in Boolaroo. Mean concentrations are similar across each sampling area

Publically accessible areas

In addition to residential properties, soil samples (n = 32) were collected from a range of other specified land uses across Boolaroo and its immediate surrounds. This land is categorised here as open space (including roadside verges, parklands and vacant blocks) had a mean lead concentration of 778 mg/kg lead (median = 620 mg/kg) (Table 2).

For these samples, the NEPM 1999 (2013) health investigation level Recreational C guideline (i.e. public open space such as parks, playgrounds, playing fields, secondary schools and roadside verges) for lead in soils (600 mg/kg) was exceeded in 13 of 23 samples. No other element exceeded the relevant Australian soil guidelines.

Sports fields are considered separately to open space even though they are also subject to Recreational C soil metal guidelines because children are more likely to interact with exposed soil surfaces. The data from sports field sampling show environmental lead levels exceed guidelines with a mean lead concentration of 5130 mg/kg (median = 1275 mg/ kg) (Table 2). The pattern of elevated soil metal concentrations is also reflected in playground and school soils (Table 2), which have a mean lead value of 812 mg/kg (median = 920 mg/kg) compared to the NEPM 1999 (2013) HIL-A value of 300 mg/kg. The HIL-A guideline includes children's day care centres, preschools and primary schools.

The non-residential community areas reveal a consistent pattern of lead-contaminated soil, with values ranging from 99 mg/kg to 17,500 mg/kg with a mean of 1330 mg/kg (median = 640 mg/kg) (Supplementary Data S5). The sports ground from where the sample containing 17,500 mg/kg of lead was taken had been filled with slag from the former PCCS, which is known to be rich in multiple metals (Morrison 2003) and also highly bio-accessible (Batley 1992; Morrison and Gulson 2007). Sites more distal to the former PCCS footprint contain lower soil lead concentrations (Figs. 1, 4), which parallels soil data collected during the operational phase of the smelter (Galvin 1992; Willmore et al. 2006).

Community areas including parks, playgrounds, schools and open spaces were not included in the LAS. This study investigated community areas excluded by the LAS to comprehensively delineate the leadexposure risk across Boolaroo. The data show that a

Table 2 Statistical data for open space (roadside verges, parklands vacant blocks), sports fields and playgrounds/schools samples

Sampling area		Antimony	Arsenic	Cadmium	Lead	Zinc
Open space (mg/kg), $n = 23$	Mean	2.2	17.7	11.9	778	1146
	Median	2.2	14.0	9.2	620	950
	SD	1.5	10.6	10.8	622	741
	Min	0.0	5.0	0.7	99.0	250
	Max	5.0	39.0	37.0	2040	2590
Sports fields (mg/kg), $n = 4$	Mean	12.7	67.3	8.9	5130	9930
	Median	4.2	28.5	6.1	1275	4205
	SD	19.0	88.9	8.3	8275	13,458
	Min	1.5	12.0	2.5	470	1410
	Max	41.0	200	21.0	17,500	29,900
Playgrounds/schools (mg/kg), $n = 5$	Mean	3.1	35.8	9.7	812	1936
	Median	3.7	18.0	9.9	920	1330
	SD	2.7	53.1	8.0	723	2388
	Min	0.0	4.5	1.7	100	220
	Max	6.6	130	20.0	1830	6090
	IVIAX	0.0	150	20.0	1830	6090

Fig. 4 Soil and dust lead concentrations from Boolaroo homes and community areas plotted against distance from the centroid of the PCCS site, illustrating a decrease in contamination with distance from the former smelter



number of community areas contain lead concentrations unacceptable for regular community use. Lead contamination of child play areas is not uncommon, particularly in industrial towns (Haugland et al. 2008; Mielke et al. 2011; Taylor et al. 2013, 2014b). Playground equipment has been identified as a pathway for lead exposure in children where dust deposited on the equipment collects on the hands of playing children (Taylor et al. 2013, 2014b). Although playing sports on grass-covered sporting fields would limit lead exposure to players, there is a reasonable risk that grass will be degraded during play or seasonally, increasing the risk of exposure to leadcontaminated soils (Carr et al. 2008). High total lead concentrations and the well-established bio-accessibility of lead in community areas around Boolaroo (Kim et al. 2009) strongly suggest that unacceptably elevated environmental lead contamination is more prevalent than that was addressed by the LAS.

Residential vacuum dust

Vacuum dust indicates a contemporary exposure pathway with sites containing very high concentrations of lead; one site returned a total extractable lead concentration of 1320 mg/kg (vacuum dust mean = 495 mg/ kg, median = 380 mg/kg, n = 17) (Supplementary Data S3). Properties in close proximity to the former PCCS generally contain higher concentrations of vacuum dust lead (Fig. 4), which is not surprising given that smelter atmospheric emissions were a significant source of contaminated dust (Morrison 2003). Lead bioaccessibility of household vacuum dust (n = 17) was also elevated (mean = 92 %, median = 90 %). Total extractable lead and bio-accessible lead concentrations in household vacuum dusts were also strongly correlated (r = 0.97, p < 0.00001). While these relationships may be an artefact of the extraction methods, these values are in agreement with those reported recently by Kim et al. (2009) in a separate assessment of bio-accessibility and phyto-availability of smelter-contaminated soils from the Boolaroo area and also concur with Morrison and Gulson (2007).

The Bunker Hill Superfund Site in Idaho, USA, was subject to a similar clean-up as Boolaroo to reduce lead in the environment (von Lindern et al. 2003b). At Bunker Hill, lead in household dust was sourced predominately from soil lead contamination around this site. Relevantly, research shows that up to 40 % of the dust inside houses is sourced from soil surrounding the home, which is then carried inside on shoes (Dixon et al. 2006, Hunt et al. 1992; 2006, Murgueytio et al. 1998, Stanek and Calabrese 1995). An estimated 40–50 % of a child's elevated blood lead level in the Bunker Hill Superfund Site area was attributed to household dusts (von Lindern et al. 2003a, b).

Assessment of effective management strategies

It is evident that despite the Boolaroo LAS, high concentrations of lead in the living environment in

Boolaroo persist. One of the most apparent failures of the LAS approach is the absence of postabatement soil analysis in order to measure the efficacy of the programme. Post-abatement assessment is fundamental to evaluate the work to reduce environmental metals exposures, and such an assessment would have revealed that the nominated properties approach used by the LAS did not achieve its goal. The strategies employed by the LAS of shallow soil capping, mulching or grass covering are insufficient to mitigate the risk of lead exposure in the long term. Management of high-risk lead-exposure sites in New Orleans, USA, involved laying a brightly coloured water permeable layer over exposed contaminated soils and capping with a minimum of 15 cm of certified clean fill (Mielke et al. 2011). This procedure placed a physical and visual barrier between the contemporary users of the site and the contaminated soil layer. Similar abatement strategies were adopted in Boston, USA, where 15 cm of soil was removed and a geotextile barrier was put in place and then capped with a minimum of 20 cm of clean soil and grass (Aschengrau et al. 1994). The Baltimore Lead in Soil Project adopted the protocol of removing the top 15 cm of soil and replacing it with clean fill (Farrell et al. 1998). In Zamfara State, Nigeria, which has been identified as one of the biggest lead poisoning incidents in history, a clean-up protocol similar to that of Boston and Baltimore was applied. Soils with lead concentrations above 1000 mg/kg were removed and replaced with clean (<100 mg/kg lead) soil, and soils between 400 and 1000 mg/kg lead were capped with 8-cm hard packed clean (<100 mg/kg lead) soil (Blacksmith Institute 2011). Despite significant financial constrictions, the protocol applied in Zamfara State, combined with community awareness and education, is estimated to have reduced environmental lead ingestion by 98 % (Blacksmith Institute 2011).

One Australian location where environmental lead contamination clean-up and exposure reduction were successful was at the coastal town of Esperance in Western Australia, which was the site of extensive contamination arising from wind-blown dust distribution from the lead ore shipping ports in 2007 (Gulson et al. 2009). After extensive soil removal (a minimum of 20 cm depth and to achieve concentrations below 300 mg/kg) and hard surface cleaning, the town was deemed to have successfully recovered from the incident and declared lead free (Government of Western Australia 2011).

In another recent example, soils around the still operational Hayden-Winkleman smelter in Arizona, USA, were remediated where values exceeded 23 mg/ kg arsenic, 400 mg/kg lead and 9300 mg/kg copper (US EPA 2012). The agreement between the US EPA and the smelter company, ASARCO, required that soil clean-up was to be completed to these concentrations or to a depth of four feet (1.2 m). The US EPA undertook soil sampling and analysis to verify effectiveness of clean-up at the base of excavated areas. Where soil concentrations still exceeded clean-up standards at a depth of four feet (1.2 m), a coloured barrier was laid at the base to alert anyone digging at this depth that the soil was still contaminated. Remediated properties were back-filled with clean soil and re-landscaped to its original condition.

These abatement strategies were effective clean-up methods because either they completely removed contaminated soil or a thick physical barrier was used to limit contact between contaminated soil and the human environment, reducing the opportunity for exposure to high concentrations of lead in soil. In order to apply the same rigorous, world's best practice approach to the lead-contaminated soil clean-up in Boolaroo, i.e. total removal of the potential lead-exposure risks from children, as was conducted in Boston (15 cm of contaminated soil), it will require approximately 234,000 m³ of soil to be removed (calculated by determining the exposed soil surface area on each property within the LAS boundary).

Evaluating the success of the LAS through monitoring blood lead concentrations

Elevated blood lead levels in mining and smelting communities are often attributed to additional environmental sources including leaded petrol and paint (Gulson et al. 1996). Prior work examining blood lead source apportionment at Boolaroo illustrates that these additional sources contribute little to blood lead levels at Boolaroo (Gulson et al. 2004). Further, the elemental correlations between concentrations of soil antimony and lead (r = 0.86, p < 0.00001) and cadmium and lead (r = 0.87, p < 0.00001) demonstrate a single smelter point source and not one derived from former lead petrol emission or old lead paint. Unsurprisingly, similar arguments have often been

promulgated in lead mining and smelting towns as part of an institutional approach to downplaying risk (Taylor et al. 2011, 2015; Sullivan 2014). Regardless of the contributions of these additional sources, residential soils in Boolaroo remain a modifiable lead-exposure risk, with the quality of the soil far below that reasonably expected for a contemporary living environment.

A dedicated assessment programme of blood lead concentrations in the community surrounding the PCCS had not been carried out since 2006, although continued NSW population health surveillance data revealed a continued declining blood lead concentration trend (NSW Health 2014). No specific blood lead assessment was conducted post-LAS to quantify the efficacy of the work although "the mechanisms to test whether abatement or remediation has been successful in the case of lead contamination in soil is to assess the level of lead in blood" (pers. comm. Coffey, NSW EPA 2014). Following the release of provisional results and conclusions from this study to the NSW Government in late 2014, the NSW EPA determined that it was necessary to establish an expert work group to evaluate the effectiveness of the LAS and other remediation activities relating to lead contamination arising from the former Pasminco lead smelter located at Boolaroo, NSW (NSW EPA 2015). The assessment includes the new blood lead surveillance programme targeted at children under 5 years of age from the Boolaroo community, initiated in 2015 (NSW Health 2015b).

Lessons from the LAS

There is a growing need to develop effective contaminated site rehabilitation approaches (Trasande and Liu 2011). Central to all clean-up efforts is the need to protect vulnerable populations, predominantly children. Given the near universal acceptance that there is no safe exposure limit for lead, it would be prudent to consider strategies to mitigate risks permanently, which provide a margin of safety in soil concentrations and avoid approaches that rely on self-protection and education strategies, which have been shown to be ineffective (Yeoh et al. 2012). The current analysis and evaluation of the LAS offer important lessons for future contaminated site clean-up attempts. It is evident that the approach applied by the LAS was insufficient for effective clean-up due to two primary reasons:

- The LAS did not capture the full extent of the contamination problem in Boolaroo. The data show that environmental lead contamination is more widespread and pervasive than the localised works in residential front and back yards. Multiple exclusions of the LAS scheme including public spaces and schools have resulted in significant lead contamination sinks remaining within the urban environment. Failure to also consider the migration of contaminated soil and dust around the urban environment and provide a clean-up strategy that prevents future re-entrainment and contamination has resulted in an unacceptable legacy in Boolaroo.
- 2. There was no post-LAS assessment to determine the effectiveness of the strategy. This study shows significant environmental lead contamination persists following completion of the LAS. If a post-LAS assessment had been conducted, it would have been apparent that the approach adopted by the LAS was not appropriate for the residential setting.

Given that the extent of environmental contamination and associated health impacts is increasing on a global scale, it has been argued that there is an intergenerational health pandemic (Adeola 2012; Edelstein 2004; Grandjean and Landrigan 2014, Hardoy et al. 2013). Even applying the precautionary principle as a minimum standard, it is clear that we should not place communities at risk of long-term illness and disease as a result of failed or insubstantial environmental rehabilitation initiatives. The embodied costs to society (socially and economically) far outweigh the costs of proper, permanent and effective intervention (Grandjean et al. 2012; Pichery et al. 2011; Trasande and Liu 2011).

Conclusion

This study demonstrates that despite the implementation of the LAS, elevated and unacceptable lead contamination surrounding the former PCCS site remains. Lead-contaminated soils in residential properties within the LAS zone have not been adequately abated to achieve lead concentrations below the soil guideline levels. The examples of international environmental clean-up approaches presented in this study illustrate the shortfalls of the LAS "cap and cover" approach. The data in this study, when compared to the expectations of current approaches and environmental standards, lead us to conclude that the goal of the LAS to reduce the lead contamination to concentrations that are within "*acceptable limits for everyday living*" has not been achieved, particularly when benchmarked against world's current best practice (Zines 2007, p. 5).

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Paper Twelve

Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes

Dong, C., Taylor, M.P., **Kristensen, L.J.** & Zahran, S. (2015). *Environmental Pollution*, 207, 345-356.

Supplementary Information in Appendix K

This study examines the effect on educational performance and developmental outcomes arising from lead and other toxic metal mining operations, where significant lead emissions are occurring. While there are multiple studies worldwide assessing the health effects of lead exposure, this study looks directly at the link to lead exposure from dust and soil and educational performance in an Australian mining community. This provides the connection between measurement of lead in the environment, in this case from the studies 'Unravelling the 'miner's myth' that environmental contamination in mining towns is naturally occurring' (Paper Six, page 77) and 'Environmental arsenic, cadmium and lead dust emissions from metal mine operations: Implications for environmental management, monitoring and human health' (Paper Eight, page 100) to the consequences on childhood health.

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Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes

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ABSTRACT

Arsenic, cadmium and lead in aerosols, dusts and surface soils from Australia's oldest continuous lead mining town of Broken Hill were compared to standardised national childhood developmental (year 1) and education performance measures (years 3,5,7,9). Contaminants close to mining operations were elevated with maximum lead levels in soil: 8900 mg/kg; dust wipe: 86,061 μ g/m²; dust deposition: 2950 μ g/m²/day; aerosols: 0.707 μ g/m³. The proportion of children from Broken Hill central, the area with the highest environmental contamination, presented with vulnerabilities in two or more developmental areas at 2.6 times the national average. Compared with other school catchments of Broken Hill, children in years 3 and 5 from the most contaminated school catchment returned consistently the lowest educational scores. By contrast, children living and attending schools associated with lower environmental contamination levels recorded higher school scores and lower developmental vulnerabilities. Similar results were identified in Australia's two other major lead mining and smelting cities of Port Pirie and Mount Isa.

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1. Introduction

The metalliferous mining history of Australia dates to the 1840s, when lead (Pb) and silver was discovered in Glen Osmond, South Australia (Drew, 2011). The minerals resource industry continues to play an important role in the Australian economy, contributing approximately 10% to gross domestic product (Roarty, 2010). Environmental contamination arising from mining and smelting operations is a worldwide concern (Nriagu, 1994; Malm, 1998; Ghose and Majee, 2000; Mighall et al., 2002; Zhang et al., 2012; Hang and Kim Oanh, 2014). In Australia, environments have been severely contaminated with metals (e.g. arsenic (As), cadmium (Cd), copper (Cu), Pb and zinc (Zn)) from ore mining and processing (e.g. Cartwright et al., 1976; van Alphen, 1999; Morrison and Gulson, 2007; Taylor et al., 2014a,b).

The effects of environmental exposures on children's health have been reported widely outside Australia (Schwartz et al., 1986; Lanphear et al., 1998; Selevan et al., 2003; O'Bryant et al., 2011; Ciesielski et al., 2013). However, in Australia, there has been a

* Corresponding author. *E-mail address:* mark.taylor@mq.edu.au (M.P. Taylor). relative paucity of research examining the impacts from mining and smelting emissions on educational and behavioural outcomes in children. The available research has focused largely on impacts of environmental Pb contamination at Port Pirie (McMichael et al., 1988; Baghurst et al., 1992; Tong et al., 1996; Burns et al., 1999). Earl et al. (2015) examined the effect of Pb on children's cognitive abilities in both Port Pirie and Broken Hill using a small cohort of 106 children with a mean age of 7.96 years. Therefore, an opportunity exists to utilize existing national education and development measures to evaluate possible linkages between environmental toxic metal exposures (e.g. As, Cd and Pb) and childhood outcomes (ACARA, 2008; AEDC, 2013). Although less well studied than Pb, several studies have shown As and Cd exposure in children and adults can also result in neurocognitive impairment (Calderon et al., 2001; Wright et al., 2006; O'Bryant et al., 2011; Ciesielski et al., 2013).

Broken Hill, Australia, contains the world's largest silver-leadzinc mineral deposit and has been mined since the discovery of ore in 1883 (Solomon, 1988). Lead poisoning in Broken Hill was reported as early as 1893 (Thompson et al., 1893). Previous studies about environmental contamination were conducted between the 1990s and early 2000 (e.g. Gulson et al., 1994). Systematic







investigation of childhood blood lead levels commenced in 1991, thereafter a general decrease in childhood blood lead levels has been recorded (Lesjak et al., 2013). However, since 2010 the proportion of children over the recently withdrawn national guideline of 10 μ g/dL increased from 12.6% (2010), 13% (2011) to 21% (2012 and 2013) (Lesjak et al., 2013; NSW Government, 2014). The recent rises in the percentage of children exceeding 10 μ g/dL may be due in part, to greater participation in annual blood lead monitoring programs following efforts to increase sample size by NSW Health. The recent increase in Broken Hill childhood blood lead levels stimulated further environmental contamination studies and attention from the New South Wales (NSW) Government in regard to persistent problem of elevated blood lead in children (Taylor et al., 2014b; Kristensen et al., 2015; Kristensen and Taylor, in review; Humphries, 2015).

This research was undertaken in the context of recent rises in childhood blood lead levels in Broken Hill and the newly revised Australian blood lead intervention level of 5 μ g/dL (NHMRC, 2015). The study applies an ecological approach to assess the spatial relationship between the potential risk of harm from environmental neurotoxic metal and metalloid hazards (As, Cd and Pb) and children's behavioural and educational performance.

2. Materials and data

2.1. Sampling and materials

Surface soil samples (0–2 cm) were collected from a total of 57 sites across the city covering six primary school catchments (SC) (Fig. 1). School catchments are used to guide parents to which primary school is appropriate for their home address. However, it is not an absolute guide as a small number of children attend schools in other catchments. Soil samples collected from school catchments and public spaces, were sieved to <2 mm using stainless steel sieves before analysis. From the 57 sites sampled, 34 surface and 29 corresponding sub-surface soils (>30 cm) were analysed for As, Cd and Pb using a PerkinElmer Elan DRC II ICP-MS at the ChemCentre, Western Australia (WA) and the National Measurement Institute (NMI), Sydney. At the remaining 23 sites, sampled surface soils were analyzed in their bulk form for total Pb concentration using an Olympus Delta Premium 40 kV portable X-Ray Fluorescence (pXRF).

In addition, site-specific sampling was undertaken at selected locations in order to understand in more detail contamination of environments accessed directly by children (Fig. 1). This comprised 34 surface soil samples and 30 dust wipes from a local high school (A9, Fig. 1, Supplementary Table S1 and S2) and four domestic residences (Fig. 1). Surface dust wipes were collected and analysed using established procedures (American Society for Testing and Materials, 2003; Taylor et al., 2014b). Analysis of these site-specific soil and dust wipes samples was conducted at NMI.

Duplicate analysis at the ChemCentre returned averaged relative standard deviation (RSD) 6% for As, 3% for Cd and 1% for Pb, while averaged RSD returned by NMI was 2% for As and Pb, 3% for Cd. Recovery rates at ChemCentre were measured using NRCC reference material PACS-2 (marine sediment) with recovery rates for As 103%, Cd 114% and Pb 102%. Recovery rates at NMI were measured using in-house reference material AGAL-10 (Hawkesbury River Sediment) and sample matrix spiking. Recovery rates for the AGAL-10 reference material for As, Cd, and Pb were 101%, 101% and 98%, respectively and 101%, 108% and 99%, respectively for matrix spikes. Dust wipe blanks returned <0.1 μ g/wipe for As and <0.05 μ g/wipe for Cd and Pb, all of which were below the laboratory limit of reporting. Recovery rates for pXRF analysis were measured using two standard reference materials NIST 2710a (Montana soil I) and

2711a (Montana soil II) with recovery rates of 109% for Pb. Analysis of a blank (SiO₂) returned <0.5 mg/kg for Pb.

2.2. Ambient air quality data

Perilya Limited, a base metals mining and exploration company extracting zinc, lead and silver in Broken Hill, is the current main source for As, Cd and Pb emissions in Broken Hill (NPI, 2014a). The company has nine dust deposit gauge stations (DDG) associated with the active Perilya southern operations to measure total dust fall and its total Pb content (EPA, 2012). Perilya also has two high volume air samplers (HVAS) for Total Suspended Particulates (TSP) and total Pb concentration in the TSP fraction, which are located on and around Perilya's southern Broken Hill operations site (EPA, 2012). From the available data (Perilya Limited, 2015), three DDG stations and one HVAS station were selected for this study, namely licence point (LP)3, LP4, LP6 and LP12, respectively, because they are located close to or immediately adjacent to urban residential areas of Broken Hill (Fig. 1). Ambient air quality data (HVAS data) covers the period from May 2012 to May 2014, with samples collected every 6th day (Perilya Limited, 2015). Dust deposition samples (DDG) are collected over a 30-day period (Standards Australia, 1998). Perilya's inactive northern operation also has DDG and HVAS stations, but these are located on the mining lease and not within the urban environment (Perilya Limited, 2015). Within the central portion of the ore body in Broken Hill, the current operating mining company, CBH Rasp Mine, also has their own air quality monitoring stations. However, the stations with available data are not located within Broken Hill's urban environment (CBH Resources Limited, 2012). Hence the data from northern operation of Perilya and CBH Rasp Mine are not included here because they do not characterise exposures specifically in the urban environment.

2.3. Australia Early Development Census (AEDC) data

The Australia Early Development Census (AEDC) is a nationwide measure to provide a snapshot of early childhood development in the first year of full-time school (normally aged 5–6 years) (AEDC, 2013). The developmental areas measured are physical health and wellbeing, social competence, emotional maturity, language and cognitive skills and communication skills and general knowledge (AEDC, 2013).

The AEDC reports are categorised according to national, state and local government areas, along with more detailed geographic information at the level of AEDC communities within local government areas (AEDC, 2013). The data and associated maps are based upon a child's home address. In the AEDC reports, Broken Hill is divided into three geographic areas: Broken Hill Central (encompassing primary school catchments SC5 and SC6), Broken Hill North (encompassing SC1, SC2 and part of SC3) and Broken Hill West (encompassing SC4 and part of SC3) (Supplementary Fig. S3). The AEDC results may be influenced by socio-economic factors. In order to make a more accurate evaluation of children's vulnerability, the relevant Socio-Economic Indexes for Areas (SEIFA) as developed by the Australian Bureau of Statistics (ABS) (ABS, 2013) were used to standardize the AEDC values:

$$AEDC_{std} = \frac{AEDC_{local}}{AEDC_{national}} \times \frac{SEIFA_{local}}{SEIFA_{national}}$$
(1)

where *AEDC_{std}* is the standardized value; *AEDC_{local}* is the vulnerability of local community; *AEDC_{national}* is the vulnerability of national community; *SEIFA_{local}* is the SEIFA score of local community and *SEIFA_{national}* is the national average score. The SEIFA scores are



Fig. 1. Locations of surface soil samples collected from the six school catchments in Broken Hill. Dust gauges (LP3, 4 and 6) and a high volume air sampler (HVAS) (LP12) from Perilya's licence monitoring are also shown. Soil samples HS4, HS5 and Soil_23 are included in school catchment SC5 to evaluate soil Pb concentrations.

based on the Australian Census 2011 data (Supplementary Table S4).

2.4. National Assessment Program – Literacy and Numeracy data

The National Assessment Program – Literacy and Numeracy (NAPLAN) is an annual assessment for students in school years 3, 5, 7 and 9, which has been a routine part of the Australian school calendar since 2008 (ACARA, 2008). Publicly available NAPLAN data is accessible at school level (ACARA, 2015). The educational domains tested are reading, narrative writing, language conventions (spelling, grammar and punctuation) and numeracy, with all results reported across a scale ranging from 0 to 1000 score points (ACARA, 2008).

The NAPLAN data is based upon where a child attends school, not their place of residence, in contrast to AEDC data. NAPLAN data is available for ten schools (A1–A10) in Broken Hill, 8 of which are primary schools (A1–A8; covering school years 3 and 5). The other two are high schools (A9, A10; covering school years 7 and 9) (school list is available in Supplementary Table S5). NAPLAN data from 2008 to 2013 was analysed for nine of the ten schools. School A8 was excluded from the analysis because it caters for geographically isolated students (e.g. those residing on remote sheep or cattle stations) within a radius of approximately 300 km from Broken Hill. This school's education program is delivered remotely. The seven primary schools involved in this study (A1–A7) cover the six school catchments in Broken Hill (Fig. 1).

In order to account for the potential adverse influence of socioeconomic factors on school outcomes, the NAPLAN Index of Community Socio-Educational Advantage (ICSEA) was integrated into the analyses (ACARA, 2013). The ICSEA measure allows for comparisons to be made between schools that are matched according to their socio-educational advantage (ACARA, 2013). Similar schools are defined by matching a school's ICSEA value to a group of up to 60 schools containing students from statistically similar backgrounds (ACARA, 2013). Schools with students who have similar levels of educational advantage will have similar ICSEA values, even though schools in their group may be located in other parts of Australia and may have different facilities and resources (ACARA, 2013). This enables a more direct comparison between schools in Broken Hill to schools with students from similar backgrounds across Australia. A ratio is applied here to examine NAPLAN data for differences between Broken Hill schools and similar schools across Australia:

NAPLAN ratio =
$$\frac{\sum_{i=2008}^{2013} (N_i - S_i)}{\sum_{i=2008}^{2013} S_i}$$
(2)

where *NAPLAN ratio* is the ratio in one domain (e.g. reading), N_i is the NAPLAN data in the same domain (e.g. reading) of one school in *i* year. S_i is the NAPLAN data in the same domain (e.g. reading) of similar schools in *i* year.

3. Results and discussion

3.1. Contemporary environmental metal exposures

3.1.1. Lead in airborne particulates

According to the National Pollutant Inventory (NPI), estimated atmospheric Pb emissions between 2012 and 2013 (26,000 kg) from Perilya Limited rank it third in Australia and first in NSW (NPL 2014a). From May 2012 to May 2014, lead in air measured as TSP Pb recorded at Licence point 12 (LP12) displayed consistently higher values between the months October to January, for both years (Supplementary Fig. S6). These months returned a maximum of 0.707 μ g/m³ and an average of 0.487 μ g/m³ compared to a maximum of 0.357 μ g/m³ and an average of 0.189 μ g/m³ in the other months (Supplementary Table S7). Seasonality of dust resuspension has been associated with warming and drying in northern hemisphere summers which can create seasonal shifts in lead exposure in children (Laidlaw et al., 2012, 2005). Broken Hill has a low annual rainfall (~260 mm/yr) and hot dry summers where temperatures can reach 46.8 °C (Bureau of Meteorology, 2015). For the only full year of data available, 2013, average TSP Pb was $0.313 \,\mu\text{g/m}^3$, with maximum $0.707 \,\mu\text{g/m}^3$. The Australia national air quality standard for TSP Pb is set at a maximum value of 0.5 μ g/m³ averaged over a year. The role of short-term spikes is not considered in the standard, but it is worth noting that Streeton's (2000) review of health data for the formulation of Australian air quality standards recommended that: "ambient lead levels should be held in the range of $0.3 - 0.5 \ \mu g/m^3$ on a mean moving monthly (or as an annual) standard, but not to exceed 0.5 μ g/m³ at any time" (Streeton, 2000, p. 33).

Compared with the other two Perilya dust gauge sites i.e., LP4 and LP6, lead dust loading was elevated at LP3 over the available comparable data period (August 2013 to May 2014) (Supplementary Fig. S8). Values ranged from 166 to 597 μ g/m²/day of dust Pb, and Pb loading peaked at 597 μ g/m²/day in December 2013 (Supplementary Table S7). For comparison, the Australian

Standard AS 4361.2-1998 (Standards Australia, 1998) provides a maximum outdoor value as a one off measurement for dust Pb in a wipe of 8000 μ g/m². The LP3 data indicates adjacent areas would take approximately 13 days to exceed this standard. There is currently no licence requirement for maximum dust Pb deposition. However, applying the Pb clean-up goal of 400 μ g/m² used by WA Health (WA Government, 2011), this value would be exceeded on a daily basis between September 2013 and January 2014. Daily average dust Pb loading values recorded at LP3 were never below the German TA Luft standard (TA Luft, 2002) for Pb deposition (100 μ g/m²/day) (Supplementary Fig. S8).

Surface dust wipe Pb data from school A9 located in central Broken Hill, ranged from 3298 to 86,061 μ g/m² (median 13,837 μ g/ m^{2}) (Table 1). The maximum value recorded is more than 215 times the Pb clean-up goal of 400 μ g/m² (WA Government, 2011). Although houses are likely to be cleaned more frequently than school surfaces, maximum dust Pb wipe values in the sampled homes distant from Broken Hill Central also exceeded the Pb cleanup goal (WA Government, 2011) (Table 1), suggesting that contemporary dust deposition continues to pose a significant potential pathway for Pb exposure. Compared with the four properties, As (maximum 687 μ g/m²) and Cd (maximum 404 μ g/m²) values in school A9 dust wipes were elevated by comparison to the daily equivalent values provided in the TA Luft (2002) (As $-4 \mu g/$ m^2/day ; Cd – 2 $\mu g/m^2/day$). Dust wipe data is detailed in Supplementary Table S9. Recently, Taylor et al. (2014b) showed that the most dust-contaminated playgrounds were also located in the Broken Hill central area.

3.1.2. Soil concentrations

Surface soil Pb concentrations measured using ICP-MS range from 46 to 8900 mg/kg (Supplementary Table S1), which are consistent with the portable XRF data that ranges from 45 to 6925 mg/kg (Supplementary Table S2). The average surface soil Pb level of each school catchment reveals that the highest soil Pb is in Broken Hill Central (median Pb 2272 mg/kg) (Table 2), which encompasses school catchments SC5 and SC6 (Fig. 1). School catchment SC3 in the west of Broken Hill returned the lowest surface soil Pb level (median Pb 116 mg/kg). The Australian National Environment Protection Measures guideline for Pb in soil for residential, preschools and primary schools (defined as Health Investigation Level (HIL) A) is 300 mg/kg (NEPM, 2013). For parks, playgrounds, secondary schools and footpaths (defined as HIL C) the value is 600 mg/kg (NEPM, 2013). The eight Broken Hill primary schools (A1–A8) are distributed across the six school catchments,

Table 1

Lead, As, Cd concentrations (median values and range) in dust wipes and surface soil for school A9 and four properties in Broken Hill. Residential A – The recommended soil concentration values for gardens and accessible soil (home grown produce <10% fruit and vegetable intake (no poultry), including childcare centres, preschools and primary schools. Residential C – covers public open spaces such as parks, playgrounds, playing fields (e.g. ovals), secondary schools and footpaths (National Environment Protection Measure (NEPM), 2013).

	School A9	House 1	House 2	House 3	House 4	Residential A guideline	Residential C guideline
Dust wipe Pb ($\mu g/m^2$)	13,837 $[n = 13]$ (3298-86,061)	356 [n = 5] (129–2467)	132 [n = 3] (125–444)	822 [n = 3] (600-2551)	279 [n = 6] (52.8–17,889)	NA	NA
Dust wipe As $(\mu g/m^2)$	130 [n = 13] (41.0-687)	6.3 [n = 5] (2.0-48.7)	4.9 [n = 3] (2.2-7.7)	17.8 [n = 3] (15.0–74.0)	7.0 [n = 6] (0.9–122)	NA	NA
Dust wipe Cd ($\mu g/m^2$)	46.3 [n = 13] (12.1-404)	1.1 [n = 5] (0.7-8.0)	1.4 [n = 3] (1.1-1.7)	4.0 [n = 3] (3.5–11.1)	4.7 [n = 6] (0.8-63.3)	NA	NA
Soil Pb (mg/kg)	705 [n = 22] (190–2200)	100 [n = 3] (15-280)	420 [n = 3] (250-1130)	140 [n = 3] (14-300)	2160 [n = 3] (360-2260)	300	600
Soil As (mg/kg)	9.4 [n = 22] (3.8-26.0)	3.2 [n = 3] (1.1–3.6)	5.1 [n = 3] (4.5–16.0)	2.7 [n = 3] (1.8–3.0)	11.0 [n = 3] (3.0–15.0)	100	300
Soil Cd (mg/kg)	2.85 [n = 22] (0.9-8.2)	0.6 [n = 3] (0.5-0.7)	1.5 [n = 3] (1.2–5.1)	0.7 [n = 3] (0.5-0.9)	8.4 [n = 3] (7.2–98.0)	20	90

Notes: NA - not available.

Table 2

Lead, As and Cd concentrations in <2 mm particle size fraction of surface soil samples collected from school catchments. Lead concentrations include combined ICP-MS and portable XRF data (Supplementary Table S1, Supplementary Table S2). Arsenic and cadmium concentrations are calculated only according to ICP-MS data (Supplementary Table S1). Soil samples HS4, HS5 and Soil_23 (Fig. 1) are included in SC5. Background As and Cd data are from Kristensen and Taylor (in review).

School catchments	Pb (mg/kg)	As (mg/kg)	Cd (mg/kg)
	Median (range)	Median (range)	Median (range)
SC1	787 (45 - 2890) [n = 8]	16.0(4.4 - 29.0)[n = 3]	12(1.4 - 17.0)[n = 3]
SC2	157(50-530)[n=8]	5.0(2.3-6.1)[n=4]	1.2 (0.9 - 1.9) [n = 4]
SC3	116(46 - 170)[n = 5]	3.6(2.0-5.0)[n=3]	0.6(0.6-0.7)[n=3]
SC4	279(175 - 1340)[n = 5]	8.0(7.1 - 8.1)[n = 3]	2.0(1.0-2.0)[n=3]
SC5	2272 (617 - 8900) [n = 25]	37.0 (2.0 - 150) [n = 19]	12.0 (1.8 - 37.0) [n = 19]
SC6	1132 (248 - 1300) [n = 6]	12.0(9.9 - 14.0)[n = 2]	3.9 (3.9 - 3.9) [n = 2]
Background	97(12-2410)[n=29]	4.9(2.2-22.0)[n=29]	0.25(0.1-7.0)[n=29]



Fig. 2. Australian Early Development Census (AEDC) results across the different geographic areas for Broken Hill standardized according to the Australian Bureau of Statistics SIEFA (Socio-Economic Indexes for Areas, ABS, 2013) index for Broken Hill.

indicating that all the primary schools are likely to contain or at least be surrounded by soils in excess of the 300 mg/kg guideline. Across Broken Hill, surface soil As and Cd returned median values of 16 mg/kg and 4.9 mg/kg, respectively. No school catchment exceeded the HIL A for As (100 mg/kg) or Cd (20 mg/kg) (NEPM, 2013) (Table 2). Kristensen and Taylor (in review) calculated median Broken Hill soil Pb background based upon samples from >30 cm depth at 97 mg/kg. Background soil median As and Cd values are 4.9 mg/kg and 0.25 mg/kg, respectively (Table 2; Supplementary Table S10). Surface soil As, Cd and Pb concentrations from school catchments SC1, SC4, SC5 and SC6 all display elevated concentrations compared to background values. The two school catchments with the lowest soil values (SC2 and SC3) are the most distant with respect to the mining operations (Fig. 1).

The median value of soil Pb within the grounds of school A9 was 705 mg/kg (Table 1; Supplementary Table S11), exceeding the Australian HIL C soil Pb guideline of 600 mg/kg for secondary schools. Soil As and Cd did not exceed the relevant Australian guidelines. However, comparison of surface soil As, Cd and Pb to background concentrations shows that values at school A9, House 2 and House 4 were elevated (Table 1; Supplementary Table S11).

3.2. AEDC results

The proportion of children developmentally vulnerable in all five areas measured by the AEDC in Broken Hill is higher than the national average (Supplementary Table S4). The data shows that children from Broken Hill Central are 41.4% more likely to be developmentally vulnerable in one of more of the areas tested by the AEDC (Supplementary Table S4).

Standardised AEDC results show that children from Broken Hill as a whole are more likely to be vulnerable in two or more areas compared to the Australian level (Fig. 2). Within Broken Hill, the data show that children from Broken Hill Central are more vulnerable in each of the AEDC areas. The proportion of children vulnerable on two or more areas in Broken Hill Central is 2.6 times as high as the Australian level (Fig. 2; Supplementary Table S12). This area is characterised by the highest soil and dust As, Cd and Pb levels (Table 2; Supplementary Fig. S6; Taylor et al., 2014b). By contrast, children from Broken Hill North and West catchments, which have lower soil and dust metal and metalloid values, have AEDC scores across the five areas closer to the Australian level.



Fig. 3. Box-whisker plots comparing the five educational domains measured in Broken Hill school children. Diamond boxes represent the six-year averaged Australian NAPLAN data for the respective educational domains. NW: narrative writing, G&P: grammar and punctuation.

3.3. NAPLAN results

NAPLAN data (2008–2013) (Supplementary Table S13) for Broken Hill and the six-year averaged values for Australia across all five assessed educational domains are shown in Fig. 3.

The results (Fig. 3) show that Broken Hill students across all age groups assessed perform below the average for Australian schools. Broken Hill students in year 7 and year 9 perform significantly worse in each of the five domains. The NAPLAN data for years 3 and 5 are closer to the average value of all Australian schools. Across all four years (i.e., year 3, year 5, year 7 and year 9) of the NAPLAN assessment program, Broken Hill children's performance in narrative writing is the lowest performing measure of all the five domains tested compared to the national average (Fig. 3).

The NAPLAN ratios from the five measured domains across Broken Hill's seven assessed primary schools (A1–A7) are displayed in Fig. 4. The two secondary schools (A9 and A10) enrol students from across all the primary school catchments (Fig. 1). Hence, we only focus on the primary schools here. School A1 located in SC5 (the area with the highest soil and dust Pb level) display lower NAPLAN scores in all of the educational domains except for spelling, even after accounting for the potential influence of socio-economic factors (Fig. 4). Lower NAPLAN scores were also observed in school A2 located in SC1, which ranks third for soil Pb (median 787 mg/kg exceeding the HIL C value of 600 mg/kg). However, the two schools A3 and A7 from SC6 with elevated soil As, Cd and Pb have higher NAPLAN scores compared to similar schools (Supplementary Fig. S14). Interestingly, primary school A7 from SC6 is a religious school that draws its students from across the whole of Broken Hill, which would have the effect of homogenising variances across school catchments.

3.4. Relationship between environmental contamination exposure and potential risk

Environmental Pb in Broken Hill has previously been shown to be highly bioavailable with soils at 41–84% and household dusts 17–100% of total lead (Gulson et al., 1994). Given that the adverse health effects of Pb exposure are considered to be a universal problem, this implies Broken Hill children are likely to experience intelligence impairments and decrements. To quantify risks from the contamination identified here, the association between NAPLAN test scores and soil metal accumulation in school catchment areas was examined. To achieve this, we execute a series of regression models where NAPLAN scores are regressed on soil metal exposure risk, adjusting for school-level socioeconomic characteristics, student grade and year fixed effects. Given the test scores are clustered at the school-level, we estimate the following



Fig. 4. Ratio of NAPLAN data for years 3 and 5 from Broken Hill schools (A1–A7) compared against NAPLAN data from comparable schools (based upon equivalent ICSEA (Index of Community Socio-Educational Advantage) values (ACARA, 2013). Positive values indicate where Broken Hill schools perform better in NAPLAN compared to similar schools. Negative values indicate a lower NAPLAN performance in Broken Hill schools compared with similar schools. NW: narrative writing, G&P: grammar and punctuation.

random effects generalized least squares model:

$$Y_{jt} = \beta_0 + \beta_1 M_j + \beta_2 I_{jt} + \Gamma_1 G_j + \Gamma_2 Z + u_j + e_{jt}$$
(3)

where, *Y* is the average score across subjects in school *j* in time *t*, M_j is the median metal soil level in school catchment area *j*, I_{jt} is the Index of Community Socio-Educational Advantage (ICSEA) of school *j* in time *t*, G_j is dummy variable = 1 for fifth grade scores,

and *Z* is the year of the test score. The random effects model residual is divided in two parts: 1) a school-specific error component, given by u_j ; and 2) a test score component, given by e_{jt} . The school-specific residual u_j captures the combined effects of omitted school characteristics that may drive test scores. Both residual terms are assumed to be Gaussian.

Regression results are in Table 3. Reported coefficients capture the expected change in test scores with unit increases in predictors

Table 3

Random effects generalized least squares coefficients predicting NAPLAN scores against soil contamination measures.

	(1) Coefficients	(2) Coefficients	(3) Coefficients	(4) Coefficients
School ICSEA	0.328***	0.308***	0.265***	0.307***
	(0.057)	(0.0539)	(0.060)	(0.055)
Soil Pb	-0.010**			
	(0.006)			
Soil As		-0.896***		
		(0.283)		
Soil Cd			-2.364***	
			(0.751)	
Soil metals				-3.249***
				(1.077)
Constant	93.35*	115.9**	156.2***	105.1**
	(54.34)	(52.47)	(58.74)	(51.83)
R^2	0.895	0.906	0.904	0.904
ρ	0.176	0.117	0.154	0.130
Wald χ^2	661.13	701.41	708.21	695.47
N	84	84	84	84
N School	7	7	7	7

Notes: Standard errors in parentheses, ***p < 0.01, **p < 0.05, *p < 0.1; Models include fixed effects for grade (with 3rd grade as our reference grade) and year (with 2008 as our reference year).

(soil metals). Column 1 shows that a mg/kg increase in school soil Pb statistically significantly reduces test scores by 0.010 points (95% CI: -0.019, -0.001). To give the soil Pb coefficient greater meaning, consider a decrease in soil Pb from 2272 to 116 mg/kg reflecting the difference in soil Pb exposure risk facing children at school A1 versus school A4, respectively. Holding all other factors constant, if children at school A1 were exposed to the lower level of soil Pb exposure risk enjoyed by their counterparts at school A4, their average NAPLAN test scores would increase an estimated 20 points (from a predicted 412.3 to 432.9 points). An increase of 20 NAPLAN points in moving from the maximum to the minimum in soil Pb risk is equivalent, in effect, to a 60-point increase in school ICSEA score $(\beta = 0.328)$, which summarizes the socio-educational advantage of a school. A 60-point increase in school ICSEA amounts to a full (sample) standard deviation increase in socio-educational advantage.

Columns 2 and 3 report coefficients for soil As and Cd, respectively. Other things held constant, we find that a unit increase in As in school catchment area soils decreases average NAPLAN test scores by 0.896 points (95% CI: -1.45, -0.34). Similarly, results in column 3 indicate that average NAPLAN test scores decline by an expected 2.36 points (95% CI: -3.84, -0.89) per mg/kg increase in soil cadmium exposure risk. Following Zahran et al. (2012) Column 4 reports results where school test scores are regressed on the standardized sum of Pb, As, and Cd in school catchment area soils, adjusting for school socio-economic status, grade and year fixed effects. The cumulative exposure to As, Cd and Pb per mg/kg unit increase in the standardized sum of soil metals depresses test scores by 3.25 points (95% CI: -5.36, -1.14).

Fig. 5a–c, traces the predicted loss in subject scores at various levels of metal accumulation (Pb, As, Cd) in school catchment area soils. Predicted scores are derived from 15 repetitions of Equation (3) involving 3 metals (Pb, As, Cd) and 5 subject test scores (reading, narrative writing, spelling, grammar and punctuation, and numeracy). Across panels, predicted NAPLAN test scores are on the y-axis, and the level of soil metals in school catchment areas is on the x-axis. In each example, five connected lines intersect the space, reflecting the expected test score in each domain, given a level of soil metals. Predicted scores are derived by delta-method and by fixing all other model covariates at their sample means.

Across all metals, we find that the relationship between subject test scores and metals in school catchment soils is downward sloping. Intriguingly, and consistent with Zahran et al. (2012), soil metals appear to impact numeracy scores more negatively than language-related skills. In Fig. 5a for example, at 250 mg/kg (e.g. equivalent to school A6) of Pb in catchment area soils, the predicted score in numeracy is 427 and 434 in spelling. At 2500 mg/kg (e.g. equivalent to school A1) of Pb in catchment area soils, the predicted scores in numeracy and spelling decrease to 400 and 419, respectively. In both absolute and percentage terms, the expected decrease in numeracy (27 points, 6.4%) is greater than the decrease in spelling (14 points, 3.4%).

The SEIFA standardized AEDC data show that Broken Hill children are more vulnerable and have lower school performance. In addition, Broken Hill Central, the most contaminated area (soil and dust As, Cd, Pb), has the largest proportion of children developmentally vulnerable in all five areas (Fig. 2). In terms of NAPLAN data, schools A1 and A2, located in the most contaminated school catchments SC5 and SC1 ranking third for soil Pb levels in Broken Hill, also display lower values (Fig. 4). These findings are consistent with the relationship between elevated blood lead and educational outcomes established in the literature (Bellinger et al., 1992; Miranda et al., 2007; Zahran et al., 2009; Amato et al., 2012; McLaine et al., 2013; Zhang et al., 2013).

3.5. Comparison to other major Australia lead mining and smelting cities

Mount Isa and Port Pirie are Australia's two other major lead mining and processing communities in Australia. Mount Isa Mines Ltd (MIM) and Nyrstar Port Pirie Pty Ltd (Nyrstar) are ranked as Australia's leading point sources for atmospheric Pb with 110,000 kg and 46,000 kg emitted between 2012 and 2013, respectively (NPI, 2014b,c). In addition, MIM ranks first for atmospheric emissions of As and Cd, while Nyrstar ranks 13th for As emissions and 11th for Cd emissions in Australia (NPI, 2014b,c). Taylor et al. (2014a) reported 2011 24-h maximum TSP values for Pb-in-air and As-in-air in Mount Isa were significantly elevated at 12.8 μ g/m³ and 2973 ng/m³, respectively. Recent studies have demonstrated elevated surface soil and dust contamination of the urban environment in Mount Isa are linked to mining and smelting operations (Munksgaard et al., 2010; Taylor et al., 2010; Mackay et al., 2013; Taylor et al., 2014a). At Port Pirie, environmental emissions are equally problematic with 24-h maximum TSP values for Pb-in-air and As-in-air at 22.57 µg/m³ (2011) and 250 ng/m³ (2009) (Taylor et al., 2014a). Elevated Pb in surface dust and soil and associated elevated blood lead values in children have been identified previously (South Australia Health, 2013; Simon et al., 2015; Taylor et al., 2013, 2015).

The corresponding AEDC results of Mount Isa and Port Pirie are provided in Supplementary Table S15. Compared with the Australian standard level (AEDC_{std}, Equation (1)), children from Mount Isa and Port Pirie are also more vulnerable across most of five areas (Supplementary Table S16), which is consistent with delayed neuropsychological development associated with Pb exposures in the Australian context (McMichael et al., 1988; Baghurst et al., 1992; Tong et al., 1996, 1998; Burns et al., 1999; Earl et al., 2015). More specifically, north Mount Isa, the area immediately adjacent to mining and smelting operations, AEDC outcomes are notably worse than other areas of the city (Supplementary Table S16). This is consistent with elevated soil Pb concentrations and associated contaminant depositions from smelter and mine site emissions (Taylor et al., 2010; Mackay et al., 2013; Taylor et al., 2014a). The proportion of children vulnerable in this area of Mount Isa in two or more of the AEDC areas of early development assessment is 2.5 times the national average. Children from Port Pirie also display greater vulnerability in the areas of physical health and wellbeing,



Fig. 5. Predicted test scores by subject by soil metal exposure risk. (a) Predicted NAPLAN school scores (adjusted for socio-economic advantage) versus soil Pb. (b) Panel B: predicted NAPLAN school scores (adjusted for socio-economic advantage) versus soil As. (c) Panel C: predicted NAPLAN school scores (adjusted for socio-economic advantage) versus soil Cd. Predicted scores are derived by fixing all other covariates at their sample means.

social competence, emotional maturity, and language and cognitive skills compared to national average values.

Australia's National Health and Medical Research Council (NHMRC) recently lowered the blood Pb intervention value to 5 μ g/dL (NHMRC, 2015). Implementation of 5 μ g/dL for intervention means ~50% of children under 5 years of age in the major Australian lead mining and smelting towns of Broken Hill, Port Pirie and Mount Isa will have a blood Pb in excess of the new reference value (Taylor et al., 2014c). The implication is that a large proportion of these children are likely to be at risk of neuro-behavioural damage (Jusko et al., 2008; Mazumdar et al., 2011; Lucchini et al., 2012; Earl et al., 2015). In light of the reduction in acceptable blood Pb levels along with recent research into ongoing exposure risks (Taylor et al., 2014b), the NSW Government announced in early 2015 AUD\$13 million to "*rejuvenate the Broken Hill Environment Lead program to address the issue of blood lead levels in local children*" (Humphries, 2015).

4. Conclusions and study limitations

There are some limitations to the study's research findings in addition to those associated with ecological research of this nature. The NAPLAN data is limited to school level. While students from each school are drawn predominantly from their corresponding catchments (~95%), there is some variance, which was not able to be accounted for. In addition, the measures of exposure from environmental contaminants are not based on individual exposures but are derived from neighbourhood samples. None-theless, this sampling approach has been shown previously to a reliable predictor for childhood blood lead measures (Zahran et al., 2013).

Environmental analysis of soil and dust samples in Broken Hill reveal ongoing potential exposures to As, Cd and Pb. Compared with the Australian national average levels, Broken Hill school children, especially those residing in Broken Hill Central, are classified as being more vulnerable in all of the five AEDC areas tested, even after adjusting for socio-economic measures. Similar outcomes are also observed in Australia's other major lead mining and smelting communities (Mount Isa and Port Pirie), which is consistent with other international studies of childhood exposure to environmental toxicants. The NAPLAN data shows that Broken Hill primary school students from areas characterised by highest soil and dust Pb levels perform poorly relative to equivalent Australian schools. Notwithstanding the aforementioned limitations, the combination of the AEDC, NAPLAN and environmental data imply strongly that metal contamination of the urban environment is a likely contributing factor to blood lead exposures and consequently, educational outcomes, even after accounting for standard social and economic factors. Given that these environmental exposures are a modifiable risk factor, it is not an unreasonable expectation that if these risks are mitigated adequately as part of a health and welfare strategy, potential outcomes will improve for the community of Broken Hill.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.09.037.

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CHAPTER 5: Synthesis of Research

The principal aim of this thesis was to investigate and measure sources of lead emissions and depositions in Australia and assess their impacts on both the environment and human health in a contemporary context. In order to achieve this, this thesis has identified and quantified current lead emissions in addition to previously unknown volumes of historical emissions, and has evaluated the effectiveness of regulations pertaining to lead exposure. Despite the wealth of studies on the multitude of adverse human and environmental aspects of lead contamination conducted in Australia through the 1980s and 1990s, there has been a marked paucity of interest and improvements to address contemporary exposures from current emissions and legacy contamination.

Environmental regulation and monitoring has changed little since the initial implementation. The lead in soil and the lead in drinking water guidelines have remained unchanged since 1996 (National Health and Medical Research Council (NHMRC) 1996; National Environment Protection Agency (NEPC) 1999) and the lead in air and surface dust guidelines unchanged since 1998 (National Environment Protection Council (NEPC) 1998; Standards Australia 1998). Additionally, measurement of BLL has seen a general decline in the number of children getting tested in recent years (Lesjak et al. 2013; Simon et al. 2015a). There has been very little independent research into and understanding of the current state of lead exposure from lead emissions in Australia. Most of the environmental monitoring is undertaken by industry whose data is difficult to access as it is deemed as proprietary information and suppled directly to state EPAs.

Exposures from ongoing emissions from mining and smelting operations form the primary contemporary lead sources, yet they currently receive limited attention and effective action. Current annual lead emission volumes from mining and smelting operations reach between 100 and 500 tonnes for an individual operation (Mount Isa Mines) with over 1200 facilities reporting lead emissions to the National Pollutant Inventory (NPI 2015a). The top three lead emitters for 2014, Mount Isa, Qld, Port Pirie, SA and Broken Hill, NSW each have significant populations between 14,000 to 20,500, that include developmentally vulnerable children aged 0-4 years (Australian Bureau of Statistics (ABS) 2014) who are particularly susceptible to adverse effects from exposure to toxic emissions (Needleman 2004; Canfield and Jusko 2008).

With the current, but essentially localised, focus with monitoring resources concentrating on contemporary industry outputs, the impact of historical lead emissions has largely been neglected. This is in part due to the success in removing lead from sources such as paint (1997) and petrol (2002) that have eliminated primary exposures (Donovan 1996; Cook and Gale 2005). However, the removal of the major pathway of lead exposure is not the conclusion to the problem. It is well established that not only does lead remain in the environment, but that the toxicity does not diminish with time (World Health Organisation (WHO) 1995; Semlali et al. 2004). Historical emissions have the potential to contribute to

BLLs through accumulation of lead in soil and dust (Zahran et al. 2013; Gulson et al. 2014). With the now near universally accepted paradigm that there is no safe level of lead exposure in the body (World Health Organisation (WHO) 2010b), these historical lead emissions need to be considered in a contemporary context.

Despite numerous studies having been conducted in Australia and internationally, lead remains one of the most ubiquitous pollutants worldwide (Nriagu and Pacyna 1988; Larsen et al. 2012). Ongoing emissions globally and the timeless toxicity of lead maintain its position as a major public health concern (World Health Organisation (WHO) 2010a). Average blood lead levels of Australians are now estimated to be below 5 μ g/dL (National Health and Medical Research Council (NHMRC) 2015) following the removal of lead in petrol and the resultant reduction of aerosol lead concentrations in major metropolitan centres (Department of the Environment and Heritage 2004). Yet, significant populations, especially children, around Australia continue to experience ongoing lead emissions and return elevated BLLs, not only above 5 μ g/dL but also above 10 μ g/dL (Lesjak et al. 2013; Simon et al. 2015a).

The studies undertaken as part of this thesis contribute to a more complete contemporary picture of the current state of lead in Australia, from emission volumes and regulations (Chapter Two), to measurement in different environmental media from contemporary and legacy sources (Chapter Three), to the impacts and consequences of lead to the environment and human health (Chapter Four). The research presented in this thesis demonstrates that lead exposure remains an ongoing environmental and human health issue in Australia. The studies presented in this thesis have not only measured total concentrations of environmental lead (*inter alia* other co-emitted contaminants) they have apportioned sources to historical and ongoing emissions. An underpinning research goal, has been to raise the issue of legacy and contemporary exposures more directly in the public health arena. The intent of the research has been to use evidence-based data to persuade industry and government authorities to further reduce and ultimately eliminate ongoing emissions and undertake appropriate remedial action to protect against historical emissions.

5.1 Historical emissions causing contemporary risks

Leaded petrol emissions have been identified previously as being responsible for elevated BLLs in Australia (Donovan 1996; National Health and Medical Research Council (NHMRC) 2009). While this is a reasonable assumption in locations where there are no other major sources of lead emissions, petrol (and/or paint) has been promoted as a major source in locations with historical or ongoing mining and smelting operations (Woodward-Clyde 1993). This argument has taken advantage of the lack of information on the volumes of lead emissions from petrol consumption in Australia over the period of its use from 1932-2002 (Cook and Gale 2005). Chiaradia et al. (1997) concluded that 90 % of lead in urban areas was sourced from leaded petrol, a source that was driven by the fact that 75 % of the lead used in petrol was emitted through the exhaust (U.S. EPA 1986).

Recent studies conducted in the United States of America (US) demonstrated the ongoing exposure and health effects from leaded petrol emissions despite the phase out of leaded petrol almost twenty years ago (Mielke et al. 2010; Mielke et al. 2011). These studies showed that the consequence of emitting five million tonnes of lead from leaded petrol continued to expose children in urban areas to fine dust-lead rich particles, which is subject to re-entrainment in the environment (Laidlaw et al. 2012). By contrast, Australia's situation with respect to total lead emissions from petrol combustion was previously unknown, despite our own extensive usage of leaded petrol. Consequently, it was not possible to evaluate its effects as a component of contemporary lead exposures.

5.1.1 Leaded petrol emissions

Paper One (Chapter Two) in this thesis collated the largest and most complete collection of historical leaded petrol records which were used to calculate lead emissions resulting from 70 years of leaded petrol consumption in Australia (Kristensen 2015). This is the first study in Australia to account completely for total lead emitted from a single lead source. Assigning emission volumes for individual states and territories in the pre-1958 period was hindered by lack of available records. However, the most prominent years of leaded petrol consumption (i.e. post 1958) and the associated emissions were calculated within state and territories to determine the locations and time period most affected by leaded petrol emissions.

The calculated 240,510 tonnes of lead released across Australia from petrol combustion pales in comparison to volumes released in the US, which is not unexpected considering the population disparities between the two countries. Population was shown to be a key factor in driving the consumption of leaded petrol and the consequent emissions. The emissions from Australia's two most populous states, NSW and Victoria, alone were so dominant that regulations to the allowable lead content in petrol in the 1970s implemented in these states had a marked impact on Australia's total lead emissions. These initial regulations proved effective at reducing lead emissions, although it was the more stringent regulations imposed Australia wide on the lead content in petrol throughout the 1990s coupled to the introduction of unleaded petrol in 1985 that resulted in the most dramatic reduction in lead emissions (Australian Environment Council 1977; Kristensen 2015).

Paper One (Kristensen 2015) also highlights the effectiveness of strict regulations for reducing and eliminating lead emissions. The success of the complete phase out of leaded petrol in Australia has seen ambient air lead concentrations fall well below guidelines (Department of the Environment and Heritage 2004) with concomitant decreases in childhood blood lead levels (Figure 5.1), a pattern that was paralleled internationally (Annest et al. 1983; Thomas et al. 1999). The calculated quantities of lead released into the Australian environment from petrol combustion provides context with which to evaluate the level of current lead emissions as well as potential contemporary exposures via these legacy sources.



Figure 5.1: Declining mean blood lead levels (BLL) in Australian children living in capital cities and lead emissions. Blood lead data from literature (Bloom et al. 1974; Garnys et al. 1979; De Silva and Donnan 1980; Gan et al. 1982; Hopper et al. 1982; McBride et al. 1982; Cooney et al. 1989; Fett et al. 1992; Donovan 1996; Cowie et al. 1997) and petrol lead emissions from Kristensen (2015).

Contemporary exposures to historical lead emissions can be measured and identified in urban communities via the use of lead concentrations and isotopic compositions. Studies conducted into contemporary lead exposure in Sydney determined that soil lead, containing lead from petrol, was the main source of exposure to residents (Laidlaw et al. 2014). Investigation of the direct exposure pathways of elevated BLLs over five years in Sydney found significant relationships not only to soil lead, but to lead contained in interior house dust (Gulson et al. 2014). These two recent studies in Sydney demonstrate BLLs from contemporary exposures are directly linked to historical emissions from leaded petrol.

Further contemporary exposures to historical emissions exist beyond the significant reservoir of lead found in soil. Paper Three (Chapter Three) showed atmospheric deposition to be the major driver to lead content in wines from McLaren Vale and Langhorne Creek, South Australia, over the last six decades. Apportionment of the source of lead using lead isotopes revealed leaded petrol, from atmospheric emissions and depositions, as the dominant contributor to lead in the wine (Kristensen et al. 2016). The primary purpose of this study was to use wine as a proxy in order to reconstruct atmospheric lead conditions beyond the availability of lead reported in air monitoring data and to evaluate the influence of multiple industrial sources to the regional air shed.

Significant reductions to the lead concentration in wine were concordant with regulations imposed on the lead content in petrol (Kristensen 2015; Kristensen et al. 2016). Low concentrations $(1 - 5 \mu g/L)$ in wine below Australian drinking water guidelines of 10 $\mu g/L$ (National Health and Medical Research Council (NHMRC) 2011) were evident in wine post leaded petrol, despite the proximity of local lead mining operations to the McLaren Vale and Langhorne Creek wine regions. Although there are also guidelines relating to the

maximum allowable lead concentration in wine (International Organisation of Vine and Wine (OIV) 1995), these guidelines were not formulated on the basis of acceptable impact on health, rather they were lowered in response to levels achievable by the wine industry (Médina et al. 2000), which reflected falling atmospheric lead levels from the reduction of lead in petrol (Kristensen et al. 2016).

Paper Three (Chapter Three) also showed the legacy of leaded petrol emissions to the environment, including its effect on Australia's agriculture and produce. It demonstrated that the argument that historical lead sources are resolved and in the past is incorrect. Complete quantification of leaded petrol emissions (Kristensen 2015) and the identification and measurement of petrol lead in wine (Kristensen et al. 2016), has enabled a more developed understanding of the overall impacts of atmospheric lead concentrations resulting from leaded petrol emissions in Australia.

Historical lead emissions, distributed throughout Australian soils and dusts, still contribute to contemporary exposure as they are subject to natural cycling processes and remobilisation. Emissions of naturally occurring metals, including lead, from natural process such as fire have been calculated to be in the range of 12 thousand tonnes per year (Nriagu 1989). With the added burden of contaminants to the environment, concern is growing regarding toxic smoke and particulates from bushfires (Weinhold 2011; Kristensen and Taylor 2012). The potential for environmental stores of historical lead emissions to be remobilised through fire events has been demonstrated in north and south America (Odigie and Flegal 2011; Odigie et al. 2015), as well as Australia (Kristensen et al. 2014).

Paper Four (Chapter Three) was the first study in Australia to show that industrial lead is remobilised during bushfires and that it represents a small, but additional potential source of exposure. Although the lead concentrations measured were low, they were released from purportedly pristine environments in Australia, raising concern as to the potential remobilisation of toxic substances during fire events stored in more contaminated regions of Australia (e.g. Mount Isa, Port Pirie, Sydney). This issue warrants further consideration given Australia's vulnerability to extreme wildfire events. Further, lead isotopic compositions measured in the ash samples confirmed significant portions of lead released from the bushfires were from historical leaded petrol emissions (Kristensen et al. 2014).

5.1.2 Mining and smelting emissions

Leaded petrol is not Australia's only significant former historical lead emission source as lead mining and smelting operations have started and ceased across Australia for over 170 years (Drew 2011). One notable example is the Pasminco Cockle Creek Smelter in Boolaroo, NSW which, until its closure in 2003, maintained elevated lead in air levels from the 10-20 tonnes of lead that were emitted yearly (NPI 2010). Rehabilitation of the smelter site and remediation of surrounding domestic residences commenced in 2007 under the Lead Abatement Strategy (LAS) (Ferrier Hodgson 2015). However, despite the LAS being EPA sanctioned, the effectiveness of the strategy in eliminating contemporary exposure to

historical lead emissions was never assessed adequately.

The investigation presented in Paper Eleven (Chapter Four) demonstrated the failure of the LAS in achieving its primary goal "to reduce the current potential exposure for residents of the nominated properties that could arise from previous lead dust deposition such that the exposure levels from lead dust deposition after the LAS has been completed are within acceptable limits during everyday living" (Zines 2007). The findings of Paper Eleven reveal that exposure to lead contamination from soil had not changed substantially, with no statistical difference in soil lead concentrations between pre- and post-abatement samples and between abated and non-abated houses (Harvey et al. 2015). Additionally, antimony, arsenic, cadmium and zinc soil contamination was also measured together with lead in playgrounds, sports fields and other publically accessible spaces to comprehensively evaluate the risk of toxic metal exposure across Boolaroo above 1000 mg/kg, historical lead emissions continue to be a contemporary exposure source and have the potential to cause harm to children residing in Boolaroo.

The remediation strategy presented and applied in Boolaroo was not the only option available and did not adhere to world's best practise (Dybowska et al. 2006). Successful remediation post smelter shut down or where other excessive lead contamination has occurred has been carried out in locations worldwide (Farrell et al. 1998; Blacksmith Institute 2011). The US Environmental Protection Agency is committed to remediation of hazardous waste sites through their Superfund database, the US government's dedicated contaminated land clean-up program. The towns of Hayden, Arizona hosting the Asarco smelter and Kellogg, Idaho hosting the Bunker Hill smelter are two examples of successful remediation following toxic metal contamination from smelter emissions (U.S. EPA 2015a, b). Aspects that set these cases apart from the LAS used in Boolaroo are the complete assessment of the region and the remediation of the total environment as well as long term monitoring and continual site review. The Bunker Hill site was listed as a Superfund site in 1983, yet the clean-up continues and blood lead testing is ongoing (U.S. EPA 2015b).

In response to the findings of Paper Eleven, the NSW EPA has established a Lead Expert Working Group tasked to undertake a review of the LAS (NSW EPA 2015). The Lead Expert Working Group, in addition to evaluating the LAS, will advise the EPA on "*cost effective, long term options for management of black slag and lead contaminated soils*" in Boolaroo and "*measures to protect the community from ongoing and future risks associated with legacy contamination arising from the former Pasminco lead smelter*" (NSW EPA 2015). Actions implemented to date include a blood lead monitoring program with initial testing of children (n=73) returning BLLs below the current guideline of 5 μ g/dL (Cronshaw 2015).

While mining operations in Broken Hill are still ongoing, the transport of lead and zinc ore concentrates in uncovered wagons ceased in 1996 after the EPA mandated that the rail wagons were to be covered. The extension of mining-related emissions along train lines

was first reported in the Port Pirie Lead Study (Body 1986). Evidence shows that these historical emissions endure in the environment resulting in contemporary exposure in communities along the train line (Smith 2012). Despite successful implementation of regulations to eliminate this emission source, these ore bearing trains passed through several towns with no awareness of the toxic substances contained within, as such, the ongoing exposure to lead to both people and adjoining ecosystems from historical depositions remained unknown.

Paper Five (Chapter Three) characterised the lead (and zinc) originating from the train lines and demonstrated the unchanged rate of dispersal from all train lines out of Broken Hill (Kristensen et al. 2015). While the footprint of lead emissions from rail transport of lead concentrates was focused within 150 m of the train line, Paper Five demonstrated effectively the lasting consequences of even small, but longitudinally distributed, emissions to the environment. This study demonstrated the effect of transporting toxic metals, such as lead, from mine sites on environmental quality adjacent to train lines. It is not the only example of uncovered transport problems associated with the movement of hazardous materials. Transport of lead concentrate to the Port of Esperance, WA, between 2005-2007 resulted in lead contamination in the community, including elevated BLLs (mean 7.5 μ g/dL) (Gulson et al. 2009). With half of Australia's commodities transported by rail, of which 80 % comprises iron ore and coal (Bureau of Infrastructure Transport and Regional Economics (BITRE) 2014) the potential exists for the widespread dispersion of mine products. The distribution of fine particulates escaping from uncovered rail wagons containing toxic metals causes not only health consequences at the destination port (eg. Esperance, WA (Gulson et al. 2009) and Townsville, QLD (Queensland Government 2010; Taylor 2015)), but results in an accumulation of toxic substances along the train lines.

Paper Five raised concerns that in an arid country, with regions prone to dust storms, reentrainment of surficial lead will continue to accumulate in homes, which then would have the potential to cause exposure in communities proximal to the contaminated train lines. The situation extends beyond Australia, with the fugitive losses due to the transport of lead products having caused environmental harm extending from ancient Roman mining (Renson et al. 2008) to some of the world's largest mining and smelting operations in the United States (Seeger 2008). Lead contamination ensuing from the production and train transport of mine products has affected multiple communities and environments to the extent that the United States Superfund program has been involved in the clean-up, particularly between the lead mining district and the Doe Run lead smelter in Missouri (U.S. EPA 2011, 2012b, a).

Papers Three, Four and Five (Chapter Three) regarding historical lead emissions contain the same message: that the legacy of lead continues to affect environmental quality and human health long after initial emission and deposition and highlights the difficulties facing complete elimination of exposure to lead. While these contemporary exposures to historical lead emissions are generally on a smaller scale compared to their original extent (e.g. leaded petrol emissions) or even to current emissions of lead from mining and smelting operations (e.g. Mount Isa, Port Pirie and Broken Hill), they still add to the total body burden of ingestion and inhalation of lead. Awareness of these point source exposures to historical lead emissions is important in evaluating the overall lead burden to populations and identifying sources to prevent ongoing exposure. Despite indications that these legacy exposure sources do not raise BLLs above the 5 μ g/dL guidelines (Cronshaw 2015), every effort must be made to eliminate lead exposure given the evidence there is no lower threshold to the negative health effects of lead (Earl et al. 2015).

5.2 Current emissions causing significant exposures

Ongoing emissions from mining and smelting operations, particularly in Mount Isa, Port Pirie and Broken Hill generate thousands of tonnes of lead annually (NPI 2015a). Combined, Mount Isa, Port Pirie and Broken Hill account for the longest and largest ongoing lead emissions in Australia (Figure 5.2). Lead in air levels has been monitored by industry since the 1970s (although the data is not publically accessible) and by the government in Mount Isa since 2009 (Queensland Government 2013) and in Port Pirie since 1995 (Dougherty 2006). Blood lead screening programs have been ongoing in Broken Hill since 1991 (Phillips and Hall 1994) and in Port Pirie since 1979 (Wigg et al. 1988). Despite continual environmental and blood lead monitoring, ongoing emissions are causing ongoing exposure to children in these communities. The exposures cause impairment to cognitive function including loss of IQ points which has been demonstrated to occur at BLLs below 10 μ g/dL (National Toxicology Program 2012) including specifically in Broken Hill and Port Pirie (Earl et al. 2015).



Figure 5.2: Distribution of total lead emissions (257 tonnes) around Australia for the 2013/2014 reporting period including the proportion of emissions from Mount Isa, Port Pirie and Broken Hill against state totals (NPI 2015a).

The large volumes of current lead emissions concentrated in Mount Isa, Port Pirie and Broken Hill (Figure 5.2) continue to affect environmental quality and human health. The conditions in Port Pirie have been described as "*living in a sea of lead*" (Simon et al. 2007) highlighting the inescapable nature of ongoing emissions. This thesis has demonstrated that

significant sources of ongoing exposure to children are depositions of emissions containing lead (as well as arsenic and cadmium) on playgrounds across lead mining and smelting communities (Taylor et al. 2013; Taylor et al. 2014b). The specific case studies presented in Papers Seven, Eight and Ten are discussed in section 5.2.1 for Port Pirie and section 5.2.2 for Broken Hill.

5.2.1 Port Pirie, South Australia

In Port Pirie, lead concentration in surface soils increases with proximity to the smelter with background levels not reached until well beyond the outskirts of town (de Vries et al. 1975; Cartwright et al. 1976; Merry and Tiller 1978; SA Health 2013). The rate of lead dust exposure on playgrounds determined in Paper Seven (Chapter Three) follows the soil concentration trend with highest concentrations of lead in dust on playgrounds closest to the smelter (Taylor et al. 2013). Upon completion of the study in 2011, the results were supplied to Port Pirie City Council and Nyrstar Port Pirie Smelter (hereafter referred to as Nyrstar). A washing regime for the playgrounds was implemented in 2012 jointly by Port Pirie Council and Nyrstar with 23 washes a week over nine playgrounds (Nyrstar 2015). Following peer review and formal publication of Paper Seven (Taylor et al. 2013) and subsequent media attention surrounding the results, the washing regime was revised further: forty-nine washes were to be carried out weekly on double the number of playgrounds (Nyrstar 2015). Subsequent to this research, signage has been placed in playgrounds around Port Pirie (Figure 5.3) reminding children and parents to wash hands after playing on playgrounds.



Figure 5.3: Signage put up at Foreshore Playground, Port Pirie.

While acknowledging that the changes to the washing regime were a positive response to identified lead exposure in playgrounds, the question arises as to whether this is an effective strategy considering the vast ongoing lead emissions from the smelter. The follow up study, Paper Ten (Chapter Four), assessed the efficacy of the implemented washing scheme for reducing children's exposure to toxic metals on playgrounds. The study outcomes demonstrated that the reduction to toxic dust was short term with unsafe exposures reached

within hours of washing (Figure 5.4) (Taylor et al. 2015b). A further update to the washing regime resulted in an increase to 81 washes weekly to 25 playgrounds. Other recent (2015) additions to the program included washing public seats and footpaths (2 washes weekly to 16 locations) and bus shelters (43 locations a week) in Port Pirie (Nyrstar 2015). This follow up study was critical in demonstrating the severity of the lead emissions contributing to exposure, regardless of action undertaken. Without this study, the washing of playgrounds may have been viewed as satisfactory in protecting children from exposures and led to complacency regarding exposure risk. The effect of this evidence-based research maintained pressure on the Port Pirie Council and Nyrstar, to address ongoing exposure risk from smelter emissions.



Figure 5.4: Predicted hourly lead exposure risk $(\mu g/m^2)$ from timed play following playground washing (Taylor et al. 2015b).

These two exposure studies in Port Pirie have contributed to the smelter upgrade proposal to reduce atmospheric emissions. The proposed, and recently approved, smelter upgrade project (Nyrstar 2012) has been projected to cost AU\$514 million (Evans 2014). In addition, Nyrstar has promised \$3 million per year for 10 years for the new Targeted Lead Abatement Program (TLAP) with an additional \$5 million initially to accelerate objectives of the TLAP (Nyrstar 2015). The South Australia Government has also committed \$1.5 million a year for 10 years towards the TLAP. With 20 % of BLLs in Port Pirie children still above 10 μ g/dL (Simon et al. 2015a) the smelter upgrade to reduce emissions, in addition to the funding for a program to address exposures in the community, are essential to make the necessary further progress in protecting children against ongoing lead (*inter alia* toxic metals) emissions. Yet despite these advancements, no regulations or guidelines exist to assess other health impacts from smelter emissions including arsenic, cadmium and sulphur dioxide in Port Pirie. Additionally, the Australian lead in air guideline is not enforceable at all Port Pirie air monitoring stations (Taylor et al. 2014a).

5.2.2 Broken Hill, New South Wales

The results of the first playground study in Port Pirie (Paper Seven) raised concerns regarding the exposure of children to toxic metals in playgrounds at locations where significant volumes of toxic emissions are occurring. This resulted in Paper Eight (Chapter Four) and the application of the hand wipe method being applied in Broken Hill (Taylor et al. 2014b). Similar to Port Pirie, playgrounds closest to current mining operations were found to have the highest levels of toxic metals (arsenic, cadmium and lead) in dust on playgrounds. However, at Broken Hill a smaller exposure window of 10 minutes was used yet lead concentrations found on hands after playground use was higher than those found in Port Pirie (Taylor et al. 2013; Taylor et al. 2014b).

Upon completion of the playground study in Broken Hill, the Broken Hill City Council implemented a playground washing regime and placed signage in the playgrounds (Figure 5.5) notifying users of the need to wash their hands to reduce exposure to lead (as well as arsenic, cadmium and zinc). Further, this study has also contributed to the re-implementation of the Broken Hill Lead Program with \$13 million of funding from the NSW Government (Humphries 2015). This new intervention is just as critical to Broken Hill children as is action to those in Port Pirie. Average blood lead levels in Broken Hill are the highest in Australia with the geometric mean above the current guideline of 5 μ g/dL (Lesjak et al. 2013). This assessment of exposure to children has also been utilised in other studies for assessing children's exposure to metals from sources beyond mining and smelting operations (Taylor 2015).



Figure 5.5: Signage put up at Sturt Playground, Broken Hill.

The ongoing lead emissions from mining operations in Broken Hill have impacted more than just the local playgrounds. However, the traditional message produced by the city's mining companies and disseminated through the communities is that mining has caused limited impact to the environment in comparison to natural processes. To challenge this perception in Broken Hill, Paper Six (Chapter Three) demonstrated that lead contamination, which is only found in surface soils, is a result of atmospheric depositions from mining activities (Kristensen and Taylor 2016). Additionally, through the combination of historical documents and recent geochemical analysis, it was demonstrated that the high levels of lead in soils is only a recent occurrence, i.e. post the onset of mining and resource extraction, which again can be attributed only to mining operations.

In order to utilise effectively the recent government funding provided to Broken Hill to reduce ongoing exposure to lead, it is essential to address the source of exposure, to raise awareness and to change perceptions as to the cause of lead contamination. Maintaining the attitude in the Broken Hill community that the lead contaminated soils are the result of natural mineralisation and weathering of the ore body is likely to adversely affect the efficiency and operation of the environmental lead program that has received \$13 million dollars of investment from the NSW Government. Paper Six (Kristensen and Taylor 2016) is important in directing the attention of exposure reduction action and the attitude of community members and mining companies alike.

5.3 Effectiveness of regulations in reducing exposure

Similar to Broken Hill, the source of exposure in Mount Isa was attributed to naturally occurring lead. Statements from the mining company in Mount Isa include: "*Mount Isa lies within a highly mineralised area. Lead occurs naturally within soils across the region. Therefore, when considering the issue of managing the risks associated with lead in the Mount Isa community, it must be acknowledged that lead is a naturally occurring substance in the local area.*" (Xstrata 2007). A suite of research into environmental quality at Mount Isa are responsible for lead contamination and exposure (Taylor et al. 2009; Munksgaard et al. 2010; Taylor et al. 2010; Mackay et al. 2013). In response to this evidence the mining company and Queensland government have changed their message and acknowledged their role in lead exposure from ongoing lead emissions: "We are committed to the mission of informing the local community about how to live safely in an environment where lead exists both from natural and industrial sources." (Queensland Government et al. 2013)

Yet despite this recent acknowledgement and change in attitude as to the source of lead exposure in the community, mining and smelting operation in Mount Isa continues to be Australia's biggest emitter of not only lead, but arsenic and sulphur dioxide (NPI 2015b). These emissions continue to affect air quality, yet Mount Isa's mining and smelting facilities are exempt from Queensland governmental air quality guidelines. The Environmental Authority agreement that has been put in place of government regulations allows for substantive variations from the air quality standards in Mount Isa. Paper Two (Chapter Two) demonstrated that this Environmental Authority agreement does not adequately protect children from harmful emissions and that regulations have been ineffective at reducing these emissions and exposures (Taylor et al. 2014a). The situation is not unique to Mount Isa with Nyrstar at Port Pirie also operating under a licence approval separate from existing state and federal government regulations. Additionally, the lack of enforcement of federal government regulations in these locations results in a further failure to protect children.
A recent example of the inadequacy of government regulations was demonstrated following the latest blood lead report from Port Pirie where the SA Health Director stated: "*Thanks to the efforts of the State Government together with Port Pirie Regional Council, Nyrstar and the community, the average blood lead level in children under five has significantly reduced to 4.6 \mug/dL.*" (Buckett 2015). However, media commentary on the information failed to reveal that in fact the average BLL of Port Pirie children had increased on the previous year's average. Additionally, almost half the children still presented with BLLs above the current guideline of 5 μ g/dL and the number of children above the old guideline of 10 μ g/dL had also increased slightly since the previous year (Simon et al. 2015b).

The blood lead - inhalation relationship is typically that every 1 μ g/m³ of lead in air contributes directly to 1.9 μ g/dL BLLs in children (National Environment Protection Council (NEPC) 1998; World Health Organisation (WHO) 2000). Indirectly, after considering the influence lead in air has on soil and dust lead concentrations, this increases to 5 μ g/dL (World Health Organisation (WHO) 2000). It has been shown that the risk to children having BLLs greater than 10 μ g/dL increases 36 % for every 0.01 μ g/m³ increase to lead in air (after adjustment for other sources of lead including historical paint) (Brink et al. 2013). Annual lead in air levels in Port Pirie reach up to 185 times this level (Taylor et al. 2014a) continuing to cause more than 20 % of Port Pirie children to have BLL above 10 μ g/dL despite efforts by the abatement program to minimise exposure (Simon et al. 2015a, b).

Short term lead exposures also affect health, yet guidelines do not exist on which to regulate or even bench mark short term emissions in Australia. Short term (24 hour) lead in air levels range from 12.8 μ g/m³ in Mount Isa to 22.6 μ g/m³ in Port Pirie (Taylor et al. 2014a). These levels become diluted when averaged over the standard one year average, which is in accordance with the national guideline (National Environment Protection Council (NEPC) 1998). Short term arsenic in air concentrations also exceed Queensland state guidelines of 6 ng/m³ (annual) with maximum concentrations over 24 hours of 2800 ng/m³ (Taylor et al. 2014a). Paper Two outlined the detrimental environmental quality conditions arising from the limited existence and application of governmental regulations.

Despite all the data analysed in Paper Two (Chapter Two) demonstrating the environmental quality associated with smelter emissions and regulations and licences obtained from government and industry sources, opposition and criticism about the accuracy of the information was raised by a former Queensland EPA director (Wilson 2015). To address this criticism Paper Nine (Chapter Four) considered further government and industry documents, including historical and draft documents, which outline the extent of pollution caused by the Mount Isa mine and smelting operations. These documents reveal the fact that this was known by the Queensland EPA and Mount Isa Mines companies (Taylor et al. 2015a). This evidence supports the original argument that regulation of toxic emissions in Mount Isa has not been effective and a failure to protect children's health is ongoing.

Of particular concern is the statement by Wilson (2015) that the regulations pertaining to Mount Isa emissions in restricting lead exposure to acceptable levels is successful on the basis that 95 % of children have a BLL below 10 μ g/dL. This demonstrates that the regulations are not successful in preventing harmful lead exposure as some children in Mount Isa still present with a BLL above 10 μ g/dL (Taylor et al. 2015a). Considering the new guideline of 5 μ g/dL (National Health and Medical Research Council (NHMRC) 2015), this increases the proportion of children to more than half that have been negatively impacted by smelter emissions as a result of inadequate regulation (Queensland Health 2011; Taylor et al. 2014c).

By raising these issues of ongoing lead emissions and the ineffectiveness of regulations and licences to reduce exposures, blood lead testing has recommenced in Mount Isa on a more regular basis (Stephens 2014). Although this outcome will allow a greater understanding of current BLLs in Mount Isa, it does not address the source of the problem, which are the ongoing emissions. Implementation of stringent emissions regulations and environmental guidelines with the added component of active enforcement is required, not only in Mount Isa, but in all locations across Australia that are emitting lead and other toxic substances. The effectiveness of past regulations, particularly in relation to leaded petrol, in eliminating lead emissions has been demonstrated in Papers One and Five (Kristensen 2015; Kristensen et al. 2015) as well as the successful reduction of exposure to the environment in Paper Three (Kristensen et al. 2016).

5.4 Consequences to environmental quality and human health The long legacy of lead and ongoing emissions has adversely affected both environmental quality and human health (Nriagu and Pacyna 1988). Lead is a persistent pollutant as it does not decay or decompose (World Health Organisation (WHO) 1995) and lead emissions remain dispersed in the environment. The effects of lead emissions in Australia on environmental quality have been demonstrated in this thesis from leaded petrol resulting in widespread emissions across Australia in Papers One, Three and Four (Kristensen et al. 2014; Kristensen 2015; Kristensen et al. 2016). The effects from mining activities have been demonstrated not only in and around Broken Hill in Papers Six and Eight (Taylor et al. 2014b; Kristensen et al. 2015). The effects of smelting activities has been demonstrated in Port Pirie in Papers Seven (Taylor et al. 2013) and Ten (Taylor et al. 2015b), together with Mount Isa in Paper Two (Taylor et al. 2014a) and Boolaroo in Paper Eleven (Harvey et al. 2015).

The consequences to human health from elevated BLLs caused by lead emissions are just as serious, if not more so, than the environmental impacts. The impact to environmental quality in terms of contaminated soil and water and elevated lead in air levels influences the health consequences of lead. The neurotoxic nature of lead affects brain development in children, one effect of which is a decrease in learning outcomes (Needleman 2004; Jusko et al. 2008). For example, Paper Twelve (Chapter Four) which analysed childhood educational performance using national standard testing, demonstrated that Broken Hill school students perform at significantly lower levels compared to Australian averages (Dong et al. 2015). Paper Twelve also demonstrated that poorer measurements in developmental areas including language and cognitive skills, emotional maturity and social competence were most dominant in children from areas within Broken Hill that had higher levels of lead (as well as arsenic and cadmium) contamination in soils (Figure 5.6) (Dong et al. 2015).



Figure 5.6: Predicted school test scores by subject by soil lead exposure risk (Dong et al. 2015).

With the ever increasing evidence of the effects of low levels of lead exposure and the guideline of blood lead intervention now at 5 μ g/dL, the studies conducted in this thesis bring important attention to a significant health and environmental problem. The effects of exposure are not isolated to Broken Hill and other Australian lead industry locations (Dong et al. 2015; Earl et al. 2015), but are global problems (Needleman et al. 1979; Lanphear et al. 2005; Magzamen et al. 2013; Skerfving et al. 2015). Importantly, the effects of exposure do not remit with age and the consequences often only become apparent many years after the initial lead exposure occurred (Bellinger 2011; Nriagu 2011; Dong et al. 2015; Earl et al. 2015).

5.5 Future directions to reduce exposure from environmental lead sources

Following the removal of lead from petrol, there remains a misconception that the problems relating to lead emissions have been resolved (Bellinger 2011). While some aspects, including the concentration of lead in air levels in cities have been resolved following the removal of lead from petrol, there continues to be ongoing exposures from historical and contemporary emissions of lead across Australia. The decline in BLLs of city children has been brought about through effective regulations, primarily through the removal of lead from petrol (Figure 5.7). Yet ongoing emissions are the primary driver of current elevated

BLLs in Australian children residing in affected locations including Mount Isa, Port Pirie and Broken Hill (Figure 5.7).



Figure 5.7: Declining blood lead levels (BLL) in Australian children and lead emissions. Blood lead data from literature (Bloom et al. 1974; Ouw and Bisby 1976; Garnys et al. 1979; De Silva and Donnan 1980; Gan et al. 1982; Hopper et al. 1982; McBride et al. 1982; Wigg et al. 1988; Cooney et al. 1989; Calder et al. 1990; Baghurst et al. 1992; Fett et al. 1992; Young et al. 1992; Calder et al. 1994; Phillips and Hall 1994; Donovan 1996; Cowie et al. 1997; Tong et al. 1998; Gulson et al. 2001; Mak et al. 2003; Gulson et al. 2006; Guttinger et al. 2008; Lesjak et al. 2013; Simon et al. 2015a), mining and smelting emissions from NPI (NPI 2015a) and petrol lead emissions from Kristensen (2015).

Although lead in air levels do not generally breach Australian guidelines, the existing guidelines may not be adequate in protecting people from the harmful impacts of lead emissions. Indeed, the NEPM lead in air guideline of 0.5 μ g/m³ (averaged over one year) was only implemented after the lead in air levels in Australia's populous capital cities were well below this level (National Environment Protection Council (NEPC) 1998; Department of the Environment and Heritage 2004). However, this is not the case Australia wide, with for example, Port Pirie lead in air concentrations exceeding annual NEPM guidelines every year from the implementation of monitoring to 2007 (Mitchell 2014).

International guidelines that are lower and more stringent in their allowable lead in air concentrations raise concerns that the Australian guidelines are not adequate to protect human health. The United States lead in air guideline of 0.15 μ g/m³ as a rolling three month average (U.S. EPA 2015c) is not only significantly lower, but reduces the dilution effect present in guidelines only requiring annual averages. Even lower lead in air guidelines are in effect in Europe (Austria, Belgium and Bulgaria) of 0.05 μ g/m³ (annual) (International Lead & Zinc Study Group 2014) and Israel 0.09 μ g/m³ (annual) (Israel Ministry of Environmental Protection 2011). This thesis has revealed that regulations and guidelines

are often set to be advantageous to industry and meeting their capabilities as opposed to human health protection (Taylor et al. 2014a).

In light of the substantial body of evidence of the toxicity of lead at low levels and the research demonstrating the contemporary exposures to historical and ongoing lead emissions, a complete review of relevant environmental guidelines is necessary. This review should include air, dust, sediment, soil and water standards as these are predicated on blood lead values above the new intervention standard of 5 μ g/dL along with the WHO provisional tolerable weekly intake (PTWI) of lead that has since been withdrawn (World Health Organisation (WHO) 2010b). The previous guideline established in 1979 was 1.5 μ g/m³ to be measured as a three month average. The current Australian guideline, which was updated in 1998 to be in line with the WHO, is again outdated as the guideline set by the WHO was intended to ensure 98 % of the population have blood lead levels below 10 μ g/dL, with a median of 5.4 μ g/dL (National Environment Protection Council (NEPC) 1998; World Health Organisation (WHO) 2000).

It is evident that the current national air quality guideline does not provide the necessary health protection in regards to the new lower blood lead guideline coupled to the evidence that there is no safe level of lead. Additionally, the absence of national guidelines for ambient air concentrations of arsenic and cadmium as well as short term (24 hour) lead in air guidelines restricts the capacity of regulations to protect human health comprehensively, particularly in locations adjacent to smelting facilities. The Queensland government has set annual air quality objects for arsenic (6 ng/m³) and cadmium (5 ng/m³) under the *Environmental Protection (Air) Policy 2008* (Queensland Government 2012).

Although these guidelines apply only to the state of Queensland, they are replaced locally at Mount Isa, where they are most needed, by a transitional environmental program that permits exceedances of state-wide standards (Taylor et al. 2014a). Recommendations of a maximum lead in air guideline of $0.3 - 0.5 \ \mu g/m^3$ as a moving monthly average with 0.5 $\mu g/m^3$ not to be exceeded were made in a review for the NEPC (Streeton 2000). Yet, these recommendations were not incorporated and short term lead in air concentrations above 0.5 $\mu g/m^3$, which are associated with the potential to increase BLLs, continue to be permissible because the current national air quality standard is based upon an annual average value.

Beyond the programs implemented and the funding allocations for lead programs in Port Pirie and Broken Hill, the most important aspect of the research in this thesis has been to re-awaken the awareness in communities, government and industry in regard to ongoing toxic metal contamination and contemporary exposures. Maintaining awareness, whether it relates to ongoing or historical emissions, will ensure action to eliminate exposures and improve environmental quality. With some of the highest legacy lead contamination contained in Sydney city soils, not only from the vast emissions from leaded petrol, but from the historical use of lead in paint, significant interest has been generated by the general public to understand the levels of toxic metals in their environment and to be proactive in preventing exposure. Participation in Macquarie University's free soil metals testing program, VegeSafe, has included over 850 participants from every state and territory in Australia (Macquarie University 2015). The program has engaged the community to increase awareness and address the legacy and contemporary exposure risks to lead from historical sources such as leaded petrol and paint.

Raising awareness in the scientific and public arena of the negative effects of anthropogenic activities on environmental quality and human health has been essential in bringing about positive changes in the past. One of the biggest campaigns was led by Clair Patterson for the removal of lead from petrol with which he described the emissions to be causing a *"severe chronic lead insult*" (Patterson 1965). Despite the long fought battle, Patterson's evidence-based approach was successful and changed the future of environmental research (Flegal 1998; Needleman 1998; Nriagu 1998).

The role of effective governmental regulation has long been understood to be crucial to preventing exposure and protecting children. Over 100 years ago, Australian doctor Alfred Turner discovered children were being severely poisoned by lead paint and declared "*the curative treatment consists essentially in removing the child from the source of the poison*" and that lead exposure to children is "*a matter that calls for legislative interference*". (Turner 1909; Taylor et al. 2011). In the absence of further current government regulatory action, programs like VegeSafe (Macquarie University 2015), as well as similar other national (Healthy Homes & Gardens 2015) and international programs (New York Government 2015), will allow the public to be directly involved with environmental scientists in understanding their exposure risks and executing effective action.

5.6 Conclusion

This thesis has applied an evidence-based approach to evaluate the contemporary exposures resulting from historical and ongoing lead emissions in Australia. The research presented in this thesis explores multiple, yet interconnecting, aspects relating to lead emissions. This thesis has determined the quantity of lead emissions, previously unmeasured, resulting from leaded petrol consumption and evaluated these emissions and depositions in the context of ongoing mining and smelting operations. The success of effective regulations on leaded petrol was demonstrated while the ongoing emissions from mining and smelting operations continues to adversely affect environmental quality and expose children.

The results from this thesis add to the body of work on environmental quality surrounding sources of lead emissions conducted in the 1980s and 1990s. However, this thesis provides an updated and contemporary assessment in the context of the lowered blood lead guideline and the cessation of leaded petrol consumption. A more complete understanding of the historical and current emissions of lead to the Australian environment can facilitate necessary intervention and remedial action to protect the health of Australians.

The studies in this thesis have challenged the misconception that the problem of lead contamination causing exposures from lead emissions has gone away. The research has demonstrated clearly that the problem has not been resolved, but has been inadequately

measured and in some regards ignored in Australia. This thesis has not only measured contemporary exposures of lead and identified sources of lead emissions, it has revealed additional sources and routes of exposure not previously considered. These findings have resulted in new intervention programs and have helped revise the misguided paradigm that the problem of lead has been resolved.

The recent lowering of the blood lead guideline in Australia is a step in the right direction to protecting children from the negative consequences of lead. However, there remains more to be done, including bringing the rest of Australia's environmental lead guidelines in line with more stringent international guidelines and expectations. The research included in this thesis adds to the scientific body of evidence essential to the process of developing updated environmental quality guidelines and standards in Australia.

5.7 References

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APPENDICES

Appendix A: Supplementary Information for Paper One

Supplementary Figure S1 Supplementary Table S1 Supplementary Table S2 Supplementary References

Appendix B: Supplementary Information for Paper Two

Supplementary Data S1 Supplementary Data S2 Supplementary Data S3 Supplementary Data S4 Supplementary Data S5 Supplementary Data S6

Appendix C: Supplementary Information for Paper Three

Supplementary Table S1 Supplementary Table S2 Supplementary Table S3

Appendix D: Supplementary Information for Paper Four

Supplementary Table S1 Supplementary Table S2 Supplementary References

Appendix E: Supplementary Information for Paper Five

Supplementary Table S1 Supplementary Figure S1 Supplementary Figure S3 Supplementary Figure S4 Supplementary Figure S5 Supplementary Figure S6

Appendix F: Supplementary Information for Paper Six

Supplementary Table S1 Supplementary Figure S1 Supplementary Figure S2 Supplementary Figure S3 Supplementary Figure S4

Appendix G: Supplementary Information for Paper Seven

Supplementary Table S1 Supplementary Table S2 Supplementary Table S3 Supplementary Table S4 Supplementary Figure S1

Appendix H: Supplementary Information for Paper Eight

Supplementary Table S1 Supplementary Figures S2a-e Supplementary Table S3 Supplementary Table S4 Supplementary Figure S5

Appendix I: Supplementary Information for Paper Ten

Supplementary Figure S1 Supplementary Figure S2 Supplementary Table S3 Supplementary Table S4

Appendix J: Supplementary Information for Paper Eleven

Supplementary Figure S1 Supplementary Table S2 Supplementary Table S3 Supplementary Table S4 Supplementary Table S5

Appendix K: Supplementary Information for Paper Twelve

Supplementary Table S1 Supplementary Figure S2 Supplementary Table S3 Supplementary Table S4 Supplementary Table S5 Supplementary Table S6 Supplementary Table S7 Supplementary Table S8 Supplementary Table S9 Supplementary Table S10 Supplementary Table S11 Supplementary Table S12 Supplementary References

Appendix A

Supplementary Figure S1: State marketing areas for leaded petrol sales (adapted from Australian Institute of Petroleum¹). The state marketing areas used for the sales of leaded petrol follow the state borders with the following exceptions: the Murwillumbah district in New South Wales (NSW) is included in the Queensland (QLD) state marketing area, the Broken Hill-Wilcannia district of NSW and the Murrayville district of Victoria (VIC) are included in the South Australia (SA) state marketing area, the Riverina district of NSW is included in the VIC state marketing area and the Australian Capital Territory (ACT) is included in the NSW state marketing area.



Year	Australia	Year	Australia		Year	Australia		Year	Australia	Year	A	ustralia
1932	Leaded petrol	1936«	1159.3 ML	3	1943«	1577.5 ML ⁴	1	948«	1836.6 ML ⁵	1953«	31	109.3 ML ⁶
	introduced ²	1937«	1282.0 ML		1944«	1691.1 ML ³	1	949«	1963.1 ML ⁶	1954«	37	459.4 ML ⁶
1933«	822.8 ML ⁷	1938«	1513.8 ML		1945«	1304.7 ML ⁵	1	950«	2240.4 M L ⁶	1955«	38	815.0 ML ⁶
1934«	$945.6 \mathrm{ML}^7$	1939«	1591.1 ML ⁴	5	1946«	1686.6 ML ⁵	1	951«	$2748.6 \mathrm{ML^6}$	1956«	41	133.8 ML ⁶
1935«	963.8 ML ⁷	1942«	1204.7 ML	-	1947«	1623.0 ML ⁵		952«	2966.3 ML ⁶	1957«	4	361.5 ML ⁶
Year	Australia*	$NSW^{\#}$		VIC	QLD		SA		TAS	WA		NT
1958	4807.5 ML ⁸	1639.0 MI	[8	1480.9 ML ⁸	655.9 N	ΛL^8	502.2 ML ⁸		160.9 ML ⁸	357.0 ML ⁸		11.7 ML ⁸
1959	5187.2 ML ⁹	1772.5 MI	67	1595.1 ML ⁹	714.5 N	ΛL^9	537.6 ML ⁹		172.7 ML ⁹	382.1 ML ⁹		$12.6 \mathrm{ML}^9$
1960	$5628.9 \mathrm{ML}^9$	1949.6 MI	67	1741.4 ML ⁹	765.5 N	ΛL^9	562.9 ML^9		184.8 ML^9	410.7 ML^9		14.1 ML^9
1961	5855.7 ML ⁹	2043.4 MI	67	1791.0 ML ⁹	790.7 N	ΛL^9	592.2 ML ⁹		189.1 ML^9	433.3 ML ⁹		16.1 ML^9
1962	6285.4 ML ⁹	2206.9 MI	67	1899.5 ML ⁹	855.4 N	ΛL^9	632.5 ML ⁹		203.2 ML^9	470.9 ML^{9}		17.2 ML ⁹
1963	6736.0 ML ⁹	2358.2 MI	67	2036.2 ML^9	914.1 N	ΛL^9	678.9 ML ⁹		218.2 ML^9	511.6 ML ⁹		18.8 ML^9
1964	$7308.0 \mathrm{ML}^9$	2558.2 MI	L9	2187.0 ML ⁹	1009.9	ML ⁹	739.4 ML^9		233.6 ML^9	558.6 ML ⁹		21.4 ML^9
1965	7752.8 ML^9	2705.8 MI	L9	2307.2 ML ⁹	1075.2	ML^9	790.9 ML^9		250.1 ML^9	602.4 ML^9		21.2 ML^9
1966	8053.1 ML ⁹	2802.0 MI	6]	2390.0 ML^9	1123.3	ML^9	$807.6 \mathrm{ML}^9$		$259.8 \mathrm{ML}^9$	647.1 ML ⁹		23.4 ML ⁹
1967	8492.4 ML^9	2959.5 MI	67	2506.2 ML ⁹	1181.9	ML^9	842.0 ML^9		275.8 ML^9	700.2 ML^9		26.9 ML^9
1968	8984.5 ML ⁹	3140.4 MI	L9	2635.6 ML ⁹	1249.3	ML ⁹	867.9 ML^9		286.7 ML^9	771.0 ML ⁹		$33.6 \mathrm{ML}^9$
1969	$9610.1 \mathrm{ML}^9$	3343.6 MI	L9	2790.2 ML ⁹	1349.0	ML ⁹	923.8 ML ⁹		301.0 ML^9	854.7 ML ⁹		47.9 ML ⁹
1970	$10178.8 \mathrm{ML}^9$	3564.8 MI	L9	2941.8 ML ⁹	1418.4	ML ⁹	961.8 ML ⁹		311.6 ML^9	921.0 ML^9		59.4 ML^9
1971	10706.1 ML^9	3770.4 MI	L9	3088.4 ML^9	1495.0	ML ⁹	$992.6 \mathrm{ML}^9$		321.9 ML^9	971.7 ML ⁹		66.2 ML ⁹
1972	11230.5 ML ^{9, 10}	3919.6 MI	L9, 10	3267.8 ML ^{9, 10}	1598.7	ML ^{9, 10}	1029.5 ML ^{9, 1}	10	$335.4 \text{ ML}^{9, 10}$	1007.9 ML ⁵	, 10	71.7 ML ^{9, 10}
1973	$12088.5 \mathrm{ML}^9$	4177.4 MI	L9	3474.4 ML ⁹	1785.5	ML ⁹	1122.1 ML ⁹		360.3 ML^9	1092.3 ML ⁹		$76.6 \mathrm{ML}^9$
1974	12490.8 ML^9	4311.9 MI	L9	3555.9 ML ⁹	1834.2	ML ⁹	1193.0 ML ⁹		372.3 ML^9	1140.7 ML ⁹		82.7 ML ⁹
1975	$12959.9 \mathrm{ML}^9$	4423.7 MI	67	3698.8 ML ⁹	1954.9	ML ⁹	1223.4 ML ⁹		377.5 ML^9	1198.5 ML ⁹		83.2 ML ⁹
1976	13546.6 ML ⁹	4532.5 MI	L9	3915.0 ML ⁹	2045.7	ML ⁹	1290.2 ML ⁹		394.5 ML ⁹	1275.1 ML ⁹		93.6 ML ⁹
		2553 ML^	11	2910 ML^ ¹¹	953 MI		965 ML^ ¹¹		140 ML^11	908 ML^ ¹¹		
		200.5 ML		4								4
1977	14212 ML^{12}	4792.8 MI	6]	4014.8 ML ⁹	2155.5	ML ⁹	1369.0 ML ⁹		$412.6 \mathrm{ML}^9$	1370.1 ML ⁵		97.5 ML ⁹
1978	14602 ML^{12}	4880.4 MI	67	4146.2 ML ⁹	2260.9	ML^9	1377.8 ML ⁹		$418.8 \mathrm{ML}^9$	1419.0 ML ⁵		99.0 ML ⁹
1979	14888 ML ¹²	4977.8 MI	L9	4208.6 ML^9	2364.5	ML ⁹	1371.9 ML ⁹		426.7 ML^9	1432.5 ML ⁹		105.9 ML^9
1980	14771 ML^{12} , ¹³	4977.8 MI	L9	4130.5 ML ^{9,13}	2382.3	ML ⁹	1417.1 ML ⁹		424.6 ML^9	1417.1 ML ⁹		109.5 ML^9
1981	14995 ML ^{12, 14}	5025.1 MI	L ¹⁴	4205.7 ML ¹⁴	2497.7	ML^{14}	1301.0 ML ¹⁴		417.9 ML^{14}	1432.5 ML ¹	4	115.1 ML ¹⁴
1982	15186 ML ^{12 15}	4951.8 MI	L ¹⁵	4280.0 ML ¹⁵	2642.6	ML ¹⁵	1324.7 ML ¹⁵		408.1 ML ¹⁵	1464.5 ML ¹	5, 16	114.2 ML ¹⁵
1983	15025.1 ML ¹⁷	4965.9 MI	L ¹⁷	4222.2 ML ¹⁷	2546.8	ML^{17}	1321.9 ML ¹⁷		404.1 ML^{17}	1446.4 ML ¹	6 17	117.9 ML ¹⁷
1984	15487 ML ^{1, 18}	5060.0 MI	L1	4339.0 ML ¹	2671.0	ML ¹	1371.0 ML ¹		423.0 ML^{1}	1499.0 ML ¹	61	123.0 ML^{1}
1985	15478.9 ML ^{18,19}	5026.2 MI	L ¹⁹	4355.9 ML ¹⁹	2676.5	ML ¹⁹	1366.8 ML ¹⁹		428.1 ML ¹⁹	1494.6 ML ¹	6 19	131.1 ML ¹⁹
		2408.2 MI 181 MI •2(L^20 0	2277 ML^20	986.9 N	M^{20}	863.3 ML^20		169.5 ML^20	1027.7 ML/	20	54.8 ML^20
1986	15091 ML ^{18,21 22}	4860.3 MI	L ²²	4230.3 ML ²²	2626.7	ML ²²	1344.3 ML ²²		420.7 ML ²²	1476.2 ML ¹	6, 22	132.5 ML ²²

Supplementary '	Table S1: Total	sales of leaded	petrol in A	Australia and l	by State or	Territory
(ML = Megalitres)	s)					

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$123.0 \mathrm{ML}^{12}$	$114.0 \mathrm{ML}^{23}$	$106.1 \mathrm{ML}^{24}$	$101.4 \mathrm{ML}^{25}$	91.8 ML ²⁶	87.7 ML ¹⁸	79.9 ML^{27}	69.2 ML ²⁸	85.9 ML ²⁸	57.7 ML ³⁰	52.0 ML ³¹	43.9 ML ³²	37.4 ML ³³	27.1 ML ³³	20.2 ML ³³	8.5 ML ³³	
1415.5 ML ^{16,12}	1351.8 ML ²³	1282.4 ML ²⁴	1192.7 ML ²⁵	1072.8 ML ²⁶	1004.9 ML^{18}	887.6 ML ²⁷	840.1 ML ²⁸	772.0 ML ²⁸	700.7 ML^{30}	616.1 ML ³¹	536.2 ML ³²	457.8 ML ³³	325.6 ML ³³	218.7 ML ³³	84.5 ML ³³	
394.5 ML ¹²	382.3 ML ²³	373.5 ML ²⁴	356.7ML ²⁵	329.5 ML ²⁶	314.6 ML ¹⁸	$301.1 \mathrm{ML}^{27}$	275.7 ML ²⁸	254.6 ML ²⁸	239.8 ML ³⁰	217.4 ML ³¹	193.8 ML ³²	172.2 ML ³³	143.5 ML ³³	121.4 ML ³³	52.5 ML ³³	
$1280.0 \mathrm{ML}^{12}$	1228.0 ML^{23}	1176.0 ML ²⁴	1071.2 ML ²⁵	975.9 ML ²⁶	932.4 ML^{18}	852.9 ML^{27}	731.3 ML ²⁸	652.2 ML ²⁸	595.5 ML ³⁰	537.8 ML ³¹	489.8 ML ³²	429.8 ML ³³	346.5 ML ³³	272.3 ML ³³	118.4 ML ³³	
$2492.6 \mathrm{ML}^{12}$	$2497.6 \mathrm{ML}^{23}$	2414.9 ML ²⁴	2212.1 ML ²⁵	2045.1 ML ²⁶	1965.1 ML ¹⁸	1863.3 ML^{27}	1650.0 ML ²⁸	1497.9 ML ²⁸	1387.3 ML ³⁰	1221.5 ML ³¹	$1050.7 \mathrm{ML}^{32}$	$930.0 \mathrm{ML}^{33}$	754.4 ML ³³	603.1 ML ³³	250.5 ML ³³	
4029.0 ML^{12}	3868.5 ML ²³	3692.7 ML^{24}	3328.3 ML ²⁵	2994.6 ML ²⁶	2808.7 ML ¹⁸	2662.8 ML ²⁷	2260.0 ML ²⁸	1989.5 ML ²⁸	1799.4 ML^{30}	1358.7 ML ³¹	1358.7 ML ³²	1150.5 ML ³³	901.0 ML^{33}	718.1 ML ³³	309.0 ML^{33}	
4583.3 ML ¹²	4387.7 ML ²³	4052.1 ML ²⁴	3668.0 ML ²⁵	3348.1 ML ²⁶	3120.6 ML ¹⁸	2877.5 ML ²⁷	2497.1 ML ²⁸	2219.6 ML ²⁸	2001.1 ML^{30}	1456.0 ML ³¹	1456.0 ML ³²	1184.0 ML ³³	908.8 ML ³³	682.4 ML ³³	271.2 ML ³³	
14317.6 ML ^{12,21}	13830.0 ML ²³	13097.7 ML ²⁴	11930.4 ML ^{13,25}	10857.8 ML ²⁶	10234.0 ML^{18}	9485.0 ML ²⁷	8323.3 ML ²⁸	7451.7 ML ²⁹	6781.5 ML ³⁰	5915.3 ML ³¹	5129.1 ML ³²	4361.8 ML ³³	3406.9 ML ³³	2636.1 ML ³³	1094.6 ML ³³	
1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	

*Totals may differ due to rounding #ACT included in value « Fiscal year (July-June) ^ Capital city consumption only • Canberra

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M V	WA						0.80 g/L* 0.805 g/L [#] Perth ¹¹)				0.745 g/L [#] ◆	$0.423 \text{ g/L}^{\# \times 16}$	0.798 g/L#◆	$0.564 \text{ g/L}^{\# \times 16}$	0.735 g/L [#] ◆	$0.344 \text{ g/L}^{\# \times 16}$	0.672 g/L#+	0.30 g/L	0.605 g/L ^{#+16}	0.685 g/L [#] + ¹⁶			0.50 g/L*	0.40 g/L* ⁴⁵	0.30 g/L*41,45	$0.28 {\rm g/L^{\# 13}}$	0.20 g/L^{*41}	0.1/ B/L
NT/TAS	CAT/IN						TAS: 0.64 g/L* ³⁵	$0.60 {\rm g/L^{\#11}}$	TAS: 0.50 g/L* ³⁵	TAS: 0.45 g/L* ³⁵	TAS: 0.45 g/L* ⁴¹														NT/TAS: 0.40 g/L ^{*45}	NT/TAS:	$0.30 \text{ g/L}^{*41, 45}$	NT/TAS:	0.20 g/L
C A	PC						0.79 g/L [#] Adelaide ¹¹				0.80 g/L* ⁴¹					0.65 g/L ⁴²	•	Adelaide:	2-7/g co.u			0.65 g/L* ⁴¹		0.55 g/L*	0.40 g/L* ⁴⁵	$0.30 \text{ g/L}^{*41, 45}$	$0.26 \mathrm{g/L^{\#13}}$	0.30 g/L^{*41}	U.40 B/L
OI D	Λrn						$0.672 \text{ g/L}^{\#}$ Brisbane ¹¹									0.84 g/L ⁴²	•	Brisbane:	0./4 g/L ⁻²			0.84 g/L^{*41}			0.40 g/L* ⁴⁵	0.30 g/L*41,45	$0.23 \text{ g/L}^{\# 13}$	$\begin{array}{c} 0.20 \text{ g/L}^{*41, 47} \\ 0.18 \text{ c/I}^{\#13} \end{array}$	U.10 B/L
						0.60 g/L* ³⁵	0.60 g/L [#] Melbourne ¹¹		0.50 g/L* ³⁵	0.45 g/L* ³⁵	0.45 g/L* ⁴¹					0.30 g/L^{42}	•	Melbourne: 0.30	g/L-2			0.30 g/L^{*41}		0.30 g/L*	0.25 g/L* ⁴⁵	0.20 g/L*41,45	$0.11 {\rm g/L^{\#13}}$	0.20 g/L^{*41} 0.14 $\sigma/T^{\#13}$	U.14 g/L
NSW	MCN					0.64 g/L* NSW 1 ³⁵	0.582g/L [#] Sydney ¹¹ 0.80 g/L [#] Canberra ¹¹)	0.45 g/L* NSW 1 ³⁵		0.4 g/L*NSW 1 ^{35, 40, 41} 0.84 g/L* NSW 2 ^{35, 41}														0.30 g/L* ⁴⁵	0.20 g/L* ^{41, 45}	$0.14 {\rm g/L}^{\#13}$	0.20 g/L* ⁴¹ 0.15 a/I #13	U.13 g/L
Anetralia	Austi alla	0.25-0.84 g/L+ 0.17-0.72 g/L ^{×34}	0.84 g/L* ³⁵	0.17-0.84 g/L+ 0.00-0.75 g/L ^{×36}	0.17-0.84 g/L+ 0.00-0.75 g/L ^{×37}	0.08-0.22 g/L• 0.01-0.11 g/L ^{×38}					0.40 g/L* ^{11, 39}							Unleaded petrol	available				0.15-0.40 g/L ⁴⁴					0.20 g/L* ¹³ 0.16 a/t #46	0.10 g/L
Voor	ICAL	1964	1967	1968	1969	1975	1976		1977	1979	1980	1982		1983		1984		1985		1986	1987	1990	1992	1993	1994	1995		1996	-

Supplementary Table S2: Concentration of lead in petrol in Australia and by State or Territory from 1964-2002.

	0.013 g/L^{*49}	0.005 g/L^{*49}	
			$Act \ 2000^{51}$
		Phase out ⁵⁰	uel Ouality Standards
			seulations National Fi
			complete: 0.005 g/L re
0.13 g/L ^{#48}			Leaded petrol phase out
1998	2000	2001	2002

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* Petrol regulation
Actual lead concentration averages
• Premium grade petrol
× Regular grade petrol

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Supplementary Data S1: Xstrata Mount Isa Mines Environmental Authority No. MIN102700011

This 135 page document can be viewed at: http://www.sciencedirect.com/science/article/pii/S1875963714000226

Supplementary Data S2: Xstrata Mount Isa Mines Transitional Environmental Program

This 18 page document can be viewed at: http://www.sciencedirect.com/science/article/pii/S1875963714000226

Supplementary Data S3: Graphic from the Queensland Department of Environment and Heritage Protection's online air quality system for the maximum daily lead-in-air concentrations in each month during 2012 at The Gap monitoring station, Mount Isa. Note that the red guideline value set at 2 μ g/m³ is not reflected in any of the environmental planning instruments for Queensland or the Xstrata Mount Isa Mines licence. The lead-in-air standard for all of Queensland including Mount Isa is set at a maximum of 0.5 μ g/m³ averaged over a year.



Supplementary Data S4: Graphic from the Queensland Department of Environment and Heritage Protection's online air quality system for the maximum daily arsenic-in-air concentrations in each month during 2012 at The Gap monitoring station, Mount Isa. Note that the red guideline value set at 0.3 ng/m³ is not reflected in any of the environmental planning instruments for Queensland or the Xstrata Mount Isa Mines licence. The arsenic air quality objective for Queensland is set at a maximum of 6 ng/m³ averaged over a year for Queensland with Mount Isa having a special arrangement for the period of 2012-2016 (inclusive) of 21 ng/m³, 20 ng/m³, 18 ng/m³, 17 ng/m³, 15 ng/m³ for 2012, 2013; 2014, 2015 and 2016, respectively (Paper two, Table 1).



Supplementary Data S5: Graphic from the Queensland Department of Environment and Heritage Protection's online air quality system for the maximum 1 hour sulphur dioxide air concentrations in a month during 2012 at The Gap monitoring station, Mount Isa. Unlike Supplementary Data S3 and S4, the red line demarking the relevant Queensland air quality guideline is consistent with that stated in the NEPM (1998) and the *Environmental Protection (Air) Policy, 2008,* (QLD). However, the current allowable sulphur dioxide 1 hour limit for Mount Isa is set under their special Transitional Environmental Program (Paper two, Table 1; Supplementary Data S2) at 0.9955 ppm (or 2,500 μ g/m³) until the end of 2016.



Supplementary Data S6: Snapshot of hourly metals data from 15/01/2013 from the Queensland Government's Department of Environment and Heritage Protection online air quality system. The values presented in $\mu g/m^3$ are rolling 24 hour averages. The lead and arsenic values are not indexed against the NEPM (1998) standards or the relevant *Environmental Protection (Air) Policy, 2008,* (QLD) objectives for lead- and arsenic-in-air at 0.5 $\mu g/m^3$ and 0.006 $\mu g/m^3$, respectively, averaged over a year (Paper two, Table 2). Instead and contrary to Department advice, air quality is benchmarked against the non-statutory values shown as red lines in Supplementary Data S3 and S4 of 2.0 $\mu g/m^3/24$ hours and 0.3 $\mu g/m^3/24$ hours for lead- and arsenic-in-air.



Sample	Year	Lead [µg/L]	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb
PWD63	1963	123	2.368	1.094	16.81
PWDa65	1965	75	2.362	1.087	16.77
PWDb65	1965	75	2.346	1.077	16.61
PWD66	1966	110	2.351	1.082	16.78
PWB73	1973	77	2.367	1.083	16.74
SWD73	1973	42	2.368	1.097	16.86
PWD74	1974	130	2.353	1.085	16.86
PWC75	1975	210	2.358	1.083	16.75
PWB76	1976	328	2.359	1.080	16.69
SMW78	1978	65	2.369	1.097	16.80
PMW79	1979	22	2.429	1.152	18.54
PWD83	1983	29	2.344	1.070	16.58
PMW85	1985	32	2.416	1 1 39	17.72
PWB85	1985	47	2.369	1.089	16.85
PWB86	1986	92	2 3 5 9	1.080	16.00
CWC88	1988	45	2.339	1.000	17.61
CWC89	1989	32	2.404	1.096	17.01
SWC90	1990	36	2.370	1.090	17.07
SWB90	1990	10	2.307	1.093	17.07
CWC91	1990	19	2.384	1.005	17.00
SMW02	1991	82	2.401	1.133	1/.45
SMW92 SMW03	1992	0.2	2.380	1.133	14.45
CMW03	1993	21	2.381	1.119	17.22
CIVI W 95	1993	19	2.383	1.129	17.22
SWA94	1994	10	2.400	1.109	17.74
SWC94	1994	19	2.400	1.090	17.55
SWD95	1995	10	2.391	1.090	17.57
SWC93	1995	19	2.390	1.092	17.55
SWA90	1990	10	2.410	1.124	17.24
SWD97	1997	13	2.370	1.130	17.24
SWA77	1997	13	2.330	1.114	10.97
SW D90	1998	15	2.420	1.131	17.56
SWA90	1998	0.7	2.404	1.097	17.30
SW D99	1999	10	2.424	1.111	17.90
SWA99	2000	0.0	2.400	1.100	17.01
SWD00	2000	24	2.410	1.110	10.09
SWA00	2000	4.5	2.415	1.110	10.40
SWA01	2001	5.0	2.429	1.111	18.43
SWW02	2002	3.9	2.411	1.130	17.00
SWD02	2002	3.4	2.418	1.120	1/./4
SWA02	2002	/./	2.430	1.124	10.43
SWBU3	2003	3.9	2.377	1.141	11.23
SWA05	2003	4.0	2.434	1.125	18.02
SWB04	2004	4.1	2.420	1.110	1/.00
SWA04	2004	4.8	2.389	1.145	19.20
SWA05	2005	1.9	2.442	1.104	10.31
SWBUG	2006	0./	2.412	1.125	18.00
SWA06	2006	2.0	2.452	1.124	18.11
SWAU/	2007	2.8	2.401	1.149	17.66
SWB08	2008	2.1	2.398	1.132	1/.00
SWA08	2008	3.5	2.420	1.109	18.54
SWB09	2009	3.1	2.421	1.140	17.03
SWA09	2009	3.3	2.405	1.130	17.00
2MRI0	2010	5.4	2.391	1.135	17.40

Supplementary Table S1: Lead concentration and isotopic composition of wine samples. P denotes port (shiraz grapes), S denotes shiraz variety, C denotes cabernet sauvignon variety.

SWA10	2010	3.1	2.418	1.156	17.85
SMWb10	2010	2.0	2.456	1.146	18.67
SMWp10	2010	2.3	2.452	1.148	18.54
SMWq10	2010	1.0	NA	NA	NA
SWA11	2011	1.5	2.426	1.148	17.90
SMW11	2011	1.1	NA	NA	NA
SWA12	2012	1.6	2.439	1.151	17.99

Supplementary Table S2: Lead concentration and isotopic composition of soil samples.

Soil	Description	Lead	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb
sample		[mg/kg]			
BD1	0-2 cm	26.7	1.150	2.448	18.01
	40-50 cm	10.0	1.189	2.500	18.71
BD2	0-2 cm	7.0	1.163	2.469	18.20
	40-50 cm	4.4	1.201	2.532	18.82
OT1	0-2 cm	5.2	1.163	2.455	18.20
	30-40 cm	12.7	1.242	2.543	19.91
OT2	0-2 cm	8.5	1.187	2.486	18.54
	20-30 cm	14.2	1.209	2.507	19.01
CH1	0-2 cm	5.6	1.151	2.456	18.00
	30-40 cm	6.4	1.178	2.494	18.43
CH2	0-2 cm	11.0	1.180	2.473	18.70
	20-30 cm	12.0	1.214	2.506	19.27

Supplementary Table S3: Lead concentration in corks where lead foil capsules were used.

	Lead [m	g/kg]
Sample	Top of cork	Bottom of cork
PMW79	15.9	9.7
PWD83	40.8	26.5
PMW85	552	Not detected
CWC88	54.3	16.9
CWC91	733	Not detected

Appendix D

Supplementary Table S1: Lead concentrations and isotopic compositions of ash and soil samples from three 2011 Australian bushfires: the Tostaree Fire (TS and TN), the Red Hill Fire (RH), and the Kelmscott Fire (KR). 'A' indicates an ash sample and 'S' indicates a soil sample, with the relevant depth value, e.g. TS_0-2S is a soil sample from Tostaree at 0-2 cm depth.

Sample Code	and	Sample	Pb			
Location		Туре	(mg/kg)	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb
TS_1A		Ash	17.1	1.1979	2.5039	18.753
TS_2A		Ash	1.6	1.1134	2.4016	17.228
TS_3A		Ash	2.5	1.1758	2.5375	18.317
TS_4A		Ash	3.5	1.1380	2.4255	17.677
TS_5A		Ash	1.8	1.1899	2.6118	18.568
TS_6A		Ash	6.1	1.1988	2.5474	18.750
TS_7A		Ash	6.3	1.1980	2.5038	18.624
TS_8A		Ash	1.0	1.1684	2.6001	18.216
TS_8B		Ash	2.0	1.1950	2.5642	18.644
TS_8C		Ash	3.0	1.1862	2.4985	18.579
TS_9A		Ash	7.9	1.1904	2.4928	18.638
TS_10A		Ash	12.9	1.1898	2.4882	18.597
TS_11A		Ash	22.9	1.1854	2.4826	18.536
TS_12A		Ash	17.8	1.1931	2.5002	18.587
TS_13A		Ash	11.5	1.1614	2.4730	17.957
TS_14A		Ash	5.7	1.2061	2.5674	18.815
TS_15A		Ash	10.1	1.1925	2.4947	18.635
TN_16A		Ash	14.0	1.2027	2.5032	18.792
TN_17A		Ash	3.5	1.2039	2.5521	18.925
TN_18A		Ash	4.4	1.2103	2.5984	18.986
TN_19A		Ash	24.1	1.1987	2.5065	18.707
TN_20A		Ash	5.9	1.2145	2.5953	18.986
TN_21A	la	Ash	5.3	1.2018	2.5700	18.765
TN_22A	tori	Ash	9.8	1.2031	2.5110	18.836
TN_23A	/ic	Ash	10.8	1.1968	2.5092	18.709
TN_24A	e, 1	Ash	5.8	1.2046	2.5364	18.845
TN_25A	are	Ash	36.5	1.1873	2.4799	18.612
TN_26A	ost	Ash	6.0	1.1940	2.5181	18.679
TN_27A	T	Ash	9.0	1.2034	2.5043	18.879
TS_0-2S		Soil	11.7	1.1872	2.4993	18.578
TN_0-2S		Soil	4.8	1.1817	2.5005	18.477
TS_40-50S		Soil	19.4	1.2023	2.5157	18.896
TN_40-50S		Soil	4.3	1.2123	2.5551	19.037
RH_1A	A	Ash	8.5	1.4032	2.3667	22.964
RH_2A	, W	Ash	10.8	1.5059	2.4205	24.877
RH_3A	Hill,	Ash	30.4	1.2249	2.3577	19.474
RH_4A	d F	Ash	30.6	1.5150	2.3703	25.342
RH_5A	Re	Ash	30.0	1.3550	2.4233	22.026

RH_6A	-	Ash	14.4	1.2943	2.3354	20.955
RH_7A		Ash	35.0	1.5146	2.3812	25.308
RH_8A		Ash	19.9	1.3584	2.3381	22.017
RH_9A		Ash	27.8	1.3431	2.3315	21.692
RH_10A		Ash	26.9	1.3292	2.3263	21.491
RH_11A		Ash	28.2	1.3529	2.2990	21.901
RH_12A		Ash	27.0	1.4450	2.4831	23.831
RH_13A		Ash	27.7	1.3051	2.3661	20.949
RH_14A		Ash	17.6	1.3778	2.3456	22.313
RH_15A		Ash	30.5	1.2810	2.3164	20.453
RH_0-2S1		Soil	23.0	1.2380	2.3780	19.774
RH_0-2S2		Soil#	8.3	1.2900	2.4390	20.747
RH_40-		Soil				
50S1			5.3	1.4530	2.4940	24.096
RH_40-		Soil#				
50S2			13.8	1.5623	2.4457	26.487
RH_rock1		Rock#	9.6	1.5130	2.4310	25.189
RH_rock2		Rock#	4.6	1.3590	2.4840	21.978
RH_rock3	1	Rock#	19.0	1.3930	2.4480	22.573
KR 1A		Ash	7.8	1.2117	2.5210	19.259
KR 2A	-	Ash	7.3	1.2314	2.5545	19.632
KR 3A		Ash	14.6	1.1960	2.4972	18.933
KR 4A	-	Ash	10.3	1.2314	2.4868	19.708
KR_5A		Ash	9.4	1.2005	2.4894	19.038
KR_6A		Ash	31.6	1.1951	2.4973	18.904
KR_7A		Ash	10.7	1.2139	2.5582	19.289
KR_8A		Ash	9.3	1.2209	2.4820	19.393
KR_9A		Ash	11.5	1.2418	2.4083	19.828
KR_10A		Ash	22.6	1.3433	2.4578	21.918
KR_11A		Ash	10.3	1.3718	2.6035	22.351
KR 12A		Ash	20.9	1.3189	2.4694	21.335
KR_0-2S1		Soil	16.6	1.3007	2.4253	21.110
KR_0-2S2	(A)	Soil#	13.0	1.1510	2.4570	18.083
KR 0-2S3	Ľ Š	Soil#	12.0	1.1440	2.4380	18.050
KR 0-2S4	lia	Soil#	23.0	1.1240	2.4200	17.668
KR 40-	stra	Soil				
50S1	Aus		9.4	1.3353	2.4182	21.824
KR_ 40-	m /	Soil#				
50S2	ster		7.3	1.1980	2.5030	19.157
KR_40-	Ne:	Soil#				
50S3	t, /		10.0	1.2410	2.5600	20.121
KR_rock1	cot	Rock#	13.0	1.3170	2.4360	18.797
KR_rock2	ms	Rock#	15.0	1.1830	2.5420	19.157
KR_rock3	Kel	Rock#	5.3	1.1780	2.5320	19.231

#Indicates samples that were analysed at National Measurement Institute, Sydney. All other samples were analysed at UCSC.

Supplementary Table S2: Lead isotopic composition of Broken Hill and Mount Isa ores and Australian leaded petrol. The lead isotopic compositions listed for the leaded petrol are averages of multiple samples from single studies.

Source	Reference	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb
Broken Hill ore body	Townsend et al., 1998	1.0403	2.3102	16.004
Broken Hill ore body	Chiaradia et al., 1997	1.0398	2.3170	16.003
Broken Hill ore body	Cooper et al., 1969	1.0390	2.3155	16.00
Mount Isa ore body	Cumming and Richards, 1975	1.0431	2.3197	16.120
Mount Isa ore body	Gulson, 1985	1.0432	2.3184	16.112
New South Wales petrol	Gulson et al., 1995	1.0602	2.3341	16.403
Sydney petrol 1978	Gulson et al., 1983	1.0807	2.3528	16.695
Sydney petrol 1979	Gulson et al., 1983	1.1114	2.3815	17.229
Sydney petrol 1980	Gulson et al., 1983	1.1905	2.4386	18.625
Sydney petrol 1981	Gulson et al., 1983	1.1375	2.3904	17.648
Queensland petrol 1994-95	Bollhöfer and Rosman, 2000	1.1930	2.4451	n/a
Sydney petrol 1995	Gulson, 2003	1.0712	2.3415	16.58
Sydney petrol 1996	Gulson, 2003	1.0859	2.3622	16.859
Sydney petrol 1997	Gulson, 2003	1.1093	2.3705	17.054
Sydney petrol 1998	Gulson, 2003	1.1259	2.3818	17.541
Sydney petrol 1999	Gulson, 2003	1.1149	2.3755	17.347

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Appendix E

Supplementary Table S1: Soil copper, zinc and lead concentrations and lead isotopic compositions.

Train	Direction	Distance	Soil	Cu	Zn	Ph	²⁰⁶ Ph/ ²⁰⁷ Ph	²⁰⁸ Ph/ ²⁰⁷ Ph	²⁰⁶ Ph/ ²⁰⁴ Ph
line	from	to track	denth	Cu	ZII	10	10/ 10	10/ 10	10/ 10
inte	tracks	[m]	[cm]		[mg/kg]				
Silverton	North	11	0-2	18	1200	695	1.044	2.321	16.10
			2-10	24	780	380			
			40-50	25	110	39			
		58	0-2	18	150	61	1.065	2.347	16.42
			2-10	22	88	25			
			40-50	25	59	10			
		101	0-2	14	130	48	1.072	2.347	16.58
			2-10	19	72	23			
			40-50	25	60	11	1.180	2.454	18.37
	South	11	0-2	14	270	140	1.050	2.334	16.18
			2-10	20	130	46			
			40-50	26	74	13			
		53	0-2	16	130	56	1.070	2.347	16.46
			2-10	22	81	19			
			40-50	24	51	7.4			
		101	0-2	15	96	40	1.077	2.353	16.68
			2-10	20	59	12	1 200	2 176	10.00
			40-30	19	30	1	1.209	2.470	18.82
Triple	North	1.5	0-2	30	355	65	1.081	2.366	16.67
Chance			2-10	32	290	46			
			10-20	23	320	50			
			20-30	19	74	12.5			
			30-40	20	79	12			
		(0)	40-50	1/	74	10	1.072	0.252	16.62
		00	2.10	14	270	38	1.073	2.353	10.02
			10.20	13	52	0.1			
			20-30	14	64	12			
			30-40	18	75	12			
			40-50	19	81	12			
		120	0-2	13	130	25.8	1.096	2.394	16.97
			2-10	15	65	11			
			10-20	17	67	12			
			20-30	21	78	14			
			30-40	21	71	12			
			40-50	21	61.5	10	1.190	2.484	18.54
	South	4	0-2	32	2230	325	1.051	2.328	16.21
			2-10	28	94	14			
			10-20	30	82	11			
			20-30	26	72	10			
			30-40	27	73	11			
			40-50	29	85	12			
		70	0-2	12	160	19.5	1.089	2.376	16.90
			2-10	16	270	33			
			10-20	19	59	12			
			20-30	24	65	11			
			30-40	25	00	11			
		125	40-30	15	12	12.5	1 126	2 416	17 48
		123	2-10	15	110	12.3	1.120	2.410	17.40
			2-10	1.5	110	15			
			10-20	15	40	7.3			
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			20-30	22	57	9.5			
			30-40	25	60	10.8			
			40-50	26	54	9.7	1.200	2.474	18.79
Broken	North	22	0-2	19	660	330	1.051	2.330	16.22
Hill to			2-10	12	140	110			
Sydney			40-50	21	45	42			
(Broken		61	0-2	20	500	290	1.042	2.321	16.06
H1ll)			2-10	20	63	26			
			40-50	26	67	9			
		100	0-2	17	430	310	1.044	2.326	16.10
			2-10	14	43	29			
	~ .		40-50	24	28	12	1.094	2.388	16.87
	South	23	0-2	39	1300	530	1.049	2.324	16.16
			2-10	39	280	160			
		55	40-50	66	61	27	1.046	2 222	16.12
		55	0-2	27	/40	380	1.046	2.322	16.13
			2-10	23	80	3/			
		112	40-30	20	43	200	1.042	2 2 2 2	16.07
		112	2 10	21	490	<u>290</u> 53	1.045	2.323	10.07
			40-50	18	29	11	1 1 1 5	2 401	17.22
Broken	North	10	0-2	26	190	61	1.115	2 363	16.75
Hill to	Horu	10	2-10	31	190	49	1.005	2.505	10.75
Sydney			10-20	26	170	62			
(Gorge)			40-50	28	65	24			
-		51	0-2	22	130	57	1.083	2.361	16.78
			2-10	28	74	26			
			10-20	31	60	21			
			40-50	28	59	21			
		100	0-2	24	71	28	1.143	2.421	17.73
			2-10	26	59	22			
			10-20	27	57	19			
			40-50	20	39	13	1.199	2.466	18.76
		154	0-2	8.3	35	15			
			2-10	8.7	29	12			
			10-20	9.3	28	12			
	<u> </u>		40-50	8.1	19	7.3	1.000	2.052	14.04
	South	27	0-2	11	33	110	1.088	2.372	16.86
			2-10	12	27	65			
			10-20	28	25	<u>0/</u> 50			
		33	40-30	11	25	72	1 105	2 303	17.12
		50	0.2	23	23 81	27	1.105	2.393	17.12
		50	2-10	13	51	18	1.140	2.414	17.75
			10-20	13	40	16			
			40-50	25	54	20			
		100	0-2	8.4	40	16	1.134	2.425	17.70
			2-10	7.7	35	15			
			10-20	6.4	23	11			
			40-50	8.3	19	7.6	1.214	2.504	18.80
		143	0-2	8	38	16			
			2-10	6.9	26	10			
			10-20	6.9	28	10			
			40-50	7.3	21	10			
Broken Hi	ill Ore	Sample 1					1.040	2.323	15.99
		Sample 2					1.041	2.319	16.05



Supplementary Figure S1: Soil lead and zinc concentration profiles across Broken Hill train line transect at Broken Hill.



Supplementary Figure S2: Soil lead and zinc concentration profiles across Broken Hill train line transect at The Gorge station.

Supplementary Figure S3: Soil lead isotopic compositions at either side of the rail line at Silverton, benchmarked against Broken Hill ore.



Supplementary Figure S4: Soil lead isotopic compositions at either side of the rail line at Broken Hill, benchmarked against Broken Hill ore.





Supplementary Figure S5: Soil lead isotopic compositions at either side of the rail line at The Gorge, benchmarked against Broken Hill ore.

Supplementary Figure S6: Photograph of a train moving ballast material ~ 50 mm in size, travelling to the east of Broken Hill. Note the plumes of dust coming from the ballast on the uncovered wagons. (Photo taken by M.P. Taylor 2009)



Appendix F

Supplementary Table S1: Soil lead and zinc concentrations, lead isotopic compositions and sample coordinates. Locations of samples in Broken Hill can be seen in Supplementary Figure S1. Sample labels coloured to indicate geology, blue = Sundown Group; yellow = Thackaringa Group; pink = Broken Hill Group.

Sample	Latitude	Longitude	Soil	Zn	Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb
	S31°	E141°	depth	[mg/kg]	[mg/kg]			
HS1	58'18.09"	29'8.93"	0-2	1520	2850	1.038	2.314	16.03
			2-10	600	2440	1.040	2.319	15.97
			10-20	160	590			
			40-50	85	700	1.044	2.322	16.08
HS2	58'27.65"	29'23.76"	0-2	1160	1060	1.043	2.323	16.00
			2-10	920	1070	1.042	2.320	16.05
			10-20	450	270			
			40-50	65	48	1.072	2.358	16.67
HS3	58'13.92"	29'45.03"	0-2	1060	1320			
			2-10	87	170			
			10-20	76	170			
			40-50	72	240			
HS4	57'55.15"	29'46.41"	0-2	3580	2900	1.042	2.321	16.05
			2-10	1130	900	1.041	2.315	16.05
			10-20	490	400	1.0.1.1		1.6.02
			40-50	290	190	1.044	2.320	16.03
HS5	57'58.38"	29'58.28"	0-2	2160	2080			
			2-10	86	160			
			10-20	100	600			
	5 (120 5 (11	0.6155.051	40-50	/5	100			
HS6	56'20.56"	26'55.35"	0-2	180	1/0			
			2-10	140	120			
			10-20	260	280			
CC1	50116 00"	27146 47"	40-30	200	200			
CCI	38'40.82	2/40.47	2 10	5200	3300			
			2-10	6670	3740			
CC^2	59'00 15"	27!49 78"	0.2	1730	1220			
CC2	59 00.15	27 49.70	2-10	2130	1340			
			10-20	1570	1090			
			40-50	No data	97			
CC3	59'16 65"	28'07 35"	0-2	1900	1320			
005	27 10.02	2007.35	2-10	470	250			
			10-20	88	48			
			40-50	100	53			
CC4	59'22.66"	27'31.00"	0-2	6860	3490			
			2-10	710	420			
			10-20	140	82			
			40-50	50	21			
CC5	59'32.74"	26'51.14"	0-2	10100	3420			
			2-10	550	560			
			10-20	360	280			
			40-50	48	24			
CC6	59'12.83"	27'10.25"	0-2	8720	3540			
			2-10	2060	770			
CC7	59'47.58"	26'55.10"	0-2	5730	2750			
			2-10	330	100			
			10-20	110	47			
			40-50	490	190			

	LOLE	58'43.57"	28'48.10"	0-2	530	700			
	1			2-10	420	410			
				40-50	110	97			
	LOLE	58'23.96"	28'22.95"	0-2	7100	8900			
	2			2-10	2700	3300			
				40-50	170	160			
	LOLE	57'56.29"	28'23.71"	0-2	5000	8400			
	3			2-10	1700	570			
				40-50	190	200			
	LOLE	57'23.97"	28'45.26"	0-2	9500	6300			
	4			2-10	6900	5700			
				40-50	2100	2000			
	LOLE	56'19.90"	28'05.89"	0-2	370	300			
	5			2-10	200	170			
				40-50	230	170			
	LOLE	56'02.08"	27'55.81"	0-2	275	395			
	6			2-10	190	230			
				20-25*	67	64			
	LOLW	59'21.88"	27'49.49"	0-2	1800	815	1.0416	2.316	16.04
	1			2-10	170	96	1.0500	2.240	1.5.7.1
				40-50	91	44	1.0708	2.349	16.54
	LOLW	58'44.77"	27'16.20"	0-2	3900	2400	1.0397	2.319	16.02
	2			2-10	370	270	1.0.400	2.220	1 < 1 1
				40-50	110	77	1.0488	2.328	16.11
	LOLW	58'13.61"	26'11.29"	0-2	290	200	1.0513	2.321	16.17
	3			2-10	37	23	1.0665	2 401	10.07
	LOLUI			30-40*	33	13	1.2665	2.401	19.97
	LOLW	57'37.86"	25'51.16"	0-2	86	46	1.0787	2.352	16.69
	4			2-10	100	66	1 2220	2,429	10.15
	DIUUI	50100 451	20126 641	40-50	46	15	1.2229	2.428	19.15
	BHWI	58'22.45"	26'26.64"	0-2	560	330			
				2-10	660 5 2 0	370			
				10-20	520	250			
		50147 101	2(120,2011	40-50	480	310			
	BHW2	58'47.19"	26'28.28	0-2	2500	1340			
				2-10	490	220			
				10-20	62	21			
	BUW3	55151 57"	26123 35"	40-30	230	10			
	DIIWS	55 51.57	20 23.33	2 10	230 88	55			
				30-35*	68	30			
	BHN1	56'35 52"	28'52 70"	0_2	3850	2890			
	DIINI	50 55.52	28 52.70	2-10	2320	2170			
				10-20	650	690			
				40-45*	460	420			
ł	BHN2	56'57 48"	26'48 55"	0-2	200	140			
	DIII (2	5057.40	20 40.55	2-10	270	270			
				10-20	97	79			
				40-50	39	12			
	BHN3	56'20.64"	27'44.44"	0-2	570	530			1
	BHN4	56'07 25"	28'38 27"	0-2	300	150			1
		2001.20	20 30.27	2-10	120	64			1
				10-20	97	42			1
				40-50	61	18			
	BHN5	57'03.90"	28'11.13"	0-2	2130	1060			1
	2.11.13	2, 33.70		2-10	1120	1250			1
				10-20	710	830			1
				40-50	1350	2410			1
	BHN6	57'24.64"	27'02.78"	0-2	860	1300			
1									

			0.10	600	1050			
			2-10	690	1070			
			20-25*	84	350			
BHN7	57'26.54"	28'18.03"	0-2	5160	3620			
			2-10	67	150			
			10-20	130	96			
			40-50	180	190			
BHN8	57'23.31"	27'31.04"	0-2	1320	1170			
			2-10	3110	3010			
			10-20	740	2390			
			40-50	89	61			
BHO1	Ore samples	s (galena)				1.040	2.323	15.99
BHO2						1.041	2.319	16.05
Soil1	57'34.31"	27'49.50"	pXRF	7971	1093			
Soil2	57'14.90"	27'38.20"	pXRF	298	248			
Soil3	56'53.92"	27'19.66"	pXRF	99	61			
Soil4	56'22.96"	27'23.77"	pXRF	117	77			
Soil5	57'45.76"	27'28.90"	pXRF	1150	1248			
Soil6	57'43.49"	27'00.09"	pXRF	732	429			
Soil7	58'27.87"	26'38.36"	pXRF	314	175			
Soil8	56'06.90"	26'24.77"	pXRF	496	279			
Soil9	57'22.24"	26'15.34"	pXRF	207	116			
Soil10	57'20.03"	26'44.28"	pXRF	162	58			
Soil11	56'17.95"	28'19.32"	pXRF	152	102			
Soil12	56'37.27"	28'18.27"	pXRF	47	45			
Soil13	57'05.04"	28'20.51"	pXRF	807	1017			
Soil14	56'33.77"	27'50.37"	pXRF	94	50			
Soil15	56'01.69"	27'49.60"	pXRF	269	143			
Soil16	56'41.26"	28'55.70"	pXRF	806	1243			
Soil17	56'27.03"	28'47.20"	pXRF	660	557			
Soil18	58'17.24"	27'53.14"	pXRF	9083	6925			
Soil19	58'01.09"	28'21.41"	pXRF	1516	1691			
Soil20	58'46.48"	27'58.89"	pXRF	744	617			
Soil21	58'58.27"	28'24.25"	pXRF	1270	680			
Soil22	59'07.80"	27'37.51"	pXRF	1516	1692			
Soil23	58'00.40"	29'49.59"	pXRF	3348	2272			

*The lowest sample collected due to the presence of bedrock pXRF = portable X-Ray Fluorescence



Supplementary Figure S1: Location of soil samples collected and tested in Broken Hill.

Supplementary Figure S2: Geology of Broken Hill drawn from Willis (1989) and Andrews (1922).



Supplementary Figure S3: Soil depth profiles and Surface Enrichment Ratios (SER) of select samples from Broken Hill



Supplementary Figure S4: The uncovered tailings mound produced from the central Broken Hill mine, known as Mount Hebbard (Blainey 1968). Note for scale the truck bottom right.



Supplementary References

Andrews, E. C. (1922). *The Geology of the Broken Hill District* (Memoirs of the Geological Survey of New South Wales, Vol. No. 8). Sydney, New South Wales: William Applegate Gullick, Government Printer. Willis, I. L. (1989). Broken Hill Stratigraphic 1:100 000 Geological Sheet. (1st ed.). Sydney, New South Wales: Geological Survey of New South Wales.

Blainey, G. (1968). The Rise of Broken Hill. Netley, South Australia: Macmillan of Australia.

Appendix G

Supplementary Table S1: Daily dust loadings from surface wipes. Note that rainfall was reported three days prior to Day 1 and then very early on Day 1, which may have affected loadings. The actual surface area wiped for each location was: Playground 1 - 414 cm²; Playground 2 - 900 cm²; Playground 3 - 632.5 cm²; Playground 4 - 900 cm²; Playground 5 - 900 cm²; Playground 6 - 225 cm². Values were standardised $\mu g/m^2$ to allow comparison between sites.

Dlamanand		Arsenic	Cadmium	Lead	Silver	Zinc
Playground	(PG)	μg/m ²	μg/m ²	$\mu g/m^2$	$\mu g/m^2$	$\mu g/m^2$
	Day 1	3.86	4.35	942	0.00	12800
	Day 2	3.62	3.14	628	0.00	6760
1	Day 3	0.00	3.62	507	0.00	6040
1	Day 4	0.00	4.35	411	0.00	6520
	Day 5	0.00	4.12	362	0.00	5070
	Mean	1.50	3.91	570	0.00	7440
	Day 1	3.33	2.22	333	0.00	533
	Day 2	20.0	2.33	467	0.00	1010
2	Day 3	6.44	2.33	389	0.00	1110
2	Day 4	13.3	4.22	767	1.00	2000
	Day 5	2.67	1.78	267	0.00	1440
	Mean	9.16	2.58	444	0.20	1220
	Day 1	901	206	59900	58.5	70990
	Day 2	459	120	35600	34.8	38400
2	Day 3	206	56.9	15500	17.4	16000
3	Day 4	206	63.2	16400	15.8	18000
	Day 5	117	42.7	9960	11.2	13000
	Mean	378	97.7	27500	27.5	31300
	Day 1	2.89	0.889	633	2.44	556
	Day 2	2.89	1.00	733	2.67	644
4	Day 3	0.00	0.00	211	0.667	678
4	Day 4	1.11	0.00	167	0.00	900
	Day 5	0.00	0.00	100	0.00	756
	Mean	1.38	0.378	369	1.16	707
	Day 1	0.00	0.00	8440	0.00	389
	Day 2	0.00	0.00	6560	0.00	444
5	Day 3	0.00	0.00	4220	0.00	444
5	Day 4	5.44	1.78	8780	0.778	1560
	Day 5	0.00	0.00	6890	0.00	956
	Mean	1.09	0.356	6980	0.156	758
	Day 1	7.11	0.00	418	0.00	4000
	Day 2	0.00	0.00	102	0.00	3640
6	Day 3	0.00	0.00	173	8.00	5330
6	Day 4	0.00	0.00	84.4	3.11	5780
	Day 5	0.00	0.00	37.8	2.22	6220
	Mean	1.42	0.00	163	2.67	4990

Discourse	·	Arsenic	Cadmium	Lead	Silver	Zinc
Playground		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
	Sample 1	5.50	1.70	750	2.20	460
1	Sample 2	10.0	3.70	690	1.70	1000
	Mean	7.75	2.70	720	1.95	730
	Sample 1	14.0	3.10	730	1.30	880
2	Sample 2	9.80	3.30	680	1.30	1020
	Mean	11.9	3.20	705	1.30	950
	Sample 1	45.0	11.0	2820	26.0	3470
	Sample 2	36.0	12.0	2250	3.00	3530
3	Sample 3	65.0	18.0	3340	5.60	5350
	Sample 4	38.0	8.50	1390	6.80	2500
	Mean	46.0	12.4	2450	10.4	3710
	Sample 1	5.10	1.70	570	1.00	580
4	Sample 2	1.20	bd	58.0	bd	80.0
	Mean	3.15	0.85	314	0.500	330
	Sample 1	2.10	0.740	200	bd	180
5	Sample 2	3.00	0.650	270	0.590	400
	Mean	2.55	0.695	235	0.295	290
	Sample 1	0.890	bd	24.0	bd	31.0
6	Sample 2	1.50	bd	44.0	bd	46.0
	Mean	1.20	bd	34.0	bd	38.5

Supplementary Table S2: Playground soil metal sample data. Note that values below detection (bd) were considered to be zero for statistical purposes.

S	սթյ	ple	me	nta	ary	T	abl	le S	3:	Pro	e- a	and	pc	st-	pla	ıy ł	nan	d v	vip	e d	ata	fo	r al	1 n	neta	als	an	d al	ll p	lay	gro	oun	ds.
		Zinc	$\mu g/m^2$	2820	6530	4150	5930	5930	18200	20900	13700	22200	14500	26200	79200	36600	49200	39300	10400	3820	5600	9680	7390	17200	8150	15100	45000	14200	13500	8230	8230	27100	9020
		Silver	$\mu g/m^2$	18.4	19.0	20.8	3.86	18.4	26.0	29.5	17.7	29.5	18.5	46.4	92.9	43.7	54.6	46.4	13.8	18.6	8.40	5.09	7.90	14.2	11.2	8.45	17.8	17.8	2.12	3.72	2.12	4.25	2.12
		Lead	$\mu g/m^2$	502	2550	1070	532	828	1790	5620	4010	0969	2620	19700	60900	25400	32000	25700	209	199	161	87.0	112	236	248	239	510	206	396	422	247	316	186
		Cadmium	$\mu g/m^2$	8.90	22.3	9.79	7.72	8.61	16.3	29.5	23.3	34.8	16.3	87.4	235	109	137	117	2.04	2.55	1.78	1.53	2.04	3.62	3.32	4.83	7.55	2.72	2.92	3.72	1.86	4.25	1.59
		Arsenic	$\mu g/m^2$	9.79	53.4	23.7	32.6	16.9	20.6	129	6:99	75.0	29.5	188	628	257	382	208	4.07	0.00	3.06	0.00	0.00	3.32	3.02	0.00	5.13	0.00	0.00	0.00	00.00	00.00	0.00
		U	Day	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5
	Post-play	[rlayground			1					2					3					4					5					9		
-		Zinc	$\mu g/m^2$	1600	2080	2200	4150	3860	6160	6160	4550	13400	11500	3000	2680	6280	9560	5460	8660	3060	5090	11500	6110	13600	4230	6940	67300	12400	9290	2600	4780	17500	5570
		Silver	$\mu g/m^2$	74.2	18.7	32.6	2.37	35.6	53.6	23.3	13.9	32.1	32.1	20.5	32.8	9.56	6.83	27.3	17.8	6.11	10.4	8.91	8.15	8.15	6.04	5.13	27.8	29.0	0.00	0.00	00.0	0.00	0.00
		Lead	μg/m²	86.4	38.9	38.9	83.5	77.5	35.1	40.5	70.0	105	86.0	544	380	129	126	82.3	23.2	58.9	43.6	46.2	46.2	36.6	33.6	15.5	191	87.9	24.2	37.5	32.2	50.8	29.5
		Cadmium	$\mu g/m^2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.87	1.34	6.01	1.91	0.00	0.00	0.00	0.00	0.00	0.00	1.78	1.27	1.81	0.00	0.00	2.11	0.00	2.39	3.18	1.59	2.39	1.86
		Arsenic	$\mu g/m^2$	22.0	0.00	6.53	83.1	0.00	0.00	00.00	0.00	9.37	0.00	6.28	4.10	0.00	3.82	00.0	0.00	00.00	11.5	0.00	0.00	0.00	0.00	0.00	00.00	0.00	00.00	0.00	0.00	00.00	0.00
		j.	Day	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5
	Pre-play	Disconcile	riayground			1					2					6					4					5					9		

Supplementary Table S4: Lead isotope ratios from post-play dust at Playgrounds 3, 4, and 5 and Broken Hill ore as reported in Townsend et al. (1998), Chiaradia et al. (1997), Gulson and Mizon (1979), Cooper et al. (1969).

Sample ID	²⁰⁶ Pb/ ²⁰⁷ Pb	²⁰⁸ Pb/ ²⁰⁷ Pb	²⁰⁶ Pb/ ²⁰⁴ Pb
PG3 Post-play 17/9/13	1.04	2.32	16.00
PG3 Post-play 18/9/13	1.04	2.33	16.10
PG3 Post-play 19/9/13	1.04	2.32	16.00
PG3 Post-play 20/9/13	1.04	2.31	15.97
PG4 Post-play 16/9/13	1.05	2.33	16.21
PG4 Post-play 17/9/13	1.07	2.35	16.47
PG4 Post-play 18/9/13	1.06	2.34	16.42
PG4 Post-play 19/9/13	1.06	2.33	16.10
PG4 Post-play 20/9/13	1.06	2.34	16.39
PG5 Post-play 16/9/13	1.06	2.33	16.26
PG5 Post-play 17/9/13	1.06	2.34	16.50
Broken Hill ore 1	1.04	2.31	16.00
Broken Hill ore 2	1.04	2.32	16.00
Broken Hill ore 3	1.04	2.32	16.00
Broken Hill ore 4	1.04	2.32	15.97

Supplementary Image 1: Dust accumulated from Playground 3 on right hand (top) and after hand wipe collected on left hand (bottom). Image taken by L.J. Kristensen on 17/9/2013.



Appendix H

Supplementary Table S1. Summary description of surfaces sampled for dust at each of the playground sites sampled in the study (two surfaces per site).

Location	Surface 1 - description	Surface 2 - description	Dimensions (cm) - surfaces (1) and (2)
Foreshore	Top surface	Top surface	(1) 79 x 7.0
playground	of a railing	of a climbing facility	(2) 30 x 30
Memorial	Square		(1) 30 x 30
Park	surface top	Square	(2) 30 x 30
playground	of play	surface top of	
	facility	play facility	(1) 40 x 26
Sport Park*			(2) 40 x 20
playground	Roof top of	Bench top	
	playground		(1) 31 x 32
Woodward	facility		(2) 34 x 26
Park*		Top of table	
playground	Square		(1) 30 x 25
	surface top		(2) 30 x 30
Port Augusta reference playground	of play facility	Top of table	
1 10	Bench top		

*At these sites the one of the surfaces was swapped after day because it was deemed unsuitable – the table refers to the main surfaces used over the sampling period.

Additional information on the surface sampling procedure

At each location a sample surface was sought using the following criteria: flat, horizontal, nonpainted surface with dimensions of 30 x 30 cm, which was not likely to be interfered with by anyone using the playground equipment. The selected site was measured and marked using masking tape prior to being sampled (as per the instructions for collecting dust wipes for lead determination in ASTM E 1728-03 (2003). In several cases such a surface was not available and a compromise site was selected. Where a surface area of 30×30 cm was not available, the sampled area was marked out in the same manner and the dimensions recorded. In order to minimize crosscontamination prior to each sample, a clean pair of blue nitrile gloves were worn. **Supplementary Figures S2a-e.** Images of the five playgrounds sampled in this study for hand wipe, soil and surface dust metal concentrations.



Figure S2a. Foreshore playground, Port Pirie (see Figure 1 for location).



Figure S2b. Memorial Park playground, Port Pirie (see Figure 1 for location).



Figure S2c. Sports Park playground, Port Pirie (see Figure 1 for location).



Figure S2d. Woodward Park playground, Port Pirie (see Figure 1 for location).



Figure S2e. Port Augusta reference playground, (see Figure 1 for location).

Additional information on the child-simulated play routine

L. Kristensen undertook the child-simulated play routine at each of the five playgrounds over the sevenday sample period. First, she completed a circuit through the entire playground and then repeated the movement in reverse, giving two complete circuits of the entire playground equipment. Depending on the size of the playground, this took between 5-10 minutes.

After completing two circuits through the entire playground equipment, the child-simulated play focused on the more 'fun' activities several times over, such as the slides, which is what we observed children do at playgrounds. The child-simulated play also involved crawling like other children and where children were playing on the facilities, they were copied in order to get a measure of exposure that was representative of that site. **Supplementary Table S3:** Descriptive statistics for surface soil metal concentrations (arsenic, copper, cadmium, lead and zinc) at Port Pirie and Port Augusta playgrounds, and also at the Port Pirie South Australia EPA air monitoring stations. ^aMean \pm SD.

Some samples (n = 3) returned cadmium values below the instrument detection limit of 1.0 mg/kg were estimated at zero to enable descriptive statistics to be calculated. PG – playground; AirMS – Air Monitoring Station.

ng/kg)	Range	250-420	200-11000	290-10000	44-3100	5400-16000	160-6000	1900-3600	2000-4400	280-320	24-68
Zinc (n	^a Mean	$\begin{array}{c} 320.00 \pm \\ 88.88 \end{array}$	7400.00 ± 6235.38	3593.33 ± 5549.24	1748.00 ± 1558.11	10166.67 ± 5379.901	2243.33 ± 3259.82	2466.67 ± 981.50	2966.67 ± 1266.23	300.00 ± 28.28	40.00 ± 24.33
ng/kg)	Range	97-240	96-2600	80-1900	22-560	2800- 6100	110-470	420-910	600- 6800	120-350	4.6-13
Lead (n	^a Mean	159 ± 73.37	1498.67 ± 1278.91	843.33 ± 944.79	327.33 ± 276.26	4933.33 ± 1850.23	293.33 ± 180.09	623.33 ± 255.41	3666.67 ± 3100.54	235.00 ± 162.63	7.53 ± 4.74
(mg/kg)	Range	11-61	96-2600	12-260	15-44	210-500	24-560	28-55	47-600	16-20	13-36
Copper (^a Mean	$\begin{array}{c} 35.00 \pm \\ 25.06 \end{array}$	$\begin{array}{c} 87.00 \pm \\ 58.03 \end{array}$	97.33 ± 140.93	31.33 ± 14.84	380.00 ± 151.33	205.00 ± 307.46	38.33 ± 14.57	238.67 ± 313.12	18.00 ± 2.83	21.00 ± 13.00
(mg/kg)	Range	1.1-2.4	1.4-9.7	0.0-5.7	0.0-2.5	25-57	0.0-4.5	2.5-3.9	5.5-47	1.9-4.7	0.0
Cadmium	^a Mean	1.60 ± 0.70	6.63 ± 4.55	$\begin{array}{c} 2.30 \pm \\ 3.00 \end{array}$	1.27 ± 1.25	44.33 ± 17.01	2.00 ± 2.29	3.17 ± 0.70	$\begin{array}{c} 23.83 \pm \\ 21.17 \end{array}$	3.30 ± 1.98	0.0
(mg/kg)	Range	4.6-5.3	8.1-66	3.5-53	6.5-16	56-120	6.7-19	14-25	16-200	8.5-14	3.1-29
Arsenic	^a Mean	5.07 ± 0.40	44.37 ± 31.60	20.27 ± 28.35	12.17 ± 5.01	95.33 ± 34.43	11.40 ± 6.64	18.33 ± 5.86	$\begin{array}{c} 87.00 \pm \\ 98.93 \end{array}$	11.25 ± 3.89	15.70 ± 12.96
	Location of soil samples (n)	Foreshore PG (3)	Memorial Park PG (3)	Sports Park PG (3)	Woodward Park PG (3)	Ellen Street AirMS (3)	Frank Green Park AirMS (3)	Pirie West Primary School AirMS (3)	Oliver Street AirMS (3)	Surface pit samples Magor Road, Port Pirie River (2)	Port Augusta Reference Site PG (3)

												-
Mean	Wind	Direction		z	Z	SE-E	Е	NE	NNE	Z	Z	
Mean	Wind	Speed	(km/h)	23	18.5	11.5	14	10.5	18.5	19	24	17.5
Mean	(lead - $\mu g/m^3$)			2.9	0.76	1.2	2.93	5.9	13.65	11.68	10.23	6.62
Oliver Street	(lead - $\mu g/m^3$)			*	0.95	*	*	*	*	*	*	0.95
Pirie West	Primary	School	(lead - $\mu g/m^3$)	2.15	0.29	0.09	0.34	1.29	4.73	4.46	*1	1.87
Frank Green	Park (lead -	μg/m ³)		*	0.19	*	*	*	*	*	*	0.19
Ellen Street	(lead -	μg/m³)		3.68	1.86	2.31	5.51	10.51	22.57	18.90	10.23	10.27
Sample Day				Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	
Sample Date				25/06/2011	26/06/2011	27/06/2011	28/06/2011	29/06/2011	30/06/3011	01/07/2011	02/07/2011	Mean

*Indicates no available data; *1 Data normally collected on this day but sample machine run time was less than the criteria period set by South Australia EPA.

Supplementary Table S4: Environment Protection Authority South Australia lead-in-air data and meteorological data collected at air monitoring stations in Port Pirie for the study period in June-July 2011. Lead-in-air data is recorded in μ g/m³ and is collected as total suspended particulates.

Supplementary Figure S5: Lead-in-air measurements in 2011 for the Environmental Protection Authority South Australia's four monitoring sites in the city of Port Pirie, South Australia. The dashed line represents the Australian (NEPM, 1998) lead-in-air standard of 0.5 μ g/m³. Ellen Street and Pirie West Primary School are monitoring every day for 24 hours, whereas the Frank Green Park and Oliver Street sites are monitored every sixth day for 24 hours.



Appendix I

Supplementary Figure S1: Port Pirie Playground Cleaning Schedule, updated August 1st 2012.

Port Pirie Playground Cleaning Schedule

Community Playgrounds	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
Flinders View Playground Ellen St	Part Piris Regional Connell	Part Pirie Regional Council	Part Picke Regional Council	Pert Pirie Ergional Council	Part Pine Regional Council	Norstar Ter, for them Water Carl	Nyrstar Ten far them Water Cart
Memorial Park Playground Memorial Dve	Part Pirie Regional Conneil	Port Pirie Regional Council	Part Firle Reparal Connel	Port Pirie Regional Council	Port Pirie Regional Council		
Netball Courts Playground Grey Tce						Nyritar Ten for them Water Cart	
Port Football Club Playground Wandearah Rd					Nyrstar Ten for them Water Cart		
Solomontown Beach Playground	Nyustar Ten for theor Water Cart	Port Pirie Regional	Nyrstar Ten for them Water Cart		Nyrstar Ten far them Water Cart		
Tennis Club Playground The Terrace					Nyvistar Ten for them Water Cart		
Tennyson Park Playground Federation Rd, Pirie West	Nyrstar Ten for them Water Cart						
Woodward Park Playground Halliday St		Part Pirie Regional Council	Nyrster Ten for them Water Cart				
Kindergarten Playgrounds							
Solomontown Kindergarten Playground Three Chain Rd	Nynstar Ten for therm Water Cart						

Nyrstar en far them

This symbol represents that the playground is cleaned by the Port Pirie Regional Council. This symbol represents that the playground is cleaned by the Nyrstar, Ten for them Water Cart

All Playground cleaning is completed in the mornings Last updated Wednesday August 1st, 2012 Supplementary Figure S2: Port Pirie Playground Cleaning Schedule, updated May 7th, 2013.

Updated 7th May, 2013 - Join www.facebook.com/tenforthem to be updated automatically

Port Pirie Playground Cleaning Schedule

Community Playgrounds	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
Flinders View Playground Ellen St	Port Pice Regional Causel	Port File	Port Price	Port Pine	Port Pirie	Nyrster Thumbs up for low levels Weter Cart	Nyrstar Thumbs up For law levels Wester Cart
Memorial Park Playground Memorial Dve	Port Pirie	Port Pirie	Port Price Negovariant	Port Pine	Port Pirie	Nyrster Thumbs up för low levels Water Cart	Nyrstar Thumbs up Ser law levels Woter Cart
McDonalds Main Road						Nyrster Thumbs up for low levels Wester Cart	
Netball Courts Playground Grey Tce					Nyrstar Thumbs up for low levels Water Cart		
Port Football Club Playground Wandearah Rd	Nyrstar Thumbs up for low levels Water Cart		Nyrstar Thumbs up for low levels Water Cart		Nyrstar Thumbs up fir low levels Water Cart		
Solomontown Beach Playground		Port Pirie Reporting	Nyrstar Thurnbs up for low levels Vulster Cart		Nyrstar Thumbs up far low levels Vulater Cart		Nyritar Thumbs up for low levels Water Carl
Tennis Club Playground The Terrace				Nyrstar Thurb's up for low levels Water Cart			
Tennyson Park Playground Federation Rd, Pirie West	Nyrstar Thumbs up for low levels Water Cart		Nyrster Thumbsi up for low levels Water Cart		Nyrstar Thumbs up fir low levels Water Cart		
Woodward Park Playground Halliday St	Nyrstar Thumbs up far low levels Water Cart	Port Pirie	Nyrstar Thumbs up far law levels Water Cart		Nyrstar Thumbs up fur low levels Water Cart		
Kindergarten & School Playgrounds							
Airdale Primary School Anzac Road		Nyrstar Thumbs up for low knels Water Cart					
Bubble & Squeak Childcare Centre Kingston Road							Nyrstar Thumbs up for low levels Woster Cart
Ellendale Kindergarten First Street		Nyrstar Thumbs up for low levels Water Cart				Nyrster Thumbi up far low levels Water Cart	
Halliday St Kindergarten Halliday Street		Nyrster Thurnbs up för low levels Water Cart		Nyrstar Thurebs up far lovels Water Cart			Nyrster Thumbi up for law levels Woter Cart
Mid-North Education Centre David Street	Nyrstar Thumbs up far low levels Wister Cavt						
Port Pirie Childcare Centre First Street	Nyrstar Thumbs up for low levels Water Cart		Nyrstar Thumbs up for low levels Water Cart		Nyrstar Thombs up for Iow Inels Water Cart		
Pirie West Primary School Goode Road	Nyrstar Thumbs up for low levels Water Cart		Nyrstar Thumbs up for low levels Water Cart		Nyrstar Thambs up for low levels Water Carl	Nyrster Thambi up for low levels Water Cart	
Solomontown Kindergarten Playground Three Chain Rd	Nyrster Thumbs up for law levels Water Cart			Nyrstar Thurbs up far law leves Water Cart			
Solomontown Primary School Three Chain Road							Nyrstar Thurdsi ap for low levels Woter Cart



This symbol represents that the playground is cleaned by the Port Pirie Regional Council.



This symbol represents that the playground is cleaned by the Nyrstar, Thumbs up for low levels Water Cart

All Playground cleaning is completed in the mornings

Supplementary Table S3. 24 hour surface dust wipe metal loadings (arsenic – As, cadmium – Cd, copper – Cu, lead – Pb and zinc - Zn) recorded over the 5 days study period at Port Pirie. Samples which returned values below detection limit of 0.001 μ g/wipe were estimated at zero to enable statistical calculations.

	Element	Foreshore playground	Memorial Park playground	Sports park playground	Woodward Park playground
Mean ± SD	As	30.81 ± 21.82	18.75 ± 21.64	0.26 ± 0.22	2.45 ± 2.23
	Cd	4.25 ± 4.45	3.49 ± 3.01	0.001* ± 0.004*	0.91 ± 0.64
	Cu	89.02 ± 53.98	111.53 ± 91.87	12.56 ± 6.54	32.75 ± 10.07
	Pb	849.46 ± 618.17	2377.38± 2753.95	28.32 ± 19.59	209.99 ± 134.40
	Zn	1340.42 ± 689.16	1530.28 ± 894.99	238.73 ± 157.83	758.06 ± 271.35
Median	As	21.80	11.86	0.17	2.23
	Cd	1.76	2.54	0.00	1.05
	Cu	95.41	74.30	10.68	31.23
	Pb	650.02	1197.84	26.73	169.31
	Zn	1556.48	1358.79	189.00	755.76
Range	As	6.7-74.3	0.9-73.7	0.0-0.7	0.01*-6.1
	Cd	0.3-13.5	1.2-11.4	0.0-0.01*	0.0-2.1
	Cu	16.0-189.4	42.7-344.8	6.0-25.3	15.3-47.2
	Pb	176.6-1871.2	375.5-9646.3	6.4-61.3	68.8-449.3
	Zn	471.5-2522.7	726.0-3622.9	70.1-554.3	458.2-1329.2

*Where rounding results in a value of zero, the first fractional number is recorded.

Supplementary Table S4. Metal loadings (arsenic – As, cadmium – Cd, copper – Cu, lead – Pb and zinc - Zn) on pre- and post-play hand wipes collected from Port Pirie over the 5 days study period. The mean difference in metal loadings between pre- and post-play values at each location are also provided. Samples which returned values below detection limit of 0.001 μ g/wipe were estimated at zero to enable statistical calculations.

	Element	Foreshore	Memorial Park	Sports Park	Woodward Park
		playground	playground	playground	playground
		Pre-play ha	nd wipe samples (µ	$\iota g/m^2$)	
Mean ±	As	4.53 ± 3.68	1.27 ± 1.07	0.46 ± 0.77	6.26 ± 3.94
SD	Cd	5.27 ± 2.88	9.27 ± 10.68	0.74 ± 0.77	2.32 ± 1.58
	Cu	89.03 ± 32.92	74.38 ± 22.34	102.16 ± 34.49	104.87 ± 34.15
	Pb	567.63 ± 471.80	147.02 ± 75.18	98.01 ± 76.39	255.13 ± 173.69
	Zn	2909.63 ±	2800.64 ±	1680.48 ±	3561.80 ±
		598.01	801.27	325.03	791.58
Median	As	3.05	0.98	0.15	4.36
	Cd	5.70	4.97	0.42	2.27
	Cu	86.42	68.53	89.23	114.50
	Pb	364.28	165.92	75.13	221.00
	Zn	3075.91	2788.56	1567.28	3859.61
Range	As	1.2-11.9	0.0-2.8	0.0-2.0	3.2-14.1
	Cd	1.5-9.3	1.5-33.0	0.0-2.0	0.5-4.9
	Cu	53.7-142.3	46.1-121.9	71.3-165.1	60.6-155.6
	Pb	179.0-1511.8	43.4-235.1	19.9-237.1	114.3-615.0
	Zn	1741.0-3624.5	1686.2-3807.7	1377.9-2208.6	2349.7-4408.2
		Post-play ha	and wipe samples ($\mu g/m^2$)	
Mean ±	As	70.99 ± 17.92	20.20 ± 10.53	26.58 ± 12.88	7.23 ± 3.62
SD	Cd	17.94 ± 6.24	12.30 ± 6.65	6.46 ± 5.35	21.91 ± 15.89
	Cu	336.33 ± 72.88	151.56 ± 61.01	166.06 ± 79.56	95.10 ± 31.43
	Pb	$4409.49 \pm$	2092.29 ±	955.53 ± 710.54	402.54 ± 233.66
		929.31	1245.37		
	Zn	7337.27 ±	$4880.38 \pm$	$7857.66 \pm$	$4816.84 \pm$
		2993.65	1831.43	4565.44	2034.21
Median	As	64.43	18.72	28.51	8.41
	Cd	16.74	12.50	5.56	19.95
	Cu	323.91	148.30	159.19	110.16
	Pb	4088.35	1830.44	768.19	442.09
	Zn	6785.42	5048.22	7856.47	5923.34
Range	As	50.5-103.0	6.4-38.3	9.4-44.1	3.4-12.0
	Cd	11.7-27.6	2.5-23.3	0.8-12.5	2.3-49.6
	Cu	250.9-443.9	68.8-247.0	78.8-290.7	53.5-129.3
	Pb	3532.5-6027.6	671.8-4397.1	308.7-2178.8	163.2-736.1
	Zn	4564.9-13760.3	1863.8-7778.1	2893.0-13969.3	2415.0-6733.2
	Me	an increase in metal	loadings on hands	post-play (µg/m ²)	
	As	66.47	18.93	26.13	0.97
	Cd	12.67	3.03	5.72	19.59
	Cu	247.30	77.18	63.89	-9.78
	Pb	3841.87	1945.27	857.52	147.41
	Zn	4427.64	2079.74	6177.17	1255.04

Appendix J

Supplementary Figure S1: Soil lead (a) Sample Point Values and (b) Grid Mean Values concentrations collected during the 1992 soil survey. Source Dames and Moore (1994a). Grid cells are 200 x 200 m.

	-	-												1 1
	992	146	365	124	6820	72	93	188	233				5	1
	183	147	231	324	190	168	210	111	507		1		0	
	187	242	287	353	353	556	242	36	61		1			
	159	328	668	524	482	758	571	144	-	'	14.04			
	8910	647	1630	832	941	754		104	132					
						/34	2880	258	972					
		561	0390	617	P	519	1110	1002	361			115	92	116
	207	947	2500	1610		1940	1095	445	870	N 158	N 196	155	85	20
	395	647	1200	2	P	-	4460	1120	549	611	181	405	01	23
	94	2610	3270	1	-	P		2180	1710	1510	0.02	105	91	
	452	5460		P	P	P	P			1310	002	154	96	230
	4640		2	P	p	P	P	3400	427	1370	232	876	94	63
	1040	992	3040	P	P	P	P	2960	1710	1430	314	65	25	
	7400	2740	4090	P	P	P		3480	1215	1710	763	369	461	
	10260	642	1800	1	21460	8530	1310	2570	917	1830	653	701	635	
	8920	2630	474	674	2050	1090	296	303	1240	1000				
	224	244	2730	1250	6380			100	1240	2000	396	634	N	
					0.00	/11	491	761	745	N	м	N	N	
	782	1825	162	350	1115	5290	744	Q			L	L	1	71
	756	135	173	111	888	537	230	791		I	ŒΥ			
	959	564	1100	15210	1710	1160	1780	449	1120		Q Q Pa	arry	o Meta	ls-S
	583	1740	739	3670	952	421	486	257	168	N	No	samp.	le	
	250	624	4140	267	196									
00					290	256	315	395	246					
00	1030	663	2980	6000	1890	2260	78	67						

Note:

(a)

Sample taken at top left corner of each grid.
Results expressed in ppm (parts per million).

Fig. 23 Soil Lead - Grid Mean Values

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. .'

367	222	261	1940	1888	136	1221	440	l l			15	•
					150	1.22	440		*		¢	
190	227 .	299	380	392	294	205	234	1	• ,1		1	
229	381	458	428	537	532	253	98					
2511	818	914	695	734	1241	968	382					
2641	2357	2417	797	738	1316	1313	648					
541	2650	2829	1114	1230	1166	913	670	463	177	155	112	Т
540	1.3.24	1770										
243	1324	1770	P	P	2498	1780	746	547	288	236	184	
937	3182	4735				2587	1390	1095	796	406	187	t
2154	5447		P	P	P	2790	1929	1254	999	536	305	+
2884	3161	F	P	P	P	3180	2124	1234	837	372	265	+
3941	2713	P 3565	P	P.	P	3220	2341	1516	1054	378	230	+
5761	2210	2045	P	P.	P	1			1			1
5201	2310	2945	P	14995	4920	2453	2046	1418	1239	622	542	
5613	1387	983	8061	8283	2807	1120	1258	1,497	1220	596	657	1
3005	1520	1282	2589	2558	647	463	762	1328	1198	515	+	1
769	1240	1123	2274	3374	1809	665	753		+		+	-
875	575	200	616	1958	1700	588			1	1	1	
604	494	4150	4480	1074	927	813	787	-				
962	1036	5180	5386	1068	962	743	499	-				
799	1811	2204	1271	456	370	1363	267	-				
						1000				KE	Y	
642	2102	3347	2088	1151	727	214	209	1		P	Pasm	11

Note:

Numbers represent mean values of soil lead samples taken at the 4 intersection points of each grid area.
Results expressed in ppm (parts per million)

*

11 0		1		1	1		
GPS Co-ordina	ates	Site	Antimony	Arsenic	Cadmium	Lead	Zinc
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
151.6252042	-32.95001777	S1SF	10	52	38	3,810	2,510
151.6252042	-32.95001777	S1SB	6.6	43	43	2,590	3,130
151.6268233	-32.95098369	S2SF	< 0.5	4.9	1.1	45	190
151.6268233	-32.95098369	S2SB	4.5	43	25	2,010	3,160
151.624632	-32.951278	S3SF	5.9	28	29	1,960	2,480
151.624632	-32.951278	S3SB	6.6	55	42	2,510	3,920
151.6208552	-32.95099963	S4SF	19	23	7.3	2,630	2,750
151.6208552	-32.95099963	S4SB	2.7	22	7.2	700	1,190
151.6205994	-32.95100324	S5SF	3	13	7.9	690	960
151.6205994	-32.95100324	S5SB	2	14	6.6	540	970
151.6267028	-32.95251557	S6SF	2.5	16	11	950	1,410
151.6267028	-32.95251557	S6SB	2.1	17	13	880	1,280
151.6265774	-32.95249488	S6aSF	3.4	15	17	1,060	2,040
151.6265774	-32.95249488	S6aSB	3.4	16	19	1,340	1,740
151.6255153	-32.95263217	S7SF	2	8.8	11	950	770
151.6255153	-32.95263217	S7SB	1	9.1	4.2	320	610
151.6255326	-32.95275625	S8SF	2.5	14	16	1,440	1,660
151.6255326	-32.95275625	S8SB	2.2	16	15	1,150	1,860
151.6246207	-32.95271317	S9SF	4	12	16	1,290	1,140
151.6246207	-32.95271317	S9SB	10	42	26	3,410	2,040
151.6225704	-32.95186125	S10SF	2.4	12	7.5	630	1,220
151.6225704	-32.95186125	S10SB	9	16	13	1,610	1,590
151.6205507	-32.95188033	S11SF	1.5	18	5.9	470	610
151.6205507	-32.95188033	S11SB	3.2	23	12	840	1,330
151.6212238	-32.95181716	S12SF	1.6	18	6.2	540	730
151.6212238	-32.95181716	S12SB	2.4	16	8.8	690	900
151.619887	-32.95279439	S13SF	1.2	11	4.6	360	550
151.619887	-32.95279439	S13SB	2.3	13	7.2	580	890
151.6240625	-32.95293802	S14SF	7.1	12	21	2,120	1,120
151.6240625	-32.95293802	S14SB	2.2	15	12	770	1,640
151.62197	-32.954022	S15SF	1.6	14	4.3	360	680
151.62197	-32.954022	S15SB	4	21	11	940	1,860
151.6343456	-32.93635946	S16SF	1.5	17	6.1	420	900
151.6129705	-32.97585992	S17SF	< 0.5	3.7	1.1	120	260
151.6129705	-32.97585992	S17SB	0.53	5	1.5	100	350
151.6275967	-32.95079784	S18SF	11	49	55	4,230	5,840
151.6275967	-32.95079784	S18SB	0.78	8.4	6.4	310	940

Supplementary Table S2: Residential soil metal and metalloid concentrations.

S = residential site code. SF = front yard soil, SB = back yard soil.

GPS Co-ordinates		Antimony mg/kg	Arsenic mg/kg	Cadmium mg/kg	Lead mg/kg	Zinc mg/kg	Bioavailable Lead mg/kg
151.6252042	-32.95001777	4.7	6	13	380	2,900	580
151.6268233	-32.95098369	4.6	13	16	1,070	1,940	850
151.624632	-32.951278	9	270	16	950	2,030	890
151.6208552	-32.95099963	12	11	3.1	150	780	140
151.6267028	-32.95251557	4.1	4.7	2	120	700	86
151.6265774	-32.95249488	7.5	6.8	9.8	380	1,240	390
151.6255153	-32.95263217	9.4	21	10	800	2,070	720
151.6255326	-32.95275625	6.6	9.2	6.7	480	2,830	350
151.6246207	-32.95271317	2.6	9.3	7	410	940	360
151.6225704	-32.95186125	3.9	9.5	6.1	370	840	300
151.6212238	-32.95181716	33	2.2	1.6	130	660	170
151.619887	-32.95279439	28	2.9	3.8	120	580	130
151.6240625	-32.95293802	14	6	5.4	1,320	1,260	1,010
151.62197	-32.954022	27	15	8.6	750	1,870	680
151.6343456	-32.93635946	13	7.6	4.5	290	1,430	220
151.6129705	-32.97585992	2.2	6.3	1.9	190	730	120
151.6275967	-32.95079784	2.6	32	6.1	500	1,370	460

Supplementary Table S3: Residential vacuum dust metal and metalloid concentrations.

GPS Co-ordina	ates	Site	Antimony	Arsenic	Cadmium	Lead	Zinc
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
151.6255153	-32.95263217	S7SF	2	8.8	11	950	770
		S7SF					
151.6255153	-32.95263217	2mm	1.9	6.9	8.3	710	550
151.6268233	-32.95098369	S2SB	4.5	43	25	2,010	3,160
		S2SB					
151.6268233	-32.95098369	2mm	3.4	24	14	1,240	2,000
151.619887	-32.95279439	S13SB	2.3	13	7.2	580	890
		S13SB					
151.619887	-32.95279439	2mm	1.3	8	4.5	360	550
151.6208552	-32.95099963	S4SB	2.7	22	7.2	700	1,190
		S4SB					
151.6208552	-32.95099963	2mm	4.5	31	7.9	850	1,370
151.6275967	-32.95079784	S23SF	11	49	55	4,230	5,840
		S23SF					
151.6275967	-32.95079784	2mm	5.9	29	24	2,250	10,200
151.6343456	-32.93635946	S16SF	1.5	17	6.1	420	900
		S16SF					
151.6343456	-32.93635946	2mm	1.6	20	6.5	440	1,090

Supplementary Table S4: Comparison of soil lead concentration in <180 μ m fraction to <2 mm fraction.

 \overline{S} = residential site code. SF = front yard soil, SB = back yard soil.

GPS Co-ordinates		Site	Antimony	Arsenic	Cadmium	Lead	Zinc
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
151.6229805	-32.9531	PS1	3	14	15	780	960
151.623357	-32.9421	PS2	3.6	13	26	1,520	2,590
151.623357	-32.9421	PS3	4.3	15	19	2,040	1,850
151.623357	-32.9421	PS4	2.1	12	7	700	820
151.631356	-32.9362	PS5	2.6	31	14	970	2,150
151.6227899	-32.96	PS6	2.1	12	11	750	1,220
151.628671	-32.9604	PS7	1	19	7.6	260	460
151.6270332	-32.9677	PS8	2.1	33	7.1	610	1,260
151.634222	-32.9549	PS9	4.9	13	35	1,930	1,970
151.634222	-32.9549	PS10	5	22	37	1,990	2,590
151.634222	-32.9549	PS11	3.8	30	31	1,600	1,930
151.633708	-32.9537	PS12	2.6	38	11	620	780
151.633708	-32.9537	PS13	2.3	30	12	660	870
151.633708	-32.9537	PS14	2.7	39	10	590	770
151.6236194	-32.9616	PS15	< 0.5	5	1.6	99	250
151.6236194	-32.9616	PS16	0.71	5.4	2.8	200	290
151.6236194	-32.9616	PS17	2.3	17	9.2	920	1,360
151.6408486	-32.9356	PS18	1.2	8.3	2.8	240	530
151.6401816	-32.9307	PS19	< 0.5	6.4	1.5	110	260
151.607615	-32.962	PS20	0.57	7.5	0.69	170	580
151.6411614	-32.9493	PS21	< 0.5	8.4	3.3	180	270
151.6202341	-32.962	PS22	2.2	17	5.5	580	1,650
151.6297227	-32.9309	PS23	1.3	11	3.5	380	950
151.6192389	-32.9579	SF1	6.5	33	7.7	1,970	5,990
151.6192389	-32.9579	SF2	41	200	21	17,500	29,900
151.6159087	-32.9602	SF3	1.9	12	4.4	470	1,410
151.6189572	-32.9555	SF4	1.5	24	2.5	580	2,420
151.6163805	-32.9624	PG1	0.59	4.5	1.7	130	490
151.643765	-32.9468	PG2	< 0.5	7.3	1.9	100	220
151.6226488	-32.9512	PG3	3.7	18	15	1,080	1,550
151.6226488	-32.9512	PG4	6.6	19	20	1,830	1,330
151.6199415	-32.9541	PG5	4.4	130	9.9	920	6,090

Supplementary Table S5: Non-residential soil metal and metalloid concentrations.

PS = public space, SF = Sporting field, PG = playground.

Appendix K

School codes	Primary school	Secondary school
A1	0	
A2	0	
A3	0	
A4	0	
A5	0	
A6	0	
A7	0	
A8	0	
A9		Π
A10		Π

Supplementary Table S1: Summary of Broken Hill schools.

Note: The names of schools are replaced by codes to assist in their de-identification. School information is extracted from Australian Curriculum, Assessment and Reporting Authority (ACARA), 2015.

Supplementary Figure S2: Australian Early Development Census (AEDC) local communities (blue lines) in Broken Hill. Overlain on the AEDC map coverage are the primary school catchment areas (red lines) for comparative purposes.



Supplementary Table S3: Summary of children developmentally vulnerable in different areas based on national and Broken Hill local community levels.

		Proportion of children developmentally vulnerable (%)									
Community	Number of children surveyed	Physical health and wellbeing	Social competence	Emotional maturity	Language and cognitive skills (school-based)	Communication skills and general knowledge	Vulnerable on one or more areas of the AEDC	Vulnerable on two or more areas of the AEDC	SEIFA (The index of Relative Socio- economic Disadvantage)		
Australia	289,973	9.3	9.3	7.6	6.8	9.0	22.0	10.8	960.0		
Broken Hill Central	82	24.3	24.3	20.0	12.9	28.6	41.4	31.4	868.4		
Broken Hill North	115	17.4	11.0	4.7	10.1	16.5	29.9	16.5	922.0		
Broken Hill West	50	15.2	8.7	8.7	10.9	13.0	28.3	17.4	898.4		

Note: the Australian Early Development Census (AEDC) data and Broken Hill local community SEIFA data are from Australian Early Development Census (AEDC), 2014a. The Australian national SEIFA average is from Australian Bureau of Statistics (ABS), 2013. AEDC results are typically reported as proportions of children who are regarded as 'on track', 'developmentally at risk', and 'developmentally vulnerable'. Children who score above the 25th percentile (in the top 75 per cent) of the AEDC population are classified as 'on track'. Children who score between the 10th and 25th percentile of the AEDC population are classified as 'developmentally at risk'. Children who score below the 10th percentile (in the lowest 10 per cent) of the national AEDC population are classified as 'developmentally vulnerable' (Australian Early Development Census (AEDC), 2013).
	Monthly average lead-in-air	Total c	leposited Pb (g/m ² /	(month)	Total deposited	l Pb (μg/m²/day) (original data
Date	concentration (µg/m ³)		9	<u>`</u>	calc	ulated over 30 day	/s)
	Licence point LP 12	Licence point LP 3	Licence point LP 4	Licence point LP 6	Licence point LP 3	Licence point LP 4	Licence point LP 6
May 2012	0.267	ND	0.015	0.007	ND	485	237
June 2012	0.122	DD	0.032	0.089	ND	1051	2950
July 2012	0.102	ND	<0.001	0.002	ND	ND	53
August 2012	0.357	ND	0.002	0.010	ND	81	343
September 2012	0.284	ND	0.002	0.003	ND	80	113
October 2012	0.556	ND	0.003	0.007	ND	92	223
November 2012	0.353	ND	0.005	0.006	ND	178	188
December 2012	0.316	ND	0.004	0.008	ND	117	253
January 2013	0.606	ND	0.005	0.003	ND	157	106
February 2013	0.351	ND	0.013	0.006	ND	433	200
March 2013	0.311	ND	0.005	0.004	ND	175	117
April 2013	0.160	ND	0.009	0.001	ND	309	50
May 2013	0.145	ND	0.003	0.002	ND	96	55
June 2013	0.120	ND	0.003	0.003	ND	86	112
July 2013	0.090	ND	0.003	0.009	ND	91	315
August 2013	0.177	0.005	0.002	0.010	166	72	336
September 2013	0.254	0.012	0.003	0.007	402	91	241
October 2013	0.595	0.016	0.004	0.007	530	127	223
November 2013	0.236	0.014	0.007	0.004	460	223	124
December 2013	0.707	0.018	0.002	0.003	597	81	108
January 2014	0.526	0.016	0.005	0.002	548	175	62
February 2014	0.172	0.010	0.006	0.004	323	211	121
March 2014	0.169	0.011	0.007	0.008	358	233	279
April 2014	0.056	0.004	0.006	0.003	145	204	113
May 2014	0.084	0.008	0.006	0.005	252	185	159

Supplementary Table S4: Monthly 24-h average lead-in-air concentration based on TSP (μ g/m³) and dust gauge deposited Pb (g/m²/month) recorded between May 2012 and May 2014 (Perilya Limited, 2015).

Note: *ND* – no data.

Property	Location	As (µg/m ²)	Cd (µg/m ²)	Pb (µg/m ²)
	BH_DW1_1907 (PE STOREROOM)	510.9	211.7	52919.7
School A9	BH_DW2_1907 (WINDOWSILL)	83.8	46.3	6283.5
(2012	BH_DW3_W_SILL	475.7	62.7	23495.7
samples)	BH_DW4_W_SILL	410.8	57.7	20612.8
	BH_DW5_W_SILL	552.6	71.3	27775.8
-	PE_STOREROOM WALL	86.96	30.43	10434.78
	PE_STOREROOM AIR VENT	161.33	74.76	21248.97
G 1 1 4 0	PE_STOREROOM SHELF	686.87	404.04	86060.61
School A9	WINDOW SILL 1 FAR (NR PE STORE)	52.29	16.09	13837.49
(2013	WINDOW SILL 2-4TH (NR PE STORE)	41.03	12.07	3298.47
samples)	WINDOW SILL 3-F BLOCK	58.20	20.95	7216.18
	WINDOW SILL 4-MASTER'S HOUSE	90.28	19.44	4791.67
	WINDOW SILL 5-MASTER'S HOUSE	130.37	29.33	7691.91
	SURFACE 1- ELECTRICAL BOX	48.67	8.00	2466.67
	SURFACE 2- PLAY EQUIPMENT	6.11	1.11	355.56
House 1	SURFACE 3- WATER HEATER	7.02	0.71	515.56
	SURFACE 4-FRIDGE	6.25	1.49	208.33
	SURFACE 5-BATHROOM	1.98	0.69	129.31
	WATER TANK	7.67	1.67	444.44
House 2	KITCHEN_SILL	BDL	BDL	125.32
	PIANO	2.22	1.07	131.63
	SURFACE 1_GLASS TABLE	17.78	4.00	822.22
House 3	SURFACE 2_KITCHEN SILL	15.00	3.50	600.00
House 5	SURFACE 3_WINDOW SILL_SOUTH SIDE	73.98	11.05	2551.02
	SURFACE 1 WATER TANK	122.22	63.33	17888.89
	SURFACE 2 LOUNGE DOOR	12.29	7.84	2268.43
II. 4	SURFACE 3 WINDOW SILL LOUNGE	1.65	1.50	278.97
House 4	SURFACE 4 TOP OF KITCHEN CUPBOARD	0.91	0.84	160.06
	SURFACE 5 WALL ABOVE COT	BDL	BDL	52.83

Supplementary Table S5: Arsenic, Cd and Pb concentrations in dust wipes for school A9 and four properties in Broken Hill.

Note: *BDL* – below detection limit.

School catchment	Sample name	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
	NBH1_0-2	29	17	2890
SC1	NBH5_0-2	16	12	1060
	NBH4_0-2	4.4	1.4	150
	NBH3_0-2	6.1	1.9	530
5.62	LOLE5_0-2	6	1.4	300
SC2	LOLE6_0-2	4	1.03	395
	HS6_0-2	2.3	0.94	170
	NBH2_0-2	3.8	0.61	140
SC3	BHW3_0-2	5	0.74	170
	LOLW4_0-2	2	0.27	46
	WBH1_0-2	7.1	2	330
SC4	WBH2_0-2	100	9.2	1340
	LOLW3_0-2	8	1	200
	HS1_0-2	24	4.4	2850
	HS2_0-2	12	2.1	1060
	HS3_0-2	28	3.5	1320
	HS4_0-2	59	12	2900
	HS5_0-2	18	7.3	2080
	CC1_0-2	12	4.4	660
	CC2_0-2	16	5.3	1220
	CC3_0-2	26	6.9	1320
	CC4_0-2	37	23	3490
SC5	CC5_0-2	150	37	3420
	CC6_0-2	150	27	3540
	CC7_0-2	150	17	2750
	LOLE1_0-2	6	1.8	700
	LOLE2_0-2	49	20	8900
	LOLE3_0-2	52	13	8400
	LOLE4_0-2	47	34	6300
	LOLW1_0-2	9.5	6.5	815
	LOLW2_0-2	46	13	2400
	NBH7_0-2	47	19	3620
	NBH6_0-2	9.9	3.9	1300
SC6	NBH8_0-2	14	3.9	1170

Supplementary Table S6: Arsenic, Cd and Pb concentration of 34 surface soils analyzed by ICP-MS across Broken Hill.

School catchment	Sample name	Pb (mg/kg)
	Soil_11	102
	Soil_12	45
SC1	Soil_13	1017
	Soil_16	1243
	Soil_17	557
	Soil_3	61
SCO	Soil_4	77
SC 2	Soil_14	50
	Soil_15	143
SC2	Soil_9	116
303	Soil_10	58
SC4	Soil_7	175
3C4	Soil_8	279
	Soil_18	6925
	Soil_19	1691
805	Soil_20	617
805	Soil_21	680
	Soil_22	1692
	Soil_23	2272
	Soil_1	1093
SCG	Soil_2	248
300	Soil_5	1248
	Soil_6	429

Supplementary Table S7: Lead concentration of 23 surface soils analyzed by pXRF across Broken Hill.

Note: *BDL* – below detection limit.

Supplementary Table S8: Arsenic, Cd and Pb concentrations of 29 sub-surface soil samples from depths > 30 cm used to calculate background metal and metalloid values in Broken Hill. The Pb data is from Kristensen and Taylor (2016). The As and Cd data also comes from that study but was not reported there.

Sample name	Soil depth (cm)	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
NBH1	40-50	9.7	1.9	420
NBH5	40-50	30	3.7	2410
NBH4	40-50	3.2	<0.5	18
LOLE5	40-50	4	0.75	170
HS6	40-50	2.2	0.95	280
NBH2	40-50	4	<0.5	12
BHW3	30-35	4.4	<0.5	30
LOLW4	40-50	4	0.08	15
WBH1	40-50	2.8	0.62	310
WBH2	40-50	4.9	<0.5	18
LOLW3	30-40	3	0.07	13
HS1	40-50	19	<0.5	700
HS2	40-50	3.9	0.67	48
HS3	40-50	7.5	<0.5	240
HS4	40-50	7.9	0.95	190
HS5	40-50	5.8	<0.5	100
CC2	40-50	8.3	<0.5	97
CC3	40-50	7.9	<0.5	53
CC4	40-50	5.6	<0.5	21
CC5	40-50	4.4	<0.5	24
CC7	40-50	9.8	1.6	190
LOLE1	40-50	3	0.39	97
LOLE2	40-50	4	0.42	160
LOLE3	40-50	3	0.6	200
LOLE4	40-50	22	7	2000
LOLW1	40-50	3	0.25	44
LOLW2	40-50	6	0.37	77
NBH7	40-50	11	0.69	190
NBH8	40-50	13	<0.5	61

Note: Where reported values were less than the limit of reporting i.e. Cd 0.5 mg/kg, a nominal value at 50 % of this (i.e. 0.25 mg/kg) was used for statistical purposes.

Property	Sample name	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)		
	BH1_0-2 cm	11.0	5.9	750		
	BH2_0-2 cm	7.1	2.3	440		
	BH3_0-2 cm	6.1	3.2	650		
	BH4_0-2 cm	17.0	6.6	1510		
	BH5_0-2 cm	17.0	8.2	2200		
	BH6_0-2 cm	12.0	4.6	1040		
	BH7_0-2 cm	6.1	1.9	390		
	BH8_0-2 cm	9.2	4.7	1390		
	BH9_0-2 cm	6.9	1.8	580		
	BH10_0-2 cm	7.0	3.8	740		
School A9	BH11_0-2 cm	6.8	1.3	360		
	BH12_0-2 cm	9.8	4.6	1140		
	BH13_0-2 cm	5.2	1.6	380		
	BH14_0-2 cm	3.8	0.9	190		
	BH15_0-2 cm	15.0	2.9	710		
	BH16_0-2 cm	16.0	0.9	470		
	BH17_0-2 cm	9.6	2.6	600		
	BH19_0-2 cm	10.0	2.8	700		
	BH20_0-2 cm	26.0	3.0	1510		
	BH21_0-2 cm	11.0	2.9	840		
	BH22_0-2 cm	5.1	1.0	280		
	BH23_0-2 cm	6.8	2.3	860		
	SOIL_1 BACK GARDEN	3.2	0.5	100		
House 1	SOIL_2 VEGGIE PATCH	1.1	BDL	15		
	SOIL_3 FRONT GARDEN	3.6	0.71	280		
	SOIL_1 FRONT	5.1	1.5	420		
House 2	SOIL_2 SIDE	16	5.1	1130		
	SOIL_3 BACK	4.5	1.2	250		
	SOIL_1 VEGGE PATCH	1.8	BDL	14		
House 3	SOIL_2 FRONT	2.7	0.5	140		
	SOIL_3 BACK	3	0.94	300		
	SOIL_1 VEGGIE PATCH	11	7.2	2260		
House 4	SOIL_2 BACK YARD	3	98	360		
	SOIL_3 FRONT YARD	15	8.4	2160		

Supplementary Table S9: Arsenic, Cd and Pb concentrations in soil for the school A9 and four domestic residences in Broken Hill.

Note: *BDL* – below detection limit.

Supplementary Table S10. Australian Early Development Census (AEDC) results standardized by socio-economic index of the Broken Hill central children vulnerability

		Proportion of children developmentally vulnerable (%)													
Community	Number of children surveyed	Physical health and wellbeing	Social competence	Emotional maturity	Language and cognitive skills (school-based)	Communication skills and general knowledge	Vulnerable on one or more areas of the AEDC	Vulnerable on two or more areas of the AEDC	SEIFA (The index of Relative Socio- economic Disadvantage)						
Australia	289,973	9.3	9.3	7.6	6.8	9.0	22.0	10.8	960.0						
Broken Hill Central	82	24.3	24.3	20.0	12.9	28.6	41.4	31.4	868.4						
Broken Hill North	115	17.4	11.0	4.7	10.1	16.5	29.9	16.5	922.0						
Broken Hill West	50	15.2	8.7	8.7	10.9	13.0	28.3	17.4	898.4						

							Y	ear 3							
A 1	D1	AUS	Similar	D2	AUS	Similar	D2	AUS	Similar	D4	AUS	Similar	D5	AUS	Similar
AI	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	326	400	363	346	414	384	345	400	367	332	403	361	333	397	365
2009	350	411	372	372	414	383	372	405	373	346	420	373	319	394	361
2010	335	414	353	344	419	366	362	399	347	319	417	347	306	395	346
2011	377	416	360	353	416	370	390	406	358	366	421	360	352	398	358
2012	318	420	366	350	416	373	348	414	363	334	424	364	333	396	352
2013	360	419	361	323	416	356	337	411	352	342	428	363	331	397	348
	D1	AUS	Similar	DA	AUS	Similar	DA	AUS	Similar	54	AUS	Similar	55	AUS	Similar
A2	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	360	400	366	383	414	387	372	400	370	372	403	365	368	397	368
2009	378	411	376	385	414	386	379	405	375	389	420	377	361	394	363
2010	374	414	351	376	419	363	372	399	346	359	417	344	392	395	344
2011	326	416	354	336	416	364	336	406	353	328	421	353	344	398	353
2012	350	420	358	363	416	366	345	414	360	348	424	355	337	396	345
2013	342	419	356	369	416	351	337	411	347	355	428	358	352	397	344
	D1	AUS	Similar	DA	AUS	Similar	DA	AUS	Similar	D.4	AUS	Similar	55	AUS	Similar
A3	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	425	400	377	439	414	396	420	400	379	432	403	377	403	397	377
2009	377	411	387	402	414	395	383	405	384	372	420	389	371	394	373
2010	400	414	381	408	419	393	384	399	371	394	417	380	371	395	368
2011	388	416	382	378	416	388	389	406	377	389	421	384	363	398	374
2012	413	420	388	428	416	390	421	414	384	437	424	388	422	396	369
2013	395	419	388	410	416	386	400	411	379	382	428	395	371	397	371
A 4	D1	AUS	Similar	DJ	AUS	Similar	D2	AUS	Similar	D4	AUS	Similar	Df	AUS	Similar
A4	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D3	avg	avg
2008	372	400	373	395	414	393	380	400	376	376	403	373	362	397	374
2009	382	411	383	386	414	392	398	405	381	390	420	385	372	394	370
2010	390	414	373	403	419	385	392	399	365	400	417	370	361	395	362
2011	360	416	375	359	416	383	369	406	371	369	421	376	351	398	368
2012	397	420	380	403	416	384	387	414	378	387	424	380	376	396	363
2013	391	419	383	375	416	380	393	411	374	393	428	389	361	397	366
45	D1	AUS	Similar	D2	AUS	Similar	D3	AUS	Similar	D4	AUS	Similar	D5	AUS	Similar
AJ	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D3	avg	avg
2008	416	400	393	418	414	409	409	400	392	407	403	395	397	397	391
2009	408	411	403	409	414	408	412	405	398	425	420	406	395	394	387
2010	410	414	392	421	419	402	405	399	380	417	417	391	382	395	377
2011	383	416	393	387	416	397	388	406	386	386	421	396	390	398	382
2012	456	420	399	428	416	399	448	414	393	442	424	400	419	396	378
2013	423	419	403	388	416	401	400	411	394	415	428	411	407	397	384

Supplementary Table S11: Summary of the National Assessment Program – Literacy and Numeracy (NAPLAN) data from Broken Hill schools.

16	DI	AUS	Similar	D2	AUS	Similar	D3	AUS	Similar	D4	AUS	Similar	D5	AUS	Similar
Au	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D3	avg	avg
2008	387	400	362	398	414	384	399	400	366	398	403	360	393	397	365
2009	356	411	372	418	414	382	404	405	372	371	420	373	370	394	360
2010	380	414	376	385	419	388	361	399	367	383	417	373	372	395	364
2011	330	416	362	361	416	371	359	406	360	342	421	362	350	398	359
2012	360	420	362	381	416	369	374	414	363	392	424	359	364	396	348
2013	400	419	378	385	416	375	414	411	369	407	428	383	361	397	362
		AUS	Similar		AUS	Similar		AUS	Similar		AUS	Similar		AUS	Similar
A/	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	432	400	385	455	414	403	445	400	386	450	403	386	465	397	384
2009	423	411	395	385	414	402	379	405	391	415	420	397	391	394	380
2010	410	414	417	416	419	421	358	399	400	404	417	418	369	395	397
2011	401	416	416	422	416	414	374	406	405	413	421	421	389	398	400
2012	445	420	419	426	416	413	424	414	410	443	424	422	416	396	395
2013	424	419	420	451	416	416	413	411	409	452	428	429	404	397	398
		AUS	Similar		AUS	Similar		AUS	Similar		AUS	Similar		AUS	Similar
A8	D1	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	345	400	406	373	414	419	340	400	403	368	403	409	389	397	402
2009	436	411	416	440	414	418	422	405	408	455	420	420	426	394	398
2010	393	414	433	406	419	433	377	399	413	433	417	435	388	395	411
2011	369	416	434	388	416	426	349	406	419	374	421	438	382	398	413
2012	422	420	436	410	416	425	395	414	424	399	424	440	406	396	409
2013	399	419	409	374	416	407	354	411	399	395	428	418	382	397	389
							Y	ear 5							
	54	AUS	Similar		AUS	Similar		AUS	Similar	54	AUS	Similar		AUS	Similar
AI	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	432	484	450	424	486	455	446	484	456	429	496	456	409	476	443
2009	433	494	458	423	485	452	443	487	458	425	500	458	427	487	454
2010	425	487	430	432	485	430	440	487	442	405	500	433	441	489	437
2011	440	488	441	436	483	434	461	484	441	446	499	444	436	488	448
2012	438	494	444	409	477	432	479	495	450	434	491	436	447	489	444
2013	447	502	452	406	478	417	441	494	439	442	501	438	430	486	433
		AUS	Similar		AUS	Similar		AUS	Similar		AUS	Similar		AUS	Similar
A2	D1	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	447	484	453	444	486	458	440	484	458	461	496	460	423	476	445
2009	419	494	461	409	485	455	454	487	461	430	500	462	428	487	457
2010	443	487	428	434	485	428	448	487	440	464	500	431	439	489	435
2011	461	488	435	426	483	428	459	484	436	447	499	437	433	488	444
2012	420	494	436	414	477	425	451	495	445	433	491	428	430	489	438
2013	439	502	448	411	478	411	416	494	435	439	501	433	453	486	429
	_	AUS	Similar	_	AUS	Similar	_	AUS	Similar		AUS	Similar		AUS	Similar
A3	D1	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg

2009	444	494	472	453	485	465	463	487	469	452	500	474	486	487	466
2010	486	487	458	465	485	459	537	487	464	480	500	467	487	489	461
2011	447	488	459	480	483	453	487	484	457	473	499	466	485	488	462
2012	524	494	464	504	477	449	530	495	466	487	491	457	503	489	461
2013	477	502	476	454	478	448	476	494	465	485	501	468	464	486	457
	D1	AUS	Similar	DA	AUS	Similar	D2	AUS	Similar	D4	AUS	Similar	D.5	AUS	Similar
A4	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	462	484	460	477	486	464	471	484	463	473	496	467	472	476	451
2009	498	494	468	447	485	462	478	487	466	470	500	469	474	487	463
2010	445	487	450	468	485	451	474	487	458	467	500	457	456	489	454
2011	473	488	453	433	483	447	466	484	452	465	499	459	444	488	458
2012	477	494	457	457	477	443	492	495	461	481	491	450	457	489	455
2013	474	502	471	442	478	442	452	494	460	462	501	462	431	486	452
15	D1	AUS	Similar	D	AUS	Similar	D2	AUS	Similar	D4	AUS	Similar	DS	AUS	Similar
AS	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	505	484	478	509	486	480	494	484	477	521	496	488	505	476	468
2009	488	494	486	486	485	479	503	487	480	519	500	490	490	487	479
2010	502	487	468	498	485	469	499	487	471	518	500	478	492	489	470
2011	505	488	469	487	483	462	486	484	465	510	499	477	497	488	470
2012	495	494	474	462	477	458	493	495	474	487	491	468	483	489	470
2013	492	502	489	441	478	463	469	494	478	457	501	484	469	486	470
10	D1	AUS	Similar	D2	AUS	Similar	D2	AUS	Similar	D4	AUS	Similar	Df	AUS	Similar
Ao	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	474	484	449	474	486	455	509	484	455	495	496	456	488	476	442
2009	439	494	457	424	485	452	458	487	458	435	500	458	465	487	454
2010	497	487	452	481	485	454	495	487	459	487	500	460	504	489	456
2011	458	488	442	443	483	436	480	484	442	467	499	445	483	488	449
2012	434	494	440	415	477	428	428	495	447	416	491	431	449	489	441
2013	487	502	467	474	478	436	471	494	455	466	501	457	464	486	447
17	D1	AUS	Similar	D	AUS	Similar	D2	AUS	Similar	D4	AUS	Similar	DS	AUS	Similar
A/	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	03	avg	avg
2008	510	484	470	500	486	474	498	484	472	529	496	480	478	476	461
2009	479	494	479	485	485	472	479	487	474	503	500	482	490	487	472
2010	485	487	491	526	485	489	520	487	488	504	500	504	514	489	514
2011	490	488	488	466	483	480	481	484	481	513	499	499	488	488	487
2012	518	494	492	479	477	473	501	495	489	536	491	489	492	489	486
2013	505	502	503	483	478	478	509	494	492	510	501	501	493	486	485
40	D1	AUS	Similar	D	AUS	Similar	D2	AUS	Similar	D4	AUS	Similar	DS	AUS	Similar
Að	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	484	484	489	522	486	491	452	484	486	522	496	500	471	476	479
2009	473	494	498	463	485	489	455	487	489	475	500	503	463	487	490
2010	395	487	507	413	485	501	436	487	499	386	500	519	442	489	505
2011	514	488	504	494	483	492	490	484	493	496	499	515	494	488	501
2012	530	494	508	467	477	485	454	495	501	499	491	506	496	489	500

2013	538	502	494	485	478	469	460	494	484	513	501	490	504	486	476
							Y	ear 7							
10	DI	AUS	Similar	DA	AUS	Similar	D	AUS	Similar	D4	AUS	Similar	D.5	AUS	Similar
A9	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D5	avg	avg
2008	512	536	514	520	534	511	525	539	518	509	529	504	514	545	520
2009	530	541	518	512	532	511	530	540	520	527	539	514	525	544	519
2010	528	546	514	503	533	503	539	545	516	521	535	501	527	548	516
2011	518	540	510	483	529	497	528	538	510	509	532	499	523	545	512
2012	514	542	510	459	518	488	532	543	513	517	546	515	509	538	505
2013	526	541	508	493	517	481	537	549	516	513	535	497	512	542	508
A 10	D1	AUS	Similar	D2	AUS	Similar	D3	AUS	Similar	D4	AUS	Similar	D5	AUS	Similar
Alt	DI	avg	avg	D2	avg	avg	D3	avg	avg	D4	avg	avg	D3	avg	avg
2008	516	536	519	475	534	515	512	539	521	499	529	509	513	545	524
2009	520	541	522	505	532	515	516	540	523	519	539	519	514	544	524
2010	513	546	518	492	533	507	529	545	519	507	535	505	509	548	519
2011	507	540	513	483	529	501	508	538	512	492	532	503	503	545	516
2012	514	542	512	452	518	490	522	543	515	512	546	517	509	538	507
0010	500	C 4 1	504	161	517	174	510	540	510	400	525	100	501	- 10	
2013	502	541	504	464	517	476	518	549	512	482	535	492	521	542	505
2013	502	541	504	464	517	476	518 Y	549 Tear 9	512	482	535	492	521	542	505
2013	502	AUS	504 Similar	464 D2	AUS	476 Similar	518 Y	549 Tear 9 AUS	512 Similar	482	AUS	492 Similar	521	AUS	505 Similar
2013 	502 D1	AUS avg	Similar avg	464 D2	AUS avg	476 Similar avg	518 Y D3	S49 Tear 9 AUS avg	Similar avg	482 D4	AUS	492 Similar avg	D5	AUS avg	505 Similar avg
A9 2008	D1 559	AUS avg 578	Similar avg 555	464 D2 539	AUS avg 569	476 Similar avg 540	518 Y D3 549	S49 Year 9 AUS avg 577	Similar avg 554	482 D4 546	AUS avg 569	492 Similar avg 542	D5 558	AUS avg 582	Similar avg 555
2013 A9 2008 2009	D1 559 554	AUS avg 578 580	Similar avg 555 557	D2 539 534	AUS avg 569 569	Similar avg 540 537	518 Y D3 549 575	549 Fear 9 AUS avg 577 576	Similar avg 554 552	482 D4 546 554	535 AUS avg 569 574	Similar avg 542 548	521 D5 558 561	542 AUS avg 582 589	505 Similar avg 555 562
A9 2008 2009 2010	D1 559 554 541	AUS avg 578 580 574	Similar avg 555 557 543	D2 539 534 533	AUS avg 569 569 568	476 Similar avg 540 537 527	518 Y D3 549 575 560	S49 fear 9 AUS avg 577 576 579	512 Similar avg 554 552 549	D4 546 554 544	S35 AUS avg 569 574 579	492 Similar avg 542 548 542	521 D5 558 561 549	AUS avg 582 589 585	Similar avg 555 562 550
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A9 2008 2009 2010 2011 2012	D1 559 554 541 550 553	AUS avg 578 580 574 580 575	Similar avg 555 557 543 549 541	D2 539 534 533 515 515	AUS avg 569 569 568 566 554	4/6 Similar avg 540 537 527 517 510	518 Y D3 549 575 560 555 552	S49 iear 9 AUS avg 577 576 579 581 577	512 Similar avg 554 552 549 549 545	482 D4 546 554 544 543 542	S35 AUS avg 569 574 579 572 573	492 Similar avg 542 548 542 534 538	D5 558 561 549 551 555	S42 AUS avg 582 589 585 583 584	Similar avg 555 562 550 548 549
A9 2008 2009 2010 2011 2012 2013	502 D1 559 554 541 550 553 561	AUS avg 578 580 574 580 575 580	Similar avg 555 557 543 549 541 551	D2 539 534 533 515 515 497	AUS avg 569 569 568 566 554 554	476 Similar avg 540 537 527 517 510 507	518 Y D3 549 575 560 555 555 552 565	S49 iear 9 AUS avg 577 576 579 581 577 583	512 Similar avg 554 552 549 549 545 552	482 D4 546 554 544 543 542 542	S35 AUS avg 569 574 579 572 573	492 Similar avg 542 548 542 534 538 531	D5 558 561 549 551 555 555	542 AUS avg 582 589 585 583 583 584 584	505 Similar avg 555 562 550 548 549 544
A9 2008 2009 2010 2011 2012 2013	502 D1 559 554 541 550 553 561	AUS avg 578 580 574 580 575 580 AUS	Similar avg 555 557 543 549 541 551 Similar	464 D2 539 534 533 515 515 497 D2	AUS avg 569 569 568 566 554 554 AUS	476 Similar avg 540 537 527 517 510 507 Similar	518 Y D3 549 575 560 555 552 565 D3	S49 fear 9 AUS avg 577 576 579 581 577 583 AUS	512 Similar avg 554 552 549 549 545 552 Similar	482 D4 546 554 544 543 542 542 542 D4	535 AUS avg 569 574 579 572 573 573	492 Similar avg 542 548 542 534 534 538 531 Similar	D5 558 561 549 551 555 555 D5	S42 AUS avg 582 589 585 583 584 584	Similar avg 555 562 550 548 549 544 Similar
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Note: D1-Reading, D2-Narrative writing, D3-Spelling, D4-Grammer and Punctuation, D5-Numceracy. AUS average - Australian average value, Similar average - the average value of schools with similar ICSEA value. The data is available from Australian Curriculum, Assessment and Reporting Authority (ACARA), 2015. **Supplementary Table S12:** Summary of children developmentally vulnerable in different areas based on national, Mount Isa and Port Pirie local communities levels.

		Proportion of children developmentally vulnerable (%)												
Community	Number of children surveyed	Physical health and wellbeing	Social competence	Emotional maturity	Language and cognitive skills (school-based)	Communication skills and general knowledge	Vulnerable on one or more areas of the AEDC	Vulnerable on two or more areas of the AEDC	SEIFA (The index of Relative Socio- economic Disadvantage)					
Australia	289,973	9.3	9.3	7.6	6.8	9.0	22.0	10.8	960.0					
Happy Valley/Parkside	50	4.1	8.2	6.1	8.2	0.0	12.2	8.2	1034.5					
Healy	34	2.9	11.8	11.8	5.9	2.9	14.7	11.8	1077.5					
North Mount Isa	121	16.9	19.5	16.9	14.4	19.5	36.4	25.4	1026.2					
Townview and Surrounds	134	13.2	10.1	3.1	17.8	15.5	31.0	14.0	940.4					
Port Pirie and surrounds	165	16.9	16.9	14.9	10.8	6.8	32.4	16.2	875.0					

Note: the Australian Early Development Census (AEDC) data and the local community SEIFA data of Mount Isa and Port Pirie are from Australian Early Development Census (AEDC), 2014b and Australian Early Development Census (AEDC), 2014c, respectively. Australian national SEIFA average is from Australian Bureau of Statistics (ABS), 2013.

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