Environmental and geochemical analysis of lead contamination: its sources and pathways of exposure and impact on children

Chenyin Dong

BSc. (East China Normal University)

Department of Environmental Sciences

Faculty of Science and Engineering

Macquarie University

Sydney, Australia

Thesis presented for the degree of

Doctor of Philosophy

MACQUARIE University

SYDNEY·AUSTRALIA

Cover photo:

Lead and zinc ore pile at the head of Perilya Limited's Mine in Broken Hill, NSW, Australia (photo provided by Professor Mark Taylor).

Acknowledgements

Many people and organisations have helped me with this research, and I would like to take this opportunity to say thank you to all of you for helping make this PhD possible.

Firstly, many thanks go to my supervisor Professor Mark Taylor. Without his limitless support, this thesis should be still a work in progress. Mark has helped me greatly in my PhD research, for example, assisting me in planning this research, seeking extra funds to support my study, signing various 'boring' forms, and going over my manuscripts. Mark is an incredible role model for me. His enthusiasm for his work and life has given me encouragement to pursue my goals. As a young researcher, I believe what I learn from Mark, not only limited to knowledge, will benefit myself for a lifelong period.

I would like to thank the Broken Hill Environmental Lead Program, in particular Frances Boreland and Peter Oldsen from the Broken Hill Environmental Lead Program for their help with my 12-months dust sample collection and their constructive discussions about my PhD project. Many thanks are also expressed to Dr Margaret Lesjak from the Broken Hill University Department of Rural Health and to the staff from the Broken Hill Child & Family Health Centre for helping me to obtain the Broken Hill dataset that include the last 25 years soil/dust Pb data and blood Pb data. Emeritus Professor Brian Gulson is also thanked for his valuable and practical suggestions on my study. I am also grateful to Associate Professor Sammy Zahran for his significant help in designing, developing and performing statistical analyses with respect to Papers Four and Five. Without his inputs these studies would be much diminished in terms of their insight and novelty. I am also very grateful for him hosting, training and sharing his statistical knowledge with me when I visited him at Colorado State University, USA in September 2016. I also thank the practical support from Rainbow Preschool, Broken Hill High school, Willyama High school and all homes involved in the Broken Hill sampling campaign.

I would also like to acknowledge the National Measurement Institute (NMI), in particular Drs Ping Di, Shiva Prasad, Andrew Evans, and Michael Wu for providing laboratory analysis support and advice. Nicole Vella, Nadia Suarez-Bosche, Debra Birch, and Sue Lindsay from the Macquarie University Microscopy Unit are also thanked for their assistance with scanning electron microscope analysis. I am also very grateful to Megan Wright for proofreading the final chapter drafts of this thesis.

Special thanks go to our research team, Marek Rouillon, Louise Kristensen and Paul Harvey for their assistance in the preparation of manuscripts and conferences posters and presentations. I am also grateful for having the opportunity to travel with Marek and Paul during fieldwork and conference trips. Many thanks also go to our Departmental admin team for their patience and assistance over the term of my candidature.

I am very grateful for my former supervisor Professor Weiguo Zhang, East China Normal University, who encouraged and supported unconditionally me to pursue my PhD research at Macquarie University. In particular, I thank Weiguo for hosting me when I visited Shanghai over the last few years and for our discussions about work and life in Australia and future research. Your valuable advice is very much appreciated.

Lastly, special thanks to my mum, dad and sister for your absolute support and love, which have kept me going through the hardest of times. I thank you for all your encouragement and tolerance. Much love to you all.

I also acknowledge the generous funding support from Macquarie University for my PhD studies—an International Macquarie University Research Excellence Scholarship (iMQRES No. 2014098). In addition, I acknowledge financial support from the Broken Hill Environmental Lead Program (BHELP) as part of a Macquarie University–BHELP collaboration agreement.

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, expect acknowledged. This thesis is comprised solely of my own work.

Chenyin Dong
January 2018

Abstract

Resolving the source of environmental contamination is a critical first step in planning remediation and intervention strategies to adduce exposure prevention. However, a major challenge in established mining and smelting communities is that the sources of contamination and related potential health risks are often minimised by polluters and government agencies, often using unsupported scientific claims. A significant and long-standing example of this vexed issue is the protracted dispute over contamination sources and causes of childhood blood Pb exposures in Broken Hill (New South Wales), Australia's longest-operating Pb–Ag–Zn mining city.

In order to unravel the sources, causes and impacts of contemporary Pb contamination in Broken Hill, this study applied a multiple lines of evidence approach using a combination of geochemical analyses and human health data. The methods applied included analysis of trace element concentrations in soil, dust, tailing dumps and weathered ores, their Pb isotopic and chemical compositions and the morphological characteristics of individual Pb-rich particles. The results demonstrated that Broken Hill contemporary dust Pb deposits were primarily sourced from current mining emissions as opposed to naturally weathered or legacy sources held in soil and dust around the city. Children living closest to the mining operations were found to be at an increased risk of Pb exposure due to higher dust Pb loading (mean 255 $\mu g/m^2/day$) and its high bioaccessibility (75% of total Pb). The effects of current mining emissions on the contemporary dust Pb loading were quantitatively estimated. The analysis showed that a 1% increase in distance away from the current mining operations was associated with -0.501% (95% CI: -0.728, -0.275) reduction in dust Pb loading, while a 1% increase in production intensity at the mine increased the expected amount of dust Pb loading by 1.487% (95% CI: 0.537, 2.437%).

Consistent with the dust Pb decreasing with distance away from current active mining operations, contemporary blood Pb concentrations (2011–2015) also decreased with distance (i.e. 1% increase in distance was associated with a 0.173% reduction in blood Pb concentration). Soil Pb concentrations, which are a proxy for legacy contamination from atmospheric dust depositions across the city also showed a decreasing trend away from the mining operations. Consequently, analysis of the long-term relationship between environmental Pb and blood Pb (1991–2015) revealed that both soil and dust Pb were significantly correlated with blood Pb concentrations, complicating the specific attribution of these individual sources to blood Pb exposure. To quantify the relevant sources of Pb, two

'natural experiments' were examined to separate the specific role of dust and soil Pb on children's blood Pb exposures: (a) the city's northerly prevailing wind direction; (b) the 2009 dust storm that blanketed Broken Hill soil with desert borne sands, rich in crustal elements Al, Si and Fe. The analyses showed that children living within the prevailing wind direction were at the greatest risk of elevated blood Pb compared to those living in a non-prevailing wind direction, even after adjusting for effects of residential soil Pb contamination. The role of current emissions on driving exposures was further corroborated by the fact that children's blood Pb shifted systematically with mine Pb production volumes irrespective of remedial interventions. The second natural experiment, the 2009 dust storm, showed blood Pb concentrations still decreased with distance even though soil Pb-distance gradient was reduced after the dust storm. Generalised linear regression analysis of contemporary outdoor dust Pb deposits and blood Pb concentrations corroborated dust as being a significant driver of childhood Pb exposures.

This thesis research confirms that soil Pb on its own cannot explain blood Pb distributions and that dust Pb depositions are a significant factor in driving contemporary exposures. This finding provides evidence-based support for the mitigation and remediation approaches that are likely to be the most effective in terms of reducing blood Pb exposures in children—these being a clear need to control current mining emissions in Broken Hill as has been identified in Australia's other mining and smelting communities of Mount Isa and Port Pirie. The adverse consequences of not implementing evidence-based and targeted mitigation and remediation strategies on childhood development outcomes were also evaluated in the thesis. Early childhood development indices (i.e. developmental vulnerabilities—Australian Early Development Census data; school test scores—National Assessment Program Literacy and Numeracy) showed that children from the most contaminated areas in Broken Hill had lower educational performance and higher developmental vulnerabilities, even when normalised for socio-economic status. Similarly, poor scores were identified for Australia's other Pb processing locations of Mount Isa (Queensland) and Port Pire (South Australia), indicating the urgent need to implement the highest standards to limit the impact of mining and smelting Pb emissions on adjoining communities. Finally, application of a multiple lines of evidence as used in this thesis research to establish more precisely the source(s) of exposure in mining and smelting communities could be applied to other locations. Such an approach would help to address unequivocally extant disputes over the sources, causes and impacts of environmental Pb contamination in order to better target remediation and prevention strategies.

Table of Contents

Acronyms and Abbreviations

ABC	Australian Broadcasting Corporation
ABS	Australian Bureau of Statistics
AEDC	Australian Early Development Census
Ag	Silver
As	Arsenic
BHP	Broken Hill Proprietary Company
Cd	Cadmium
CDC	Centers of Disease Control and Prevention
EDS	Energy Dispersive Spectroscopy
EPA	Environment Protection Authority
IQ	Intelligence Quotient
mg/kg	Milligram per kilogram
MP	Member of Parliament
Mt	Million tonnes
NAPLAN	National Assessment Program–Literacy and Numeracy
NEPM	National Environment Protection Measures
ng/m^3	Nanograms per cubic metre (units of metal(loid)s in air measurement)
NHMRC	National Health and Medical Research Council
NMI	National Measurement Institute
NPI	National Pollutant Inventory
NSW	New South Wales
oz	Ounce
PAHS	Polycyclic aromatic hydrocarbons
Pb	Lead
PBDEs	Polybrominated diphenyl ethers
PFOS/PFOA	Perfluorooctane sulfonate/perfluoro-octanoic acid
pXRF	Portable X-Ray fluorescence
SA	South Australia
SEM	Scanning electron microscope
µg/dL	Micrograms per gram (units of blood lead measurement)
$µg/m^3$	Micrograms per cubic metre (units of metal(loid)s in air measurement)
$µg/m^2/day$	Micrograms per square metre per day (units of in dust deposits measurement)
WHO	World Health Organization
Zn	Zinc

Author contribution to publications

Chapter 3: Applying geochemical signatures and SEM methods to identify contamination sources of mining and smelting communities

Paper One: **Dong, C.** (80%), Taylor, M. P. (20%), 2017. Applying geochemical signatures of atmospheric dust to distinguish current mine emissions from legacy sources. *Atmospheric Environment* 161, 82-89.

This paper was developed by Dong and Taylor. Fieldwork, laboratory analyses and writing were performed by Dong. Editing and reviewing were conducted by Dong and Taylor.

Paper Two: Harvey, P. J. (55%), Rouillon, M. (20%), **Dong, C.** (5%), Ettler, V. (5%), Handley, H. K. (2%), Taylor, M. P. (5%), Tyson, E. (2%), Tennant, P. (2%), Telfer, V. (2%), Trinh, R. (2%), 2017. Geochemical sources, forms and phases of soil contamination in an industrial city. *Science of the Total Environment* 584-585, 505-514.

This study was designed by Harvey, Rouillon, Dong and Taylor. Fieldwork was conducted by Harvey, Rouillon, Dong, Tyson, Tennant, Telfer and Trinh over many trips to Newcastle. Laboratory analyses were conducted by Harvey, Rouillon, Dong and Ettler. Writing was performed by Harvey and Rouillon. Editing and reviewing were conducted by all authors.

Chapter 4: Blood Pb and its response to environmental Pb

Paper Three: Childhood blood lead and the response to environmental Pb in an Australian mining community—Broken Hill. **Dong, C.** (80%), Taylor, M. P. (20%), To be submitted to *Environmental Research.*

This study was designed by Dong. Statistical analyses were conducted by Dong. Writing was performed by Dong. The text was edited and reviewed by Taylor.

Chapter 5: Influences of contemporary mining activities on childhood blood Pb and dust Pb deposits in Broken Hill

Paper Four: Blood lead effects of child exposure to contemporary emissions in an Australian mining community. **Dong, C.** (50%), Taylor, M. P. (20%), Zahran, S. (30%), To be submitted to *Environmental Health Perspectives.*

The initial concept of this paper came from Taylor. This research was developed, designed and undertaken by all three authors. C. Dong and S. Zahran undertook the study analyses. All authors have been involved in the paper writing.

Chapter 6: Influences of environmental contamination on the children educational and behavioural performance

Paper Five: **Dong, C.** (65%), Taylor, M. P. (15%), Kristensen, L. J. (5%), Zahran, S. (15%), 2015. Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioral outcomes. *Environmental Pollution* 207, 345-356.

The concept of this paper came from Taylor with development by Dong. Environmental contamination data was provided by Taylor and Kristensen. Childhood health data was compiled by Dong. Statistical analyses were performed by Zahran. Writing was performed by Dong. Editing and reviewing was done by Taylor and Kristensen.

Chapter 1: Introduction

1.1 Environmental contamination in Australia

With the development of the global economy, awareness of environmental contamination and human health exposure risk has increased among individuals, non-governmental organisations, industry and governments worldwide (Evans and Kantrowitz, 2002; Dunlap and Jorgenson, 2012). In recent times, there has been a greater focus on morbidity and mortality risks associated with global contamination, particularly in lower to middle-income countries (Landrigan et al., 2017). Given Australia's relatively short post-European history, it might be expected that pollution would be less of a concern than in centuries-old European cities, as well developing countries with a poor understanding of environmental contamination severity (Tiller, 1992). However, the upsurge of worldwide environmental contamination since the industrial revolution has resulted in significant pollution in Australia (Tiller, 1992) which encompasses a diverse range of pollutants across the continent (Langley, 2002). There are many examples of how environmental contamination has occurred in Australia, including the use of pollutants to control insects and weeds for a wide range of domestic, public health and agricultural purposes. Pesticides and herbicides have been used widely at levels which exceed the environment's ability to absorb or recycle these contaminants, and have been detected in regions across Australia (e.g. Kookana et al., 1998; Kennedy et al., 2012; Weaver et al., 2012; Allinson et al., 2017). Polybrominated diphenyl ethers (PBDEs) are an important class of flame retardants that have been used widely in a variety of consumer products, resulting in contamination caused by their usage and manufacture, as well as the waste disposal of related consumer products containing PBDEs (e.g. Toms et al., 2009; Stasinska et al., 2013; McGrath et al., 2016, 2017; English et al., 2017). In addition, contamination by polycyclic aromatic hydrocarbons (PAHs) has resulted from the combustion of organic materials, including the burning of fossil fuels, in Australia (e.g. McCready et al., 2000; Nguyen et al., 2014). Polycyclic aromatic hydrocarbons contamination is also associated commonly with fuel stations (NSW EPA, 2014), which comprise the bulk of notified sites on the NSW Environment Protection Authority's list of contaminated sites. Emerging contaminants, including those listed on the Stockholm Convention (Stockholm Convention, 2017), are becoming an increasing area of concern for regulators, particularly given that the consequences of exposure are poorly understood, and therefore generate significant apprehension amongst impacted communities (ABC News, 2017). One such group of compounds includes perfluorinated chemicals (organofluorine compounds containing only carbon-fluorine bonds). In particular, the compounds perfluorooctane sulfonate/perfluoro-octanoic acid (PFOS/PFOA), which have been used

widely in a number of industrial functions and consumer products, including firefighting foams, since the middle of the 20th century (Taylor and Cosenza, 2016), have been shown to have grossly contaminated soils and groundwater at and around multiple military bases in Australia (Parliament of Australia, 2016; NSW EPA, 2017).

There are estimated to be as many as 200,000 contaminated sites across Australia due to human activity (Langley, 2002), with a current market value of over $3 billion per annum (Naidu et al., 2015). While not all contaminated sites present a risk to human health and the environment, those that do, such as the perfluorinated chemical contaminated area of Williamtown, NSW, can have significant environmental, social and economic impacts (Taylor and Cosenza, 2016).

Environmental contamination typically arises when either the environment is unable to absorb, process or recycle "waste" products, or, the waste products themselves are not regulated and managed appropriately, resulting in elevated levels of trace elements that pose a risk to human health (Dunlap and Jorgenson, 2012).

Given that economic growth is largely dependent on the extraction and production of minerals and metals (International Resource Panel, 2011), proper management of ore production, and the manufacturing process of minerals and metals, is of paramount importance in order to limit adverse outcomes on people and the environment. Environmental contamination caused by mining and smelting activities have been reported widely (e.g. Salomons, 1995; Dudka and Adriano, 1997; Csavina et al., 2012; Li et al., 2014). Moreover, mining and smelting industries ranked second in the 2016 list of the most polluting industries (Pure Earth and Green Cross, 2016). A specific example is the use and re-use of Pb-acid batteries, battery production factories and related operations causing the release of Pb compounds into the environment in critical quantities (e.g. Chen et al., 2012; Ericson et al. 2016, 2017).

1.2 Mining in Australia

Australia is one of the world's leading nations in terms of mineral resources, with operational mines distributed across the country (Supplementary Document S1; Australian Government, 2017a). The metalliferous mining history of Australia dates back to the 1840s, when lead (Pb) and silver (Ag) were discovered in Glen Osmond, South Australia (Drew, 2011). The minerals resource industry continues to play an important role in the economy, contributing approximately 6.9% to the gross domestic product (AUD$115 billion) in 2015–2016

(Australian Government, 2017b) with approximately 60% of mining resources exported overseas (Frydenberg, 2015). There are over 1300 mining companies in Australia employing around 2% of the total workforce (estimated 220,000 people) (Garnet, 2015).

1.3 Environmental contamination issues specific to mining and smelting communities in Australia

Mining and smelting operations generate a range of contaminants from multiple sources and activities, which impact the environment and pose risks to human health. For example, widespread asbestos contamination was found in the blue asbestos mining and milling township of Wittenoom, Australia (Reid et al., 2008). Elevated sulfur dioxide and PAHs concentrations are also observed in communities with smelting activities, due to the combustion of fossil fuels (Taylor et al., 2014a; Harvey et al., 2017). In addition, the transportation and storage of mineral resources (e.g. refined and unrefined metal ores and coal) have been shown to contaminate nearby townships and areas (e.g. Gulson et al., 2012; Kristensen et al., 2015; Taylor, 2015; O'Kane, 2016). Heavy metals and metalloids (hereafter referred to as metals) contamination has been widely reported in Australian mining and smelting centres and their surrounding environments, including Broken Hill (Gulson et al., 1994a,b; Taylor et al., 2014b; Yang and Cattle, 2015); Karumba (Gulson et al., 2016); Lake Macquarie (Morrison and Gulson, 2007; Harvey et al., 2015; Morrison et al., 2016); McArthur River (Munksgaard and Parry, 1998); Mount Isa (Parry, 2000; Taylor et al., 2010); Newcastle (Harvey et al., 2017); Port Pirie (Cartwright et al., 1976; Taylor et al., 2013); Risdon smelter and Rosebery in Tasmania (Gulson et al., 1996; Priestly, 2009); and Wollongong (Young et al., 1992; Martley et al., 2004).

In order to prevent exposure pathways of heavy metal contamination, resolving contamination sources is a critical first step. Multiple studies have examined the source and impact of environmental contamination in Australian mining and smelting communities (e.g., Gulson et al., 1994b; Mackay et al., 2013; Csavina et al., 2014; Davis et al., 2016), yet ongoing disputes remain over contamination sources and subsequent health risks in adjacent communities (Taylor and Schniering, 2010; Taylor et al., 2014a; Sullivan, 2014; Spear et al., 2015). For instance, in Port Pirie, where the world's largest Pb smelter was established, the local government understood there were legacy issues of contamination at the smelting plant of Nyrstar, and had been working with all parties for many years to come to a solution. Even the town's Independent state MP, Geoff Brock announced that Port Pirie was not a contaminated town:

"I think it is unwarranted, quite frankly," he said. "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." (Taylor, 2012).

At Mount Isa (one Australia's largest zinc (Zn) and Pb mining operations), Mount Isa Mines Ltd faced similar disputes over local environmental contamination issues (Taylor and Schniering, 2010). A Pb pathways study report commissioned by Mount Isa Mines Ltd (Noller et al., 2017) released in February 2017 stimulated another round of discussion over sources of atmospheric particles (Taylor et al., 2017). In addition, smelting emissions from the Kalgoorlie Consolidated Gold Mines, in Western Australia, were summarily dismissed using the arguments that the arsenic (As) emission breaches did not pose a threat to health because the As in the ore was low compared to other ore bodies, and also that the wind direction blows emissions away from the city (ABC News, 2003). In other examples overseas, the owners of the copper (Cu) and Pb smelter in Tacoma, Washington, USA, have stated that their smelter emissions are so dispersed they could not be found in the surrounding environment, and therefore would not affect human or environmental health (Sullivan, 2014).

The dismissal of the importance or the influence of mining, smelting or industrial chemical emissions on surrounding communities could be categorised into three groups, which include the use of questionable scientific claims and disputing contamination sources (Sullivan and Green, 2016; Spear et al., 2015). The typical disputed scientific claims are as follows:

- Contamination is naturally occurring or from other sources (e.g. legacy emissions, paints or fossil fuels) rather than mining and smelting activities
- Toxic metal compounds are not bio-accessible
- Emissions from mining and smelting are blown away.

In order to effect proper and targeted clean up, any such claims need to be examined and evaluated using evidence-based science to undertake successful remediation programs.

1.4 Impacts of heavy metal contamination

Environmental metals such as As, cadmium (Cd) and Pb are neurotoxic, even at low levels of exposure (Vahidnia et al., 2007; Bellinger, 2008; Wang and Du, 2013; Mason et al., 2014; Tsuji et al., 2015). Childhood exposure pathways to these toxic metals include the ingestion and inhalation of water, food, air, soil and dust (Figure 1-1; Tong et al., 2000; Kapaj et al., 2006; Schoeters et al., 2006; Rodríguez-Barranco et al., 2013). In mining and smelting

communities, soil and dust have been shown to be important exposure pathways for children's health, especially for elevated childhood blood Pb cases (Gulson et al., 1994a; Mackay et al., 2013; Barbieri et al., 2014; Li et al., 2014). The dose-response relationship between environmental Pb (in soil and dust) and blood Pb concentrations has been observed widely outside Australia (e.g. Lanphear et al., 1998; Dixon et al., 2009; Mielke et al., 2007; Zahran et al., 2011; Bradham et al., 2017; Safruk et al., 2017). In contrast to overseas research enquiries, there has been a paucity of research in Australia examining the dose-response relationship between environmental Pb and blood Pb, and the available studies have been limited by small cohorts (Wilson et al., 1986; Baghurst et al., 1992; Fett et al., 1992; Young et al., 1992; Gulson et al., 2006; Boreland et al., 2006; Gulson and Taylor, 2017).

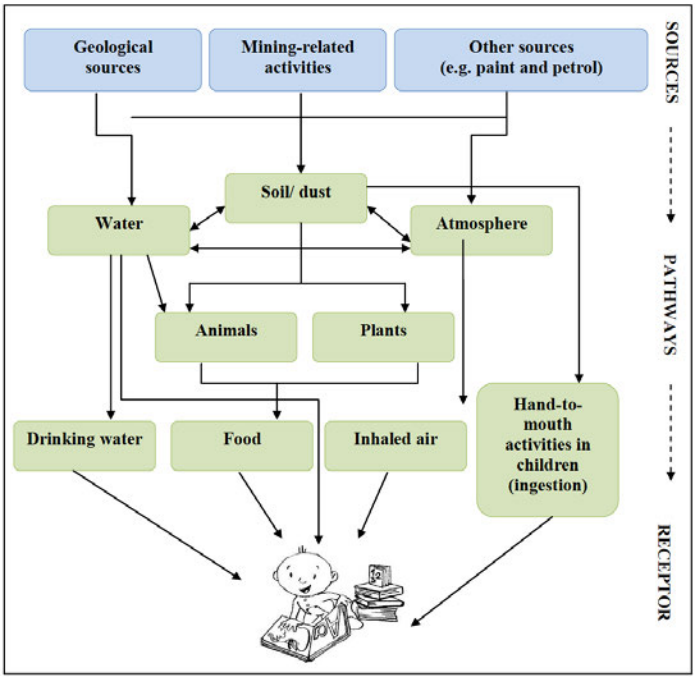


Figure 1-1. The primary exposure pathways of Pb (and other metals) from the environment to the human child receptor (Mackay, 2011).

The deleterious effects of As, Cd and Pb on children's neurological systems, behavioural and cognitive abilities have been well-documented, especially in terms of the impact of Pb on the brain (Calderón et al., 2001; Lanphear et al., 2005; Wright et al., 2006; O'Bryant et al., 2011; Ciesielski et al., 2013; Huang et al., 2016). Yet, in Australia, the relevant studies have focused largely on a cohort of children in Port Pirie, South Australia (McMichael et al., 1988; Baghurst et al., 1992; Tong et al., 1996; Burns et al., 1999; Earl et al., 2016), and were mostly completed in the 1990s, with the wider applicability of the findings remaining untested. As such, there is a need to improve the extensiveness of Australian research in these areas, and further assess the impacts of environmental contamination on children's health. Specifically, an opportunity exists to evaluate the dose-response relationship between soil and dust Pb

concentrations against blood Pb concentrations at the city scale, and determine the impacts of soil and dust contamination on children's educational and behavioural performance in other Australian mining and smelting communities.

1.5 Introduction to heavy metal contamination issues in Broken Hill

Broken Hill contains one of the world's largest Ag (silver)–Pb–Zn deposits and has been mined continuously since the discovery of ore in 1883 (Solomon, 1988). In 1893, the first blood Pb poisoning cases in Broken Hill were documented by Thompson et al. (1893). In the early 1990s, a systematic soil, dust and blood Pb screening program was established to monitor children's blood Pb concentrations (Lyle et al., 2006). From 1991 to present, there have been over 25,000 blood samples and 10,000 soil and dust samples tested in Broken Hill, making this the largest dataset of this type in Australia. Yet, despite the collection and analysis of thousands of environmental and blood Pb samples, these have never been examined as a whole. Such a dataset provides the opportunity to estimate the dose-response relationship between soil and dust Pb concentrations and blood Pb concentrations at the city scale, as well as an investigation of the role of environmental factors (e.g. wind direction and speed) and an assessment of the impacts of soil and dust Pb contamination on children's educational and behavioral performance in Broken Hill.

In Broken Hill up to 28 smelters were operating between 1886 and 1897, yet by 1897 all of the smelting operations had moved to Port Pirie (Woodward, 1965; Solomon, 1988). The mining and early smelting activities at Broken Hill have left behind a legacy of widespread Pb contamination in the adjoining residential community. From 1886 to 1897, it is estimated that at least 11,000−18,400 tonnes of lead were emitted by smelting activities (van Alphen, 1991). Furthermore, its estimated that over 200 million tonnes of ore have been extracted from Broken Hill since mining began (Morland and Webster, 1998; Perilya Limited, 2015), most of which occurred before proper environmental controls were implemented from the 1990s onwards. The consequences of occupational and community Pb poisoning were reported as early as 1893 (Thompson et al., 1893).

In the early 1990s, the Broken Hill City Council undertook a citywide survey of footpath soil contamination (Lyle et al., 2006). The Australian National Environment Protection Measure's guideline for Pb in soil at parks, playgrounds, secondary schools and footpaths (defined as Health Investigation Level C) is 600 mg/kg (NEPM, 2013). In the early 1990s survey, 37% of samples exceeded the soil Pb guideline of 600 mg/kg at Broken Hill (Supplementary Table

S2). This study (Figure 1-2) showed that the area adjacent to the mining operations was the most Pb-contaminated area, which is also confirmed by Yang and Cattle's (2015) study. Yang and Cattle (2015) investigated soil Pb bioaccessibility in Broken Hill and found the bioaccessibility ranged from 24% to 89% in topsoil, which is consistent with previous findings by Gulson et al. (1994b). Moreover, Yang and Cattle (2015) revealed an overall decreasing pattern of soil Pb bioaccessibility with increasing distance from the mining operations. Kristensen et al. (2015) demonstrated that transport of Pb and Zn ore concentrates using uncovered wagons significantly extended the environmental footprint of the local mining operations over an area extending hundreds of kilometres along the train lines that linked Broken Hill to Port Pirie. In order to reduce the exposure risk of soil contamination in Broken Hill, cracker dust, a material made from crushed volcanic rocks with low lead concentrations, was intensively applied to cap contaminated soil between 2005 and 2006, and proved to be an effective remediation strategy (Yang and Cattle, 2017). Before this, cracker dust had been widely used as a backfill material for kerbs and gutters installed since the 1940s (Yang and Cattle, 2017).

Figure 1-2. Soil Pb distribution in Broken Hill from the 1990 citywide survey of footpath soil contamination (Data from Supplementary Table S2).

More recently, a study of Pb in the playgrounds of Broken Hill revealed high levels of dust Pb loading, with a mean value of 27,500 μg/m^2 recorded close to existing southern mining operations (Taylor et al., 2014b). In addition, elevated dust As and Cd concentrations were

also observed at the same sites (Taylor et al., 2014b). The dust found on the playground equipment had Pb isotopic compositions that indicated their source was indeed the Broken Hill ore body (Taylor et al., 2014b). In addition to the two aforementioned dust monitoring studies, the two mining companies of Broken Hill are also required to collect dust samples around the Line of Lode in accordance to their Environment Protection Licenses (Perilya Limited, 2016; CBH Resources Limited, 2016). The results of their recent analyses showed that monitored sites close to mining operations had elevated dust Pb loading rates with a mean value of 378 μg/m^2/day (Dong et al., 2015). Though there are no Australian guidelines for dust Pb deposition, the Queensland state government has set a dust Pb guideline of 100 μg/m^2/day as a trigger for environmental monitoring of Mount Isa Mines (Taylor et al., 2014a). This is the same guideline value as listed in the German TA Luft (TA Luft, 2002), which has been used elsewhere as a benchmark value for assessing Pb deposition (Taylor, 2015). Recently, the benchmark of 100 μg/m^2/day was further demonstrated by Gulson and Taylor (2017). Moreover, the World Health Organisation indicated that Pb dust deposition >250 μg/m^2/day leads to increased blood Pb levels (WHO, 2000). This implies that dust Pb loading rates at sites close to mining operations in Australia exceed all acceptable values

1.6 Disputes over sources of contamination in Broken Hill

In the 1990s, a series of studies examining sources and pathways of environmental Pb were conducted in Broken Hill (Woodward-Clyde, 1993; Gulson et al., 1994a,b; Boreland et al., 2002), with the findings having recently been confirmed by additional studies (Kristensen and Taylor, 2016; Davis et al., 2016). However, there continues to remain ongoing dispute over the primary source of environmental Pb, as discussed in Section 1.3.

Initially, it was estimated that approximately 40-60 million tonnes of the Broken Hill ore body were lost due to weathering and erosion since its formation (~1.7 billion years ago) (Plimer, 1984; Gulson et al., 1994b). However, after detailed examination of the ore lenses, Webster (2006) re-estimated this loss to be less than 4.7 million tonnes. Additionally, an estimated 11,000−18,400 tonnes of Pb were emitted by smelting activities from 1886 to 1897 (van Alphen, 1991). Consequently, it has been argued that contamination in the region arose via the distribution of the naturally eroded ore and legacy emissions from historic smelting and mining activities that were distributed over the city area of Broken Hill (Kristensen and Taylor 2016). Furthermore, an estimated 240,000 tonnes of Pb was released from leaded petrol into the atmosphere during the 70-year period (1932-2002) of leaded petrol consumption in Australia (Kristensen, 2015), some of which impacted Broken Hill.

Consequently, legacy leaded petrol depositions remain one of main sources of metal contamination in Australian urban areas (Kristensen et al., 2017). In Broken Hill, leaded petrol was considered to be a significant contributor to environmental Pb in previous studies during the era of leaded petrol use (the early 1990s) (Gulson et al., 1994b). Therefore, the prevailing perspective at the time was that current mining operations were not a dominant source of Pb contamination when compared to other emissions. This view was also reflected in a 1993 report to the NSW Environment Protection Authority (EPA): '*This 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 Pty Ltd, 1993, p. 5-3).

The misconception about the source of Broken Hill environmental Pb exposure was re-circulated again in 2015 by Dr Rob Stokes, the NSW Minister for Environment (at the time) who said: '*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).

In Broken Hill, the NSW Government announced in early 2015 that AUD$13 million was to be allocated to '*rejuvenate the Broken Hill Environment Lead program to address the issue of blood lead levels in local children'*. Therefore, in order to undertake targeted and effective remediation to reduce childhood Pb levels, the precise sources (natural or anthropogenic; legacy or contemporary) and mechanisms of Pb contamination need to be resolved, unequivocally. However, research addressing this question is relatively scarce. Recently, Kristensen and Taylor (2016) applied multiple lines of evidence to assess soil contamination sources by evaluating current soil metal concentrations and Pb isotopic compositions, geological data, historical environmental assessments and old photographic evidence. The results revealed that surface soil contamination is predominantly derived from the ore body but that it is not likely to be related to natural weathering processes. However, there is still a paucity of research examining sources of contemporary dust Pb and their impact on human health. Furthermore, the recent study of dust contamination sources by Davis et al. (2016) is mainly based on Broken Hill dust deposits collected in the 1990s. In addition to the lack of clarity regarding Pb contamination sources (i.e. legacy depositions, ongoing emissions, paint and leaded petrol etc), the complexity of physico-chemical factors influencing Pb exposure risks to Broken Hill children remain poorly characterised. Relevant physico-chemical factors

influencing Pb uptake include Pb mineralogy, its solubility, the particle size of Pb-rich particles, as well as human-factors including personal behaviour and diet (e.g. NTP, 2012; NHMRC, 2015). As the Broken Hill Environmental Lead Program (BHELP) moves forward with its aim of having all children below the NHMRC upper acceptable blood Pb level of 5 µg/dL, it may be prudent to distil these additional exposure risk factors to better support targeted interventions with appropriate evidence-based data. However, if the program was to blanket remove and/or reduce Pb in the ambient environment and within residential homes to very low levels, i.e. those that mirror uncontaminated environments, then the exposure risk would be mitigated without the need to understand physico-chemical or human-related factors and their interplay on blood lead levels.

1.7 Blood Pb levels in Broken Hill

Occupational and community Pb poisoning in Broken Hill was first reported as early as 1893 (Thompson et al., 1893). The first blood Pb survey of school-aged children in Broken Hill was conducted in 1982, which found that the all the children had blood Pb concentrations < 40 ug/dL, the benchmark level of concern in Australia at the time. Nevertheless, in 1991, a systematic investigation of childhood blood Pb levels was conducted which found 86% of children had blood Pb levels ≥10 µg/dL (the upper acceptable blood Pb value from 1993 to 2015) (Lyle et al., 2006). In 1994, the NSW state government commenced the remediation of homes where children with high blood Pb levels (>15 µg/dL) lived (Lyle et al., 2006). Since this remediation, there has been an overall reduction in children's blood Pb concentrations (Figure 1-3, Lesjak and Jones, 2016). However, in recent years the proportion of children with a blood Pb level > 10 µg/dL increased from 12.6% (2010) to 24% (2015) and has remained at approximately 20-24% after 2012 (Figure 1-3; Lesjak and Jones, 2016). In 2015, Australia's National Health and Medical Research Council (NHMRC) lowered the blood Pb intervention concentration to 5 µg/dL, meaning 47% of all children and 79% aboriginal children less than 5 years of age had a blood Pb concentration greater than the new intervention guideline (Lesjak and Jones, 2016).

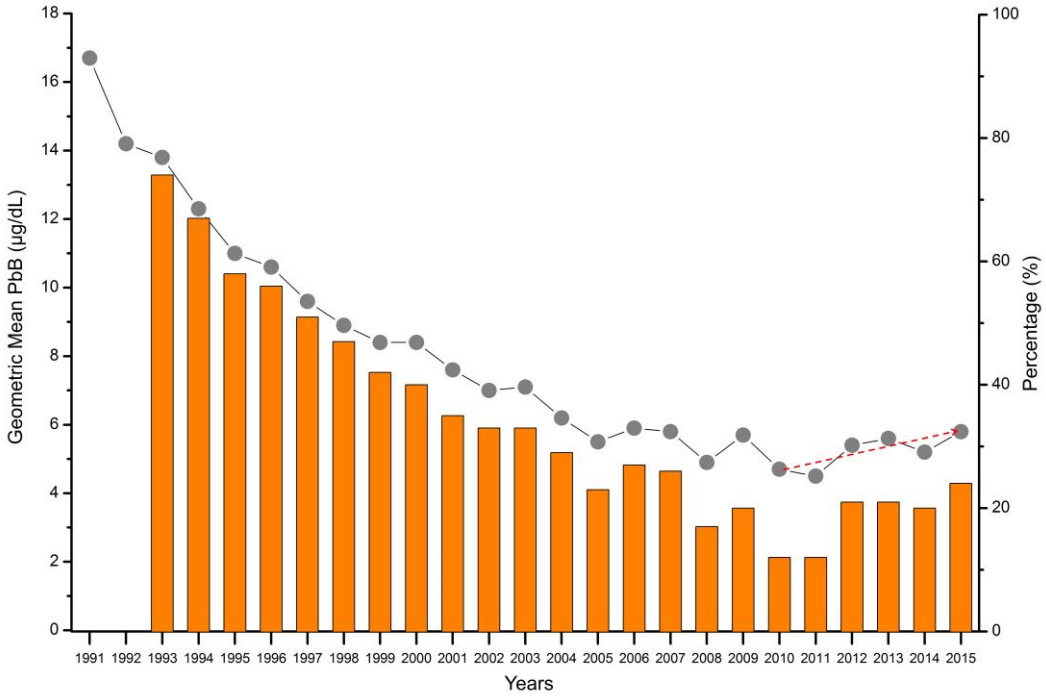


Figure 1-3. Blood Pb levels of children aged 1-4 years and percentage of children with blood Pb levels exceeding 10 µg/dL in Broken Hill, 1991-2015. Grey solid dots: Geometric mean blood Pb; Bar chart: percentage of children with blood Pb >10 µg/dL.

The Pb isotopic compositions of children's blood indicated that blood Pb cases were due to exposure from Broken Hill ores along with other sources, such as Pb-based paint and leaded petrol (Gulson et al., 1994b). However, it despite this analysis, it was still unclear if blood Pb cases were due to legacy mining and smelting emissions or contemporary mining activities through the generation of contaminated dust. Furthermore, while the dose-response relationship between environmental Pb and blood Pb has previously been estimated, the study only used a small cohort of data (Boreland et al., 2006). Therefore, an opportunity existed to evaluate the role of environmental contamination on contemporary childhood blood Pb concentrations. To evaluate this, children's blood Pb levels, as well as environmental soil and dust lead data collected at Broken Hill over the last two decades by the local Child & Family Health Centre, were analysed.

1.8 Aims

This thesis aims to examine environmental data (e.g. soil and dust Pb) and blood Pb from Broken Hill, and apply a developed integrated analysis to understand contamination sources and the drivers of blood Pb exposure. Furthermore, the data in this thesis enables a more detailed assessment of the question/debate over Pb sources. This thesis accessed over 20 years of soil and dust Pb data, blood Pb data and production rates of Broken Hill ore to estimate the dose-response relationship between mining activities, environmental Pb and blood Pb. The details of the dataset used in this research are provided in the following chapters. Section 1.4

has shown that previous studies in Australia looking at the deleterious effects of blood Pb and environmental Pb on children's behavioural and cognitive abilities have focused largely on a cohort of Port Pirie children. Thus, this thesis presents the first comprehensive examination of environmental contamination and its sources, processes and effects on children's educational and behavioural performance in Broken Hill. The outcomes of this thesis provide evidence-based data to support decision making by the BHELP, which was launched by the NSW government in 2015 to address the issue of elevated blood Pb levels in local children.

The summary aims of this thesis are as to:

a. assess contemporary soil and dust contamination in Broken Hill

b. identify legacy sources and new emissions using geochemical signatures of atmospheric dust

c. quantify the extent and impact of mining-related activities on soil and dust contamination

d. determine relationships between environmental Pb and blood Pb and evaluate impacts of other factors on blood Pb

e. evaluate the impacts of mining activities on children's blood Pb

f. evaluate the effects of environmental contamination on children educational performance and behavioural activities

g. provide scientific evidence to aid the BHELP to improve and target remediation works

h. recommend possible management interventions based on research outcomes to reduce the negative impacts of metal contamination.

In addition, the thesis also examines other sources and locations impacted by environmental contamination from industrial activity. These locations include the Australian mining and smelting communities of Newcastle, Port Pirie and Mount Isa. The relevant outcomes identify the severity of soil/dust contamination in the studied communities and provide possible approaches for other mining and smelting communities to resolve soil/dust contamination issues.

1.9 References

ABC News, 2003. Air pollution breach baffle miner. http://www.abc.net.au/news/2003-08-01/air-pollution-breach-baffles-miner/1458054 (accessed 28.05.16).

ABC News, 2017. Contamination. http://www.abc.net.au/4corners/contamination/9032140 (accessed 10.12.17).

Allinson, M., Zhang, P., Bui, A., Myers, J. H., Pettigrove, V., Rose, G., Salzman, S. A., Walters, R., Allinson, G., 2017. Herbicides and trace metals in urban waters in Melbourne, Australia (2011–12): concentrations and potential impact. Environmental Science and Pollution Research 24, 7274-7284.

Australian Government, 2017a. Minerals Basics. Geoscience Australia. http://www.ga.gov.au/scientific-topics/minerals/basics (accessed 20.06.17)

Australian Government, 2017b. Australian Industry Report 2016. Department of Industry, Innovation and Science: Canberra.

Baghurst, P. A., Tong, S. L., McMichael, A. J., Robertson, E. F., Wigg, N. R., Vimpani, G. V., 1992. Determinants of blood lead concentrations to age 5 years in a birth cohort study of children living in the lead smelting city of Port Pirie and surrounding areas. Archives Environmental Health 47, 203-210.

Barbieri, E., Fonturbel, F. E., Herbas, C., Barbieri, F. L., Gardon, J., 2014. Indoor metallic pollution and children exposure in a mining city. Science of the Total Environment 487, 13-19.

Bellinger, D. C., 2008. Very low lead exposures and children's neurodevelopment. Current Opinion in Pediatrics 20, 172-177.

Boreland, F., Lyle, D. M., Wlodarczyk, J., Balding, W. A., 2006. Lead Dust in Broken Hill Homes: Relationship between House Dust and Children's Blood Lead Levels. Environmental Health 6, 15-24.

Boreland, F., Lyle, D. M., Wlodarczyk, J., Balding, W. A., Reddan, S., 2002. Lead dust in broken hill homes—a potential hazard for young children? Australian and New Zealand Journal of Public Health 26, 203-207.

Bradham, K. D., Nelson, C. M., Kelly, J., Pomales, A., Scruton, K., Dignam, T., Misenheimer, J. C., Li, K., Obenour, D. R., Thomas, D. J., 2017. Relationship Between Total and Bioaccessible Lead on Children's Blood Lead Levels in Urban Residential Philadelphia Soils. Environmental Science & Technology 51, 10005-10011.

Burns, J. M., Baghurst, P. A., Sawyer, M. G., McMichael, A. J., Tong, S. L., 1999. Lifetime Low-Level Exposure to Environmental Lead and Children's Emotional and Behavioral Development at Ages 11–13 Years: The Port Pirie Cohort Study. American Journal of Epidemiology 149, 740-749.

Calderón, J., Navarro, M. E., Jimenez-Capdeville, M. E., Santos-Diaz, M. A., Golden, A., Rodriguez-Leyva, I., Borja-Aburto, V., Diaz-Barriga, F., 2001. Exposure to arsenic and lead and neuropsychological development in Mexican children. Environmental Research 85, 69-76.

Cartwright, B., Merry, R.H., Tiller, K.G., 1976. Heavy metal contamination of soils around a lead smelter at Port Pirie, South Australia. Australian Journal of Soil Research 15, 69-81.

CBH Resources Limited, 2016. Environment Monitoring Overview. http://www.cbhresources.com.au/files/6713/4551/1116/Monitoring_Overview_and_Criteria.pdf (accessed 19.08.2016).

Chen, L., Xu, Z., Liu, M., Huang, Y., Fan, R., Su, Y., Hu, G., Peng, X., Peng, X., 2012. Lead exposure assessment from study near a lead-acid battery factory in China. Science of the Total Environment 429, 191-198.

Ciesielski, T., Bellinger, D. C., Schwartz, J., Hauser, R., Wright, R. O., 2013. Associations between cadmium exposure and neurocognitive test scores in a cross-sectional study of US adults. Environmental Health 12: 13. https://doi.org/10.1186/1476-069X-12-13.

Csavina, J., Field, J., Taylor, M. P., Gao, S., Landázuri, A., Betterton, E. A., Sáez, A. E., 2012. A Review on the Importance of Metals and Metalloids in Atmospheric Dust and Aerosol from Mining Operations. Science of the Total Environment 433, 58-73.

Csavina, J., Taylor, M. P., Félix, O., Rine, K. P., Sáez, A. E., Betterton, E. A., 2014. Size-resolved dust and aerosol contaminants associated with copper and lead smelting emissions: Implications for emission management and human health. Science of the Total Environment 493, 750-756.

Davis, J. J., Morrison, A. L., Gulson, B. L., 2016. Uncovering pathways of metal contamination with microscopic techniques and lead isotopic tracing. Australian Journal of Earth Sciences 63, 795-803.

Dixon, S.L., Gaitens, J.M., Jacobs, D.E., Strauss, W., Nagaraja, J., Pivetz, T., Wilson, W. & Ashley, P.J. 2009, Exposure of U.S. Children to Residential Dust Lead, 1999-2004: II. The Contribution of Lead-Contaminated Dust to Children's Blood Lead Levels, Environmental Health Perspectives 117, 468-74.

Dong, C., Taylor, M. P., Kristensen, L. J., Zahran, S., 2015. Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes. Environmental Pollution 207, 345-356.

Drew, G. J., 2011. Australia's first mining era. MESA Journal 61, 42-46.

Dudka, S., Adriano, D. C., 1997. Environmental Impacts of Metal Ore Mining and Processing: A Review. Journal of Environmental Quality 26, 590-602.

Dunlap, R. E., Jorgenson, A. K., 2012. Environmental Problems. The Wiley-Blackwell Encyclopedia of Globalization.

Earl, R., Burns, N., Nettelbeck, T., Baghurst, P. 2016. Low-level environmental lead exposure still negatively associated with children's cognitive abilities. Australian Journal of Psychology 68, 98-106.

English, K., Chen, Y., Toms, L., Jagals, P., Ware, R. S., Mueller, J. F., Sly, P. D., 2017. Polybrominated diphenyl ether flame retardant concentrations in faeces from young children in Queensland, Australia and associations with environmental and behavioural

factors. Environmental Research 158, 669-676.

Ericson, B., Duong, T. T., Keith, J., Nguyen, T. C., Havens, D., Daniell, W., Karr, C. J., Hai, D. N., Tung, L. V., Ha, T. T. N., Wilson, B., Hanrahan, D., Croteau, G., Taylor, M. P., 2018. Improving human health outcomes with a low-cost intervention to reduce exposures from lead acid battery recycling: Dong Mai, Vietnam. Environmental Research 161, 181-187.

Ericson, B., Landrigan, P., Taylor, M. P., Frostad, J., Caravanos, J., Keith, J., Fuller, R., 2016. The Global Burden of Lead Toxicity Attributable to Informal Used Lead-Acid Battery Sites. Annals of Global Health 82, 686-699.

Evans, G. W., Kantrowitz, E., 2002. Socioeconomic Status and Health: The Potential Role of Environmental Risk Exposure. Annual Review of Public Health 23, 303-331.

Fett M. J., Mira, M., Smith J., Alperstein, G., Causer J., Brokenshire, T., Gulson B., Cannata, S. 1992. Community prevalence survey of children's blood lead levels and environmental lead contamination in inner Sydney. Medical Journal of Australia 157, 441-506.

Frydenberg, J., 2015. Mining and the Australian economy: the Australian Government's priorities for the mining sector. http://minister.industry.gov.au/ministers/frydenberg/speeches/mining-and-australian-economy-australian-governments-priorities-mining (assessed 20.01.17).

Garnet, A., 2015. Australia's 'five pillar economy': mining. https://theconversation.com/australias-five-pillar-economy-mining-40701 (accessed 29.06.17).

Gulson, B. L., Davis, J. J., Mizon, K. J., Korsch, M. J., Law, A. J., Howarth, D., 1994a. Lead Bioavailability in the Environment of Children: Blood Lead Levels in Children Can Be Elevated in a Mining Community. Archives of Environmental & Occupational Health 49, 326-331.

Gulson, B. L., Korsch, M., Bradshaw, A., 2016. Impact of Dust from Ore Processing Facilities on Rain Water Collection Tanks in a Tropical Environment—The Obvious Source "Ain't Necessarily So". International Journal of Environmental Research and Public Health 13, 243. doi:10.3390/ijerph13020243

Gulson, B. L., Korsch, M., Winchester, W., Devenish, M., Hobbs, T., Main, C., Smith, G., Rosman, K., Howearth, L., Burn-Nunes, L., Seow, J., Oxford, C., Yun, G., Gillam, L., Crisp, M., 2012. Successful application of lead isotopes in source apportionment, legal proceedings, remediation and monitoring. Environmental Research 112, 100-110.

Gulson, B. L., Mizon, K. J., Law, A. J., Korsch, M, J., Davis, J. J., 1994b. Source and Pathways of Lead in Humans from the Broken Hill Mining Community—An Alternative Use of Exploration Methods. Economic Geology 89, 889 – 908.

Gulson B., Mizon K., Taylor A., Korsch M., Stauber J., Davis J. M., Honway L., Wu M., Swan, H., 2006. Changes in manganese and lead in the environment and young children associated with the introduction of methylcyclopentadienyl manganese tricarbonyl in gasoline—preliminary results. Environmental Research 100, 100-114.

Gulson, B. L., Pisaniello, D., McMichael, A. J., Mizon, K. J., Korsch, M. J., Luke, C.,

Ashbolt, R., Pederson, D. G., Vimpani, G., Mahaffey, K. R., 1996. Stable lead isotope profiles in smelter and general urban communities: a comparison of environmental and blood measures. Environmental Geochemistry and Health 18, 147-163.

Gulson, B. L., Taylor, A., 2017. A simple lead dust fall method predicts children's blood lead level: New evidence from Australia. Environmental Research 159, 76-81.

Harvey, P. J., Rouillon, M., Dong, C., Ettler, V., Handley, H. K., Taylor, M. P., Tyson, E., Tennant, P., Telfer, V., Trinh, R., 2017. Geochemical sources, forms and phases of soil contamination in industrial city. Science of the Total Environment 584-585, 505-514.

Harvey, P. J., Taylor, M. P., Kristensen, L. J., Grant-Vest, S., Rouillon, M., Wu, L., Handley, H. K., 2015. Evaluation and assessment of the efficacy of an abatement strategy in a former lead smelter community, Boolaroo, Australia. Environmental Geochemistry and Health 38, 941-954.

Huang, S. Y., Hu, H., Sánchez, B. N., Peterson, K. E., Ettinger, A. S., Lamadrid-Figueroa, H., Schnaas, L., Mercado-García, A., Wright, R. O., Basu, N., Cantonwine, D. E., Hernández-Avila, M., Tellez-Rojo, M. M., 2016. Childhood Blood Lead Levels and Symptoms of Attention Deficit Hyperactivity Disorder (ADHD): A Cross-Sectional Study of Mexican Children. Environmental Health Perspectives 124, 868-874.

Humphries, K. 2015. NSW Government commits more than $13 million to reduce lead levels at Broken Hill. Media release: Kevin Humphries MP Minister for Natural Resources, Lands and Water Minister for Western NSW, 13th February 2015. http://www.epa.nsw.gov.au/resources/MinMedia/EPAMin150213.pdf (accessed 05.01.2017).

International Resources Panel, 2011. DECOUPLING NATURAL RESOURCES USE AND ENVIRONMENTAL IMPACTS FROM ECONOMIC GROWTH. United Nations Environment Programme. http://wedocs.unep.org/handle/20.500.11822/9816 (accessed 10.12.17).

Kapaj, S., Peterson, H., Liber, K., Bhattacharya, P., 2006. Human Health Effects From Chronic Arsenic Poisoning-A Review. Journal of Environmental Science and Health Part A 41, 2399-2428.

Kennedy, K., Schroeder, T., Shaw, M., Haynes, D., Lewis, S., Bentley, C., Paxman, C., Carter, S., Brando, V. E., Bartkow, M., Hearn, L., Mueller, J. F., 2012. Long term monitoring of photosystem II herbicides−Correlation with remotely sensed freshwater extent to monitor changes in the quality of water entering the Great Barrier Reef, Australia. Marine Pollution Bulletin 65, 292-305.

Kookana, R. S., Baskaran, S., Naidu, R., 1998. Pesticide fate and behaviour in Australian soils in relation to contamination and management of soil and water: a review. Soil Research 36, 715-764.

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

Kristensen, L. J., Taylor, M. P., 2016. Unraveling a ‘miner’s myth’ that environmental contamination in mining towns is naturally occurring. Environmental Geochemistry and Health 38, 1015-1027.

Kristensen, L. J., Taylor, M. P., Flegal, A. R., 2017. An odyssey of environmental pollution: The rise, fall and remobilisation of industrial lead in Australia. Applied Geochemistry 83, 3-13.

Kristensen, L. J., Taylor, M. P., Morrison, A. L., 2015. Lead and zinc dust depositions from ore trains characterised using lead isotopic compositions. Environmental Science: Processes & Impacts 17, 631–637.

Landrigan, P. J., Fuller, R., Acosta, N. J. R., Adeyi, O., Arnold, R., Basu, N., Baldé, A. B., Bertollini, R., Bose-O'Reilly, S., Boufford, J. I., Breysse, P. N., Chiles, T., Mahidol, C., Coll-Seck, A. M., Cropper, M. L., Fobil, J., Fuster, V., Greenstone, M., Haines, A., Hanrahan, D., Hunter, D., Khare, M., Krupnick, A., Lanphear, B., Lohani, B., Martin, K., Mathiasen, K. V., McTeer, M. A., Murray, C. J. L., Ndahimananjara, J. D., Perera, F., Potočnik, J., Preker, A. S., Ramesh, J., Rockström, J., Salinas, C., Sandilya, K., Sly, P. D., Smith, K. R., Steiner, A., Stewart, R. B., Suk, W. A., van Schayck, O. C. P., Yadama, G. N., Yumkella, K., Zhong, M., 2017. The Lancet Commission on pollution and health. The Lancet. http://dx.doi.org/10.1016/S0140-6736(17)32345-0.

Langley, A. J., 2002. The soiled environment: bubble, bubble, soil in trouble. Medical Journal of Australia 177, 599-603.

Lanphear, B. P., Hornung, R., Khoury, J., Yolton, K., Baghurst, P., Bellinger, D. C., Canfield, R. L., Dietrich, K. N., Bornschein, R., Greene, T., Rothenberg, S. J., Needleman, H. L., Schnaas, L., Wasserman, G., Graziano, J., Roberts, R., 2005. Low-Level Environmental Lead Exposure and Children's Intellectual Function: An International Pooled Analysis. Environmental Health Perspective 113, 894-899.

Lanphear, B. P., Matte, T. D., Rogers, J., Clickner, R. P., Dietz, B., Bornschein, R. L., Succop, P., Mahaffey, K. R., Dixon, S., Galke, W., Rabinowitz, M., Farfel, M., Rohde, C., Schwartz, J., Ashley, P., Jacobs, D. E., 1998. The Contribution of Lead-Contaminated House Dust and Residential Soil to Children's Blood Lead Levels: A Pooled Analysis of 12 Epidemiologic Studies. Environmental Research 79, 51-68.

Lesjak, M., Jones, T., 2016. Lead Health Report 2015—Children less than 5 years old in Broken Hill. Population Health Unit, NSW Government, Western NSW & Far West Local Health District. http://leadsmart.nsw.gov.au/wp-content/uploads/2016/12/Broken-Hill-Lead-Health-Report-2015-children-aged-0%E2%80%934.pdf (accessed 19.09.17).

Lyle, D. M., Phillips, A. R., Balding, W. A., Burke, H., Stokes, D., Corbett, S., Hall, J., 2006. Dealing with lead in Broken Hill−Trends in blood lead levels in young children 1991−2003. Science of the Total Environment 359, 111-119.

Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z., Huang, L., 2014. A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. Science of the Total Environment 468-469, 843-853.

Mackay, A. K., 2011. Sources, pathways and relative risks of metal contaminants in the upper Leichhardt River catchment and Mount Isa urban area. PhD thesis, Macquarie University.

Mackay, A. K., Taylor, M. P., Munksgaard, N. C., Hudson-Edwards, K. A., Burn-Nunes, L., 2013. Identification of environmental lead sources and pathways in a mining and smelting town: Mount Isa, Australia. Environmental Pollution 180, 304-311.

Martley, E., Gulson, B. L., Pfeifer, H. -R., 2004. Metal concentrations in soils around the copper smelter and surrounding industrial complex of Port Kembla, NSW, Australia. Science of the Total Environment 325, 113-127.

Mason, L. H., Harp, J. P., Han, D. Y., 2014. Pb Neurotoxicity: Neuropsychological Effects of Lead Toxicity. BioMed Research International 2014, http://dx.doi.org/10.1155/2014/840547.

McCready, S., Slee, D. J., Birch, G. F., Taylor, S. E., 2000. The Distribution of Polycyclic Aromatic Hydrocarbons in Surficial Sediments of Sydney Harbour, Australia. Marine Pollution Bulletin 40, 999-1006.

McGrath, T. J., Ball, A. S., Clarke, B. O., 2017. Critical review of soil contamination by polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs); concentrations, sources and congener profiles. Environmental Pollution 230, 741-757.

McGrath, T. J., Morrison, P. D., Sandiford, C. J., Ball, A. S., Clarke, B. O., 2016. Widespread polybrominated diphenyl ether (PBDE) contamination of urban soils in Melbourne, Australia. Chemosphere 164, 225-232.

McMichael, A. J., Baghurst, P. A., Wigg, N. R., Vimpani, G. V., Robertson, E. F., Roberts, R. J., 1988. Port Pirie Cohort Study: environmental exposure to lead and children's abilities at the age of four years. The New England Journal of Medicine 319, 468-475.

Mielke, H. W., Gonzales, C. R., Powell, E., Jartun, M., Mielke, P. W., 2007. Nonlinear association between soil lead and blood lead of children in metropolitan New Orleans, Louisiana: 2000–2005. Science of the Total Environment 388, 43-53.

Morland, R., Webster, A. E., 1998. Broken Hill lead-zinc-silver deposit. In Berkman, D. A. & Mackenzie, D. H. (Eds.), Geology of Australian and Papua New Guinean Mineral Deposits. Australian Institute of Mining and Metallurgy, Melbourne, pp. 619-626.

Morrison, A. L., Gulson, B. L., 2007. Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. Science of the Total Environment 382, 30-42.

Morrison, A. L., Swierczek, Z., Gulson, B. L., 2016. Visualisation and quantification of heavy metal accessibility in smelter slags: The influence of morphology on availability. Environmental Pollution 210, 271-281.

Munksgaard, N. C., Parry, D. L., 1998. Lead isotope ratios determined by ICP-MS: Monitoring of mining-derived metal particulates in atmospheric fallout, Northern Territory, Australia. Science of the Total Environment 217, 113-125.

Naidu, R., Bekele, D. N., Birke, V., 2015. Permeable Reactive Barriers: Cost-Effective and Sustainable Remediation of Groundwater. In: Naidu, R. and Birke, V. (Eds.), Permeable Reactive Barrier: Sustainable Groundwater Remediation. CRC Press Taylor and Francis Group, Boca Raton, Florida, pp. 1–24.

National Environment Protection Measure (NEPM), 2013. Schedule B1: Guideline on Investigation Levels For Soil and Groundwater. http://www.scew.gov.au/system/files/resources/93ae0e77-e697-e494-656f-afaaf9fb4277/files/schedule-b1-guideline-investigation-levels-soil-and-groundwater-sep10.pdf (accessed 07.12.16).

New South Wales Environment Protection Authority (NSW EPA), 2014. Technical Note: Investigation of Service Station Sites. Environment Protection Authority, Sydney.

New South Wales Environment Protection Authority (NSW EPA), 2017. Williamtown independent review. http://www.epa.nsw.gov.au/working-together/community-engagement/community-news/raaf-williamtown-contamination/williamtown-independent-review (accessed 10.12.17).

Nguyen, T. C., Loganathan, P., Nguyen, T. V., Vigneswaran, S., Kandasamy, J., Slee, D., Stevenson, G., Naidu, R., 2014. Polycyclic aromatic hydrocarbons in road-deposited sediments, water sediments, and soils in Sydney, Australia: Comparisons of concentration distribution, sources and potential toxicity. Ecotoxicology and Environmental Safety 104, 339-348.

NHMRC, 2015. NHMRC STATEMENT: EVIDENCE ON THE EFFECTS OF LEAD ONHUMAN HEALTH. https://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh58_nhmrc_statement_lead_effects_human_health_a.pdf (accessed 01.07.2017)

Noller, B., Zheng, J. J., Huynh, T., Ng, J., Diacomanolis, V., Taga, R., Harris, H., 2017. Lead Pathways Study—Air, Health Risk Assessment of Contaminants to Mount Isa City. http://www.mountisamines.com.au/en/publications/LeadPathways/Lead%20Pathways%20Study%20Air%20Report.pdf (accessed 06.11.17).

O'Bryant, S. E., Edwards, M., Menon, C. V., Gong, G., Barber, R., 2011. Long-term low-level arsenic exposure is associated with poorer neuropsychological functioning: a Project FRONTIER study. International Journal of Environmental Research and Public Health 8, 861-874.

O'Kane, M., 2016. Final Report on the Independent Review of Rail Coal Dust Emissions Management Practices in the NSW Coal Chain NSW Chief Scientist & Engineer. http://www.chiefscientist.nsw.gov.au/__data/assets/pdf_file/0008/89864/160805-FINAL-Coal-Dust-Report.pdf (accessed 01.11.17).

Parliament of Australia, 2016. Contamination of Australia's Defence Force facilities and other Commonwealth, state and territory sites in Australia. https://www.aph.gov.au/Parliamentary_Business/Committees/Senate/Foreign_Affairs_Defence_and_Trade/ADF_facilities (accessed 10.12.17).

Parry, D. L., 2000. Metals in soils and surface water in the vicinity of Mount Isa, Report to Mount Isa Mines Limited. Environmental Analytical Chemistry Unit, Northern Territory University, Darwin, Australia.

Perilya Limited, 2015. Broken Hill. http://www.perilya.com.au/our-business/operations/broken-hill. (accessed 07.12.16).

Perilya Limited, 2016. Monthly reports: environmental reporting. http://www.perilya.com.au/health--safety--environment/environment/reports (accessed 24.07.16).

Plimer, I. R., 1984. The mineralogical history of the Broken Hill lode, NSW. Australian Journal of Earth Sciences 31, 379-402.

Priestly, B. G., 2009. An assessment of health risks associated with environmental exposures in Murchison and Clemons Streets, Roseberry. School of Public Health and Preventative Medicine, Monash University.

Pure Earth and Green Cross, 2016. The World's Worst Pollution Problems 2016: The Toxics Beneath Our Feet. http://worstpolluted.org/docs/WorldsWorst2016Spreads.pdf (accessed 10.12.17).

Reid, A., Heyworth, J., de Klerk, N., Musk, A. W., 2008. The mortality of women exposed environmentally and domestically to blue asbestos at Wittenoom, Western Australia. Occupational & Environmental Medicine 65, 743-749.

Rodríguez-Barranco, M., Lacasaña, M., Aguilar-Garduño, C., Alguacil, J., Gil, F., González-Alzaga, B., Rojas-García, A., 2013. Association of arsenic, cadmium and manganese exposure with neurodevelopment and behavioural disorders in children: A systematic review and meta-analysis. Science of the Total Environment 454-455, 562-577.

Safruk, A. M., McGregor, E., Whitfield Aslund, M. L., Cheung, P. H., Pinsent, C., Jackson, B. J., Hair, A. T., Lee, M., Sigal, E. A., 2017. The influence of lead content in drinking water, household dust, soil, and paint on blood lead levels of children in Flin Flon, Manitoba and Creighton, Saskatchewan, Science of The Total Environment 593, 202-210.

Salomons, W., 1995. Environmental impact of metals derived from mining activities: Processes, predictions, prevention. Journal of Geochemical Exploration 52, 5-23.

Schoeters, G., Hond, E. D., Zuurbier, M., Naginiene, R., Van Den Hazel, P., Stilianakis, N., Ronchetti, R., Koppe, J. G., 2006. Cadmium and children: Exposure and health effects. Acta Pædiatrica 95, 50-54.

Solomon, R. J., 1988. The richest lode: Broken Hill 1883-1988. Hale & Iremonger, Sydney.

Spear, M., Thomas, R., Shrader-Frechette, K., 2015. Commentary: Flawed Science Delays Smelter Cleanup and Worsens Health. Accountability in Research 22, 41-60.

Stasinska, A., Reid, A., Hinwood, A., Stevenson, G., Callan, A., Odland, J. Ø. Heyworth, J., 2013. Concentrations of polybrominated diphenyl ethers (PBDEs) in residential dust samples from Western Australia. Chemosphere 91, 187-193.

Stockholm Convention, 2017. The 16 New POPs—An introduction to the chemicals added to the Stockholm Convention as Persistent Organic Pollutants by the Conference of Parties. http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx (accessed 10.12.17).

Sullivan, M., 2014. Tainted Earth: Smelters, Public Health and the Environment. Rutgers University Press, New Brunswick, US.

Sullivan, M., Green, D., 2016. Misled about lead: an assessment of online public health education material from Australia's lead mining and smelting towns. Environmental Health 15:1; https://doi.org/10.1186/s12940-015-0085-9.

TA Luft, 2002. Technical Instructions on Air Quality Control. In: First General Administration Regulation Pertaining the Federal Immission Control Act. http://www.bmub.bund.de/fileadmin/bmu-

import/files/pdfs/allgemein/application/pdf/taluft_engl.pdf (accessed 10.03.15).

Taylor, M. P., 2012. Lead poisoning of Port Pirie children: a long history of looking the other way. http://theconversation.com/lead-poisoning-of-port-pirie-children-a-long-history-of-looking-the-other-way-8296 (accessed 18.09.17).

Taylor, M. P., 2015. Atmospherically deposited trace metals from bulk mineral concentrate port operations. Science of the Total Environment 515-516, 143-152.

Taylor, M. P., Camenzuli, D., Kristensen, L. J., Forbes, M., 2013. Environmental lead exposure risks associated with children's outdoor playground. Environmental Pollution 178, 447-454.

Taylor, M. P., Cosenza, I. J., 2016. Review of the New South Wales Environment Protection Authority's Management of Contaminated Sites. Department of Environmental Sciences, Macquarie University. ISBN: 978-1-74138-444-4.

Taylor, M. P., Dong, C., Harvey, P., 2017. Mount Isa contamination 'within guidelines' but residents told to clean their homes. https://theconversation.com/mount-isa-contamination-within-guidelines-but-residents-told-to-clean-their-homes-72862 (accessed 19.06.17).

Taylor, M. P., Davies, P. J., Kristensen, L. J., Csavina, J. L., 2014a. 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.

Taylor, M. P., Hudson-Edwards, K. A., Mackay, A. K., Holz, E., 2010. Soil Cd, Cu, Pb and Zn contaminants around Mount Isa city, Queensland, Australia: potential sources and risks to human health. Applied Geochemistry 25, 841-855.

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

Taylor, M. P., Schniering, C., 2010. The public minimization of the risks associated with environmental lead exposure and elevated blood lead levels in children, Mount Isa, Queensland, Australia. Archives of Environmental & Occupational Health 65, 45-48.

Thompson, A. J., Hamlet, W. M., Thomas, J., 1893. Report of Board Appointed to Inquire into the Prevalence and Prevention of Lead Poisoning at the Broken Hill Silver-Lead Mines to the Honorable the Minister for Mines and Agriculture. New South Wales: Legislative Assembly. New South Wales.

Tiller, K. G., 1992. Urban soil contamination in Australia. Australian Journal of Soil Research 30, 937-957.

Toms, L. L., Hearn, L., Kennedy, K., Harden, F., Bartkow, M., Temme, C., Mueller, J. F., 2009. Concentrations of polybrominated diphenyl ethers (PBDEs) in matched samples of human milk, dust and indoor air. Environment International 35, 864-869.

Tong, S. L., Baghurst, P. A., McMichael, A. J., Sawyer, M. G., Mudge, J., 1996. Lifetime exposure to environmental lead and children's intelligence at 11-13 years: the Port Pirie cohort study. BMJ 312, 1569-1575.

Tong, S. L., von Schirnding, Y. E., Prapamontol, T., 2000. Environmental lead exposure: a public health problem of global dimensions. Bulletin of the World Health Organization 78, 1068-1077.

Tsuji, J. S., Garry, M. R., Perez, V., Chang, E. T., 2015. Low-level arsenic exposure and developmental neurotoxicity in children: A systematic review and risk assessment. Toxicology 337, 91-107.

Vahidnia, A., van der Voet, G. B., de Wolff, F. A., 2007. Arsenic neurotoxicity—A review. Human & Experimental Toxicology 26, 823-832.

van Alphen, M., 1991. The history of smelting and ore dressing in Broken Hill and the potential for mine derived lead contamination in Broken Hill. Unpublished report.

Wang, B., Du, Y., 2013. Cadmium and Its Neurotoxic Effects. Oxidative Medicine and Cellular Longevity 2013, http://dx.doi.org/10.1155/2013/898034.

Weaver, T. B., Ghadiri, H., Hulugalle, N. R., Harden, S., 2012. Organochlorine pesticides in soil under irrigated cotton farming systems in Vertisols of the Namoi Valley, north-western New South Wales, Australia. Chemosphere 88, 336-343.

Webster, A. E., 2006. The geology of the Broken Hill lead-zinc-silver deposit, New South Wales, Australia. Hobart, Tasmania: CODES ARC Centre of Excellence in Ore Deposits, University of Tasmania.

Wilson, D., Esterman, A., Lewis, M., Roder, D., Calder, I., 1986. Children's Blood Lead Levels in the Lead Smelting Town of Port Pirie, South Australia. Archives of Environmental Health 41, 245-250.

World Health Organization (WHO), 2000. Air Quality Guidelines for Europe: Second Edition. Regional Office for Europe, Copenhagen. http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf (accessed 02.11.16)

Woodward-Clyde Pty Limited, 1993. Evaluation of environmental lead at Broken Hill. Report to the Environment Protection Authority.

Woodward, O. H., 1965. A review of the Broken Hill Lead-Silver-Zinc Industry. West Publishing Corporation Pty. Ltd, Sydney, NSW.

Wright, R. O., Amarasiriwardena, C., Woolf, A. D., Jim, R., Bellinger, D. C., 2006. Neuropsychological correlates of hair arsenic, manganese, and cadmium levels in school-age children residing near a hazardous waste site. NeuroToxicology 27, 210-216.

Yang, K., Cattle, S. R., 2015. Bioaccessibility of lead in urban soil of Broken Hill, Australia: A study based on in vitro digestion and the IEUBK model. Science of the Total Environment 538, 922-933.

Yang, K., Cattle, S. R., 2017. Effectiveness of cracker dust as a capping material for Pb-rich soil in the mining town of Broken Hill, Australia. Catena 148, 81-91.

Young A. R. M., Bryant E. A., Winchester H. P. M., 1992. The Wollongong lead study: an investigation of the blood lead levels of pre-school children and their relationship to soil lead levels. Australian Geographer 23, 121–33.

Zahran, S., Mielke, H. W., Weiler, S., Gonzales, C. R., 2011. Nonlinear associations between blood lead in children, age of child and quantity of soil lead in metropolitan New Orleans. Science of the Total Environment 409, 1211-1218.

Chapter 2: Study area

Chapter One introduced environmental contamination issues related to Australian industrial activity, with a particular focus on mining and smelting communities and the paucity of research examining its activities on Australian childhood health (i.e. children's blood Pb concentrations, educational and behavioural performance). To help address this gap, Australia's longest-operating Pb–Ag–Zn mining city, Broken Hill, was selected as the primary study area for this thesis. This chapter introduces the mineral composition of the Broken Hill orebody, as well as its mining and smelting history and climate information, which likely contributes significantly to contamination of the surrounding landscape by way of aeolian transportation and deposition of trace elements, specifically metal(loid)s. The approaches to sampling and analysis are summarised in Section 2.2 of this thesis, and are provided in detail within Chapters Three, Four, Five and Six.

2.1 Study area

Broken Hill is located in far-west NSW, approximately 1100 km from Sydney (NSW), 750 km from Melbourne (Victoria), and 400 km from Adelaide (South Australia) (Figure 2-1). The population of Broken Hill is 18,856 (ABS, 2017), of which approximately 7.5% are Aboriginal and Torres Strait Islanders (ABS, 2017). The climate at Broken Hill is characterised by hot and windy desert-type weather systems, with a mean annual precipitation of 260 mm (Bureau of Metrology, 2016a). The prevailing wind direction in the summer months (December to February) is from south to north, with the reverse occurring during the winter months (June to August) (Figure 2-2). Overall, the annual prevailing wind direction is southerly (Figure 2-2).

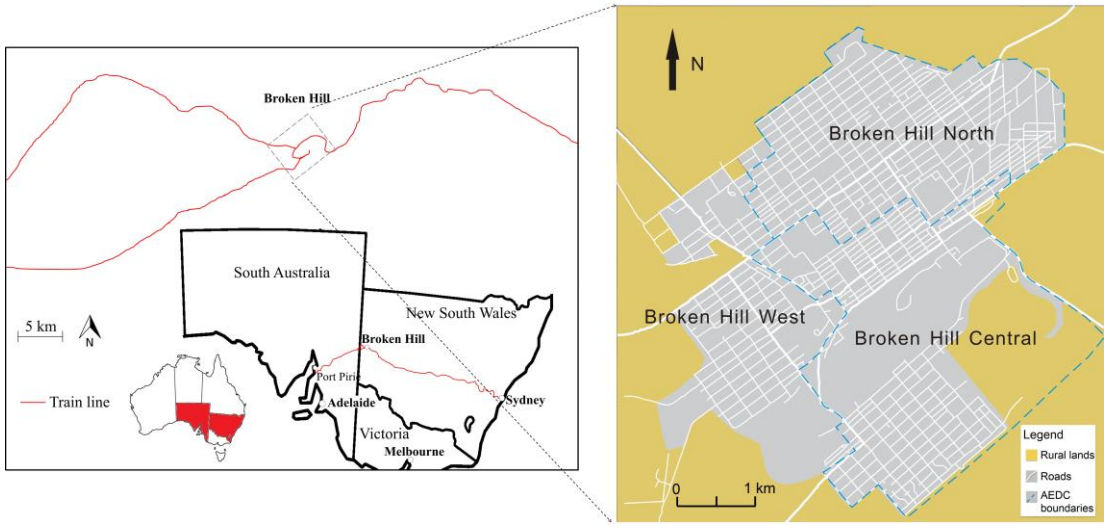


Figure 2-1. Location of Broken Hill and train lines into and out of Broken Hill. The train line map is based on Figure 1 of Kristensen et al. (2015).

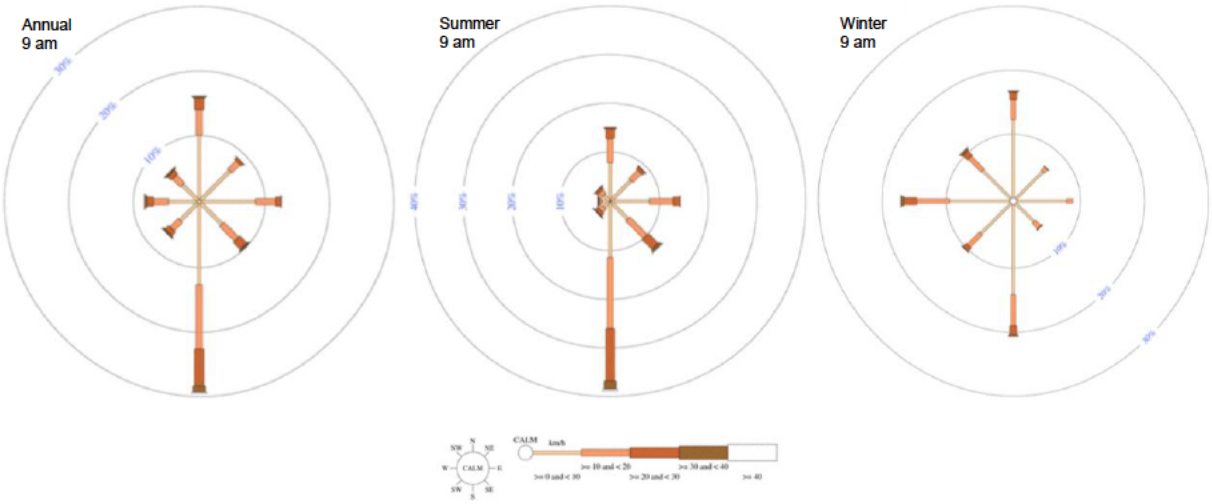


Figure 2-2. Wind roses showing mean wind speed and direction for the Broken Hill region (Bureau of Metrology, 2016b).

The Broken Hill orebody deposit (known locally as the 'Line of Lode') formed 1.7 billion years ago and is approximately 7.5 km long, 850 m in height and 250 m wide (Figure 2-3) (Page et al., 2005). Charles Rasp discovered the ore deposit in 1883, and 16 months later in 1885 high-grade Pb-Ag-Zn ore was identified there (Kearns, 1975).

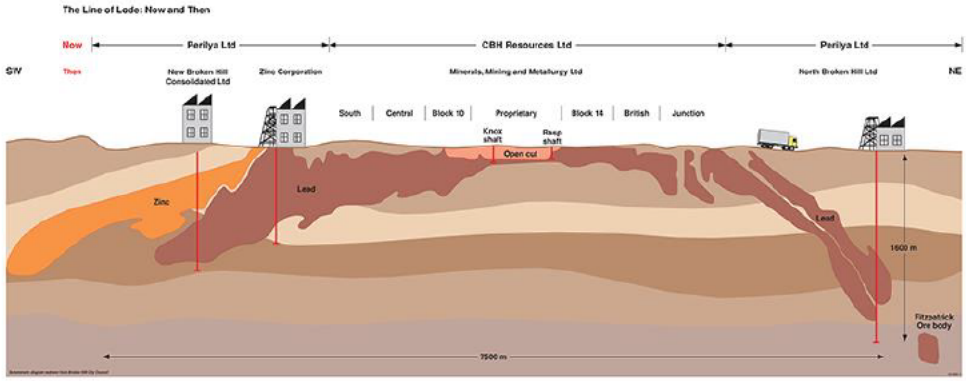


Figure 2-3. Details of the Line of Lode in Broken Hill (sourced from Crutchley et al., 2015).

The enriched Ag and Pb ore was smelted in Broken Hill from 1886 to 1897 (Figure 2-4) (Solomon, 1988; Woodward, 1965), where up to 28 smelters were in operation (Woodward, 1965). However, due to a lack of local fuel sources, the smelting operations had to be relocated (Kristensen et al., 2015). The South Australian Government took advantage of this opportunity to construct a train line to transport Broken Hill ores to Port Pirie for metal refinement (Kearns, 1972). The first train line connecting Adelaide and Port Pirie (South Australia) to Cockburn, on the NSW–South Australia border, was opened by South Australian Railways in June 1887 (Kearns, 1975). A train line on the NSW side of the border connecting Cockburn to Broken Hill via Silverton was opened in January 1888 by the privately-owned Silverton Tramway Company (Figure 2-1) (Kristensen et al., 2015), as the NSW government was not prepared to build a rail link connecting to South Australia at that time (Kearns, 1972).

Following the completion of the train lines connecting Broken Hill to Port Pirie (Figure 2-1), the first transfer of ores for smelting operations occurred in 1889. By 1897 all smelting activities had been transferred to Port Pirie (Solomon, 1988; Woodward, 1965).

Figure 2-4. Smelting activities in Broken Hill from 1886 to 1897 (Blainey, 1968).

The first ore mined and smelted (from 1886 until 1897) at Broken Hill was a Ag-rich Pb carbonate ($PbCO_3$) derived from the oxidised surface of the ore body, which was smelted in Broken Hill (Blainey, 1968). As mining went deeper, unweathered sulphide-rich ore minerals including galena (PbS) were found (Blainey, 1968). Common minerals found in the ores currently being extracted at Broken Hill are shown in Table 2-1.

Table 2-1. The contemporary common Broken Hill minerals (Morrison, 2008).

Mineral	Chemical Composition
Galena	PbS
Sphalerite	(Zn, Fe)S
Pyrite	FeS_2
Pyrrhotite	$Fe_{0\,83\text{-}1}S$
Arsenopyrite	FeAsS
Tetrahedrite	$(Cu, Fe, Ag, Zn)_{12}Sb_4S_{13}$
Chalcopyrite	$CuFeS_2$

Since its discovery, the Broken Hill orebody has produced over 250 million tonnes of high grade ore, originally containing 28 Mt Pb, 24 Mt Zn and 1 billion oz Ag, with an estimated total revenue of AUD$144 billion (calculated by average price of Zn (US$2150/t), Pb (US$2340/t) and Ag (US$38/oz)) (Hamedani et al., 2012). The wealth generated from the

Broken Hill orebody stimulated the industrialisation of mining in Australia and the formation of two of the world's largest mining companies: BHP Billiton and Rio Tinto (Blainey, 1968). Currently, mining in Broken Hill generates approximately AUD$400 million a year, which accounted for almost half of the city's gross regional product in 2012 (TravelIn, 2015).

Currently, there are two active mining companies operating in Broken Hill: Perilya Limited and CBH Resources Limited (hereafter referred to as CBH) (Figure 2-3). After more than 130 years of mining, all extractive operations are now carried out underground with the ore brought to the surface for processing and concentrating. In addition, the processing and concentrating of ores by CBH Resources Limited is conducted under a negative pressure environment to reduce dust emissions (Wilson, 2010). The impact of these current operations is indicated by estimated emissions published in the National Pollutant Inventory (Dong and Taylor, 2017). Emissions to the atmosphere of As, Cd and Pb between 2015 and 2016 from Perilya Limited were 925 kg, 250 kg and 28,473 kg respectively, ranking it 18th, 8th and 4th in Australian emission levels (Table 2-2). By contrast, CBH estimated it emitted only 95 kg of atmospheric Pb during the 2015-2016 period (NPI, 2017c). Previous studies have shown that Perilya Limited has been emitting significant amounts of toxic metal(loid)s, particularly Pb, into the atmospheric environment from 2002 to the present (Dong and Taylor, 2017). Atmospheric Pb emissions from Perilya's operations during the 2002–2014 period are estimated to be in the range of 137 tonnes (Dong and Taylor, 2017). Perilya Limited has listed two operations in Broken Hill – its northern and southern operations (Figure 2-3). The northern mining operations were closed by previous owner Pasminco Limited in February 1993. The southern mining operations are currently the only active site, though recently Perilya has indicated it intends to reopen its northern mining operations (ABC News, 2016). Hence the emissions from the southern mining operations form the focus of the contemporary environmental contamination study in Broken Hill.

Table 2-2. Atmospheric emissions estimates from Perilya (Broken Hill), Nyrstar (Port Pirie) and Mount Isa Mines (Mount Isa) (2015-2016) (NPI, 2017a, b and c). National emission rankings are shown in brackets (with the first being the highest emitter).

Location	As (kg)	Cd (kg)	Pb (kg)
Perilya (Broken Hill)	925 (19th)	250 (7th)	28,473 (3rd)
Nyrstar (Port Pirie)	1,057 (10th)	1168 (2nd)	46,788 (1st)
Mount Isa Mines (Mount Isa)	13,314 (1st)	1837 (1st)	17,675 (6th)

2.2 Materials and methods

The aims of this thesis (see Chapter One) can be categorized into two parts: 1) evaluating contemporary environmental contamination in Broken Hill and identifying legacy sources and new emissions; 2) determining influences of mining activities on children's health (i.e. blood Pb concentrations, educational and behavioural performance). To achieve these aims, multiple approaches, materials and methods were used to evaluate the available data and are detailed in Chapters Three, Four, Five and Six. In order to provide a summary of the approaches used, the relevant information is described briefly below.

In Chapter Three, twelve months of exterior dust Pb deposition samples (2014–2015) were collected from six sampling sites across the residential area of Broken Hill. Remnant gossan (weathered Broken Hill ore) and tailing dump samples, as potential sources of dust metal contamination, were also collected for analysis. Chapter Three evaluates the contemporary dust Pb deposition loading rates, and identifies its sources by examining dust, gossan and tailing dump samples for their total and bioaccessible metal concentrations, morphological characteristics of Pb particles and Pb isotopic compositions. Data relating to individuals' blood Pb concentrations, as well as Pb concentrations measured in different environmental media including soil, indoor petri-dish dust and ceiling dust (hereafter referred as Broken Hill dataset) is examined in Chapters Four and Five. The Broken Hill dataset is derived from NSW Health's systematic blood Pb investigation program that commenced in 1991, which contains in excess of 24,000 blood Pb data, as well as 10,000 soil and dust Pb data, covering the period of 1991 to 2015. Access to the Broken Hill dataset was facilitated by the Broken Hill Child and Family Health Centre (NSW Health) and approved by the Human Research Ethics Committee of NSW Health and Macquarie University (Project No. LNR/14/GWAHS/112; 5201500832).

In Chapter Four, the whole Broken Hill dataset between 1991 and 2015 was analysed to evaluate the long-term relationship between a range of environmental Pb sources (i.e. soil, indoor petri-dish dust and ceiling dust) and blood Pb concentrations. Covariate relationships associated with children's blood Pb (i.e. age, sex, ethnicity, socio-economic status and age of house) are also estimated. Environmental Pb is composed of atmospheric emissions and depositions from ongoing mining activities and also from legacy Pb held in soils, which is subject to recycling in the environment.

Chapter Five identifies and evaluates the impacts of contemporary mining activities on children's blood Pb concentrations and dust Pb loading rates using the linear regression model. Therefore, this chapter focuses on the latest available blood Pb data from Broken Hill over a five year period (2011–2015) along with dust Pb data from the Broken Hill mining company Perilya Limited, which is the highest emitter of Pb in Broken Hill. In order to evaluate the impacts of current mining activities accurately, the related parameters influencing childhood blood Pb concentrations identified in Chapter Four were also included in the data modelling.

In Chapter Six, the potential impacts from metal exposure on early childhood developmental and educational performance were examined using data obtained from the Australian Early Development Census (AEDC) and the National Assessment Program–Literacy and Numeracy (NAPLAN). Educational and behavioural measures were assessed against soil and indoor/exterior dust metals (including Pb, As, Cd) to ascertain whether any relationships existed between the variables. Developmental and educational performance data were normalised according to socio-economic status to evaluate the impacts of environmental metal (including Pb, As and Cd) contamination.

The Appendix section of the thesis contains supplementary data sets for the five studies included in the main body of the thesis along with another co-authored paper (Paper Six) published in *Environmental Pollution*. This study evaluates the use of *in situ* portable X-ray Fluorescence (pXRF) for the assessment of metal-contaminated sites compared to the more traditional approach of *ex situ* analysis via ICP-MS or an equivalent analytical method (e.g. ICP-OES). In addition, the Appendix contains two co-authored online articles published in *The Conversation*, which discuss contemporary contamination and human risks in Broken Hill and Mount Isa from lead mining and smelting operations.

2.3 References

Australian Broadcasting Corporation (ABC) News, 2016. Perilya ramps up efforts to breathe new life into old North Mine. http://www.abc.net.au/news/rural/2016-10-21/perilya-north-mine-reopen-broken-hill/7951174 (accessed 20.09.17).

Australian Bureau of Statistics (ABS), 2017. Broken Hill (C) (LGA), New South Wales. http://stat.abs.gov.au/itt/r.jsp?RegionSummary&region=11250&dataset=ABS_REGIONAL_LGA&geoconcept=REGION&datasetASGS=ABS_REGIONAL_ASGS&datasetLGA=ABS_REGIONAL_LGA&regionLGA=REGION&regionASGS=REGION (accessed 09.06.17).

Blainey, G., 1968. The rise of Broken Hill. Netley: Macmillan of Australia.

Bureau of Metrology, 2016a. Climate statistics for Broken Hill. http://www.bom.gov.au/climate/averages/tables/cw_047007.shtml (accessed 24.07.16).

Bureau of Metrology, 2016b. Wind speed and direction rose at Broken Hill. http://www.bom.gov.au/cgi-bin/climate/cgi_bin_scripts/windrose_selector.cgi?period=Annual&type=9&location=47007 (accessed 24.07.16).

Crutchley, G., Tomkins, K., Lehane, K., 2015. New visitor experiences showcase the minerals of Broken Hill. http://www.ga.gov.au/news-events/news/latest-news/new-visitor-experiences-showcase-the-minerals-of-broken-hill (accessed 21.09.17).

Dong, C., Taylor, M. P., 2017. Applying geochemical signatures of atmospheric dust to distinguish current mine emissions from legacy sources. Atmospheric Environment 161, 82-89.

Hamedani, M. L., Plimer, I. R., Xu, C., 2012. Orebody Modeling for Exploration: The Western Mineralisation, Broken Hill, NSW. Natural Resources Research 21, 325-345.

Kearns, R. H. B., 1972. Silverton, a brief history. The Broken Hill Historical Society, Broken Hill.

Kearns, R. H. B., 1975. Broken Hill 1883-1893—Discovery and Development. The Broken Hill Historical Society, Broken Hill.

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

Morrison, A. L., 2008. Scanning electron microscopy examination for particle samples. Unpublished report, Macquarie University.

National Pollutant Inventory (NPI), 2017a. 2015/2016 data within Australia—Arsenic & compounds from Facilities (Industry). http://www.npi.gov.au/npidata/action/load/emission-by-facility-result/criteria/substance/11/destination/ALL/source-type/INDUSTRY/subthreshold-data/Yes/substance-name/Arsenic%2B%2526%2Bcompounds/year/2016 (accessed 20.09.17).

National Pollutant Inventory (NPI), 2017b. 2015/2016 data within Australia—Cadmium &

compounds from Facilities (Industry). http://www.npi.gov.au/npidata/action/load/emission-by-facility-result/criteria/substance/18/destination/ALL/source-type/INDUSTRY/subthreshold-data/Yes/substance-name/Cadmium%2B%2526%2Bcompounds/year/2016 (accessed 20.09.17).

National Pollutant Inventory (NPI), 2017c. 2015/2016 data within Australia—Lead & compounds from Facilities (Industry). http://www.npi.gov.au/npidata/action/load/emission-by-facility-result/criteria/substance/52/destination/ALL/source-type/INDUSTRY/subthreshold-data/Yes/substance-name/Lead%2B%2526%2Bcompounds/year/2016 (accessed 20.09.17).

Page R.W., Stevens B. P. J., Gibson G. M., 2005. Geochronology of the Sequence Hosting the Broken Hill Pb-Zn-Ag Orebody, Australia. Economic Geology 100, 633-661.

Solomon, R. J., 1988. The richest lode: Broken Hill 1883-1988. Hale & Iremonger, Sydney.

TravelIn, 2015. Mining History of Broken Hill. https://www.travelin.com.au/articles/Mining-History-of-Broken-Hill-01105 (accessed 06.11.17).

Wilson, G., 2010. Broken Hill Operations Pty Ltd. http://www.cbhresources.com.au/files/3913/3747/8536/response-to-submissions-PPR.pdf (accessed 06.11.17).

Woodward, O. H., 1965. A review of the Broken Hill Lead-Silver-Zinc Industry. West Publishing Corporation Pty. Ltd, Sydney, NSW.

Chapter 3: Applying geochemical signatures and SEM methods to identify contamination sources of mining and smelting communities

Chapter Three presents the following two papers:

- Paper One: Applying geochemical signatures of atmospheric dust to distinguish current mine emissions from legacy sources. **Dong, C.,** Taylor, M. P., 2017. *Atmospheric Environment* 161, 82-89.

- Paper Two: Geochemical sources, forms and phases of soil contamination in an industrial city. Harvey, P. J., Rouillon, M., **Dong, C.,** Ettler, V., Handley, H. K., Taylor, M. P., Tyson, E., Tennant, P., Telfer, V., Trinh, R., 2017. *Science of the Total Environment* 584-585, 505-514.

As discussed in Section 1.4 of Chapter One, while the sources of environmental Pb contamination in Broken Hill have been previously examined, the specific source of the contamination (natural, legacy and contemporary) and their risk to human health is poorly understood. The knowledge gap regarding specific emission sources pertains not only to Broken Hill but also involves debate about contamination in several Australian and international locations (Taylor et al., 2014; NASEM, 2017; Noller et al., 2017). Polluters and government agencies have made several statements in regard to the source of contamination in Pb mining and smelting communities, such as: 'the contamination is naturally occurring' (Humphries, 2015); 'there are other sources of contamination rather than smelting and mining activities'; or that 'Toxic metal(oid)s compounds are not bioaccessible.' (Kristensen and Taylor, 2016).

Despite the long history of research at Broken Hill, research examining contemporary dust deposits in Broken Hill is more limited (Taylor et al., 2014), which restricts evidence based decision–making to assist in targeted remediation and clean up in the city. **Paper One** of Chapter Three examines contemporary dust Pb loading ($\mu g/m^2/day$), its bioaccessibility and potential sources of dust Pb particles using multiple lines of geochemical and SEM evidence. The multiple lines of evidence demonstrate that contemporary dust Pb contamination in Broken Hill is sourced primarily from current mining activities and not from weathering or legacy emissions.

Paper Two of Chapter Three investigated soil contamination and its likely sources in the industrial city of Newcastle (NSW). This study revealed that soils in household yards and public areas presented a significant hazard for exposure not only to Pb but also As and polycyclic aromatic hydrocarbons. Collectively, the studies in Chapter Three demonstrate that the methods and approaches have potential for their wider application given that similar contamination issues are present in many global industrial cities (NASEM, 2017).

References

Humphries, K., 2015. NSW Government commits more than $13 million to reduce lead levels at Broken Hill. Media release: Kevin Humphries MP Minister for Natural Resources, Lands and Water Minister for Western NSW, 13th February 2015. http://www.epa.nsw.gov.au/resources/MinMedia/EPAMin150213.pdf (accessed 05.01.2018).

Kristensen, L. J., Taylor, M. P., 2016. Unraveling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. Environmental Geochemistry and Health 38, 1015-1027.

National Academies of Sciences, Engineering, and Medicine (NASEM), 2017. Investigation Strategies for Lead-Source Attribution at Superfund Sites Associated with Mining Activities. The National Academics Press, Washington, DC.

Noller, B., Zheng, J., Huynh, T., Ng, J., Diacomanolis, V., Taga, R., Harris, H., 2017. Lead Pathways Study—Air: Health Risk Assessment of Contaminants to Mount Isa City. http://www.mountisamines.com.au/en/publications/LeadPathways/Lead%20Pathways%20Study%20Air%20Report.pdf (accessed 05.12.17).

Taylor, M. P., Csavina, J., Kristensen, L., Davies, P., 2014. Reducing the harms of toxic air in mining and smelting communities. https://theconversation.com/reducing-the-harms-of-toxic-air-in-mining-and-smelting-communities-25999 (accessed 02.11.17).

Taylor, M. P., Mould, S. A., Kristensen, L. J., Rouillon, M., 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.

Atmospheric Environment 161 (2017) 82 89

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Applying geochemical signatures of atmospheric dust to distinguish current mine emissions from legacy sources

Chenyin Dong [a, *], Mark Patrick Taylor [a, b]

[a] Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, North Ryde, Sydney, NSW 2109, Australia
[b] Energy and Environmental Contaminants Research Centre, Macquarie University, North Ryde, Sydney, NSW 2109, Australia

HIGHLIGHTS

- Multiple approaches applied to identify sources of atmospheric dust contamination.
- Broken Hill Pb in dust is highly bio accessible with a mean of 68%.
- Former sources of contamination e.g. leaded gasoline are no longer significant.
- Current mining activities contribute Pb rich dust to the urban environment.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:
Received 5 January 2017
Received in revised form
12 April 2017
Accepted 14 April 2017
Available online 21 April 2017

Keywords:
Bioaccessibility
Pb isotopes
SEM/EDS
Natural weathering
Legacy emissions
Broken Hill

ABSTRACT

Resolving the source of environmental contamination is the critical first step in remediation and exposure prevention. Australia's oldest silver zinc lead mine at Broken Hill (>130 years old) has generated a legacy of contamination and is associated with persistent elevated childhood blood lead (Pb) levels. However, the source of environmental Pb remains in dispute: current mine emissions; remobilized mine legacy lead in soils and dusts; and natural lead from geological weathering of the gossan ore body. Multiple lines of evidence used to resolve this conundrum at Broken Hill include spatial and temporal variations in dust Pb concentrations and bioaccessibility, Pb isotopic compositions, particle morphology and mineralogy. Total dust Pb loading (mean 255 $\mu g/m^2/day$) and its bioaccessibility (mean 75% of total Pb) is greatest adjacent to the active mining operations. Unweathered galena (PbS) found in contemporary dust deposits contrast markedly to Pb bearing particles from mine tailings and weathered gossan samples. Contemporary dust particles were more angular, had higher sulfur content and had little or no iron and manganese. Dust adjacent to the mine has Pb isotopic compositions ($^{208}Pb/^{207}Pb$: 2.3197; $^{206}Pb/^{207}Pb$: 1.0406) that are a close match (99%) to the ore body with values slightly lower (94%) at the edge of the city. The weight of evidence supports the conclusion that contemporary dust Pb contamination in Broken Hill is sourced primarily from current mining activities and not from weathering or legacy sources.

* Corresponding author.
E-mail address: chenyin.dong@hdr.mq.edu.au (C. Dong).

http://dx.doi.org/10.1016/j.atmosenv.2017.04.024
1352-2310/

1. Introduction

The minerals industry contributes 8.7% to the Australian gross domestic product, placing the nation as one of world's leading resource nations (Australian Bureau of Statistics, 2000; Australian Government, 2015). Despite the benefits of resource extraction and use, its adverse impacts remain a significant ongoing global concern (Thornton, 1996; Tong et al., 2000; Ericson et al., 2016; Pure Earth and Green Cross, 2016). While the consequences of toxic metal exposure is well understood (Lanphear, 2015), the sources (Kristensen and Taylor, 2016) and the subsequent health risks from ore processing and emissions on adjoining communities tend to be minimized by polluters and government agencies (e.g. Taylor and Schniering, 2010; Taylor et al., 2014a, Taylor, 2015; Sullivan and Green, 2016). Strategies used to downplay the link between contamination and mineral extraction and processing industries include using questionable scientific claims and disputing contamination sources (Sullivan, 2014; Spear et al., 2015).

Broken Hill, in far west New South Wales (NSW), contains the world's largest silver lead zinc (Ag Pb Zn) mineral deposit (Solomon, 1988). The ore deposit was discovered in 1883 and has since been mined uninterrupted (Kristensen and Taylor, 2016). Smelting of ore was conducted from 1886 until 1897 until it was relocated to Port Pirie due to a lack of local fuel sources for smelting (Woodward, 1965; Solomon, 1988). The ore processing operations have left behind a legacy of widespread Pb contamination in the adjoining residential community, with occupational and commu nity Pb poisoning being reported as early as 1893 (Thompson et al., 1893). Systematic investigation of childhood blood Pb levels commenced in 1991 at which time 86% of children had blood Pb levels ≥10 μg/dL (the upper acceptable blood Pb value until 2015) (Lyle et al., 2006).

A series of studies about sources and pathways of environ mental Pb were conducted in the 1990s (e.g. Woodward Clyde Pty Ltd, 1993; Gulson et al., 1994a,b; Boreland et al., 2002). A prevailing perspective at the time was that current mining operations were not a dominant source of contamination compared to other emis sions (Woodward Clyde Pty Ltd, 1993, p. 5 3). Nevertheless, stable Pb isotopic composition analysis indicated childhood blood Pb in Broken Hill was predominantly derived from the local ore body (Gulson et al., 1994a). Further, hand to mouth activity was subse quently shown to be an important exposure pathway for childhood lead exposure (Gulson et al., 1994b, 2004).

In 1994, the NSW State Government undertook the remediation of homes of children with high blood Pb levels (>15 μg/dL) (Lyle et al., 2006). Since this time there has been an overall reduction in children's blood Pb concentrations (Lesjak and Jones, 2015). However, in recent years the proportion of children with a blood Pb level >10 μg/dL increased from 12.6% (2010) to 21% (2012) and remained at ~20% after 2012 (Lesjak and Jones, 2015). In 2015, Australia's National Health and Medical Research Council (NHMRC) lowered the blood Pb intervention concentration to 5 μg/dL, resulting in ~50% of children under 5 years of age with a blood Pb concentration in excess of this new guideline (Taylor et al., 2014b; Lesjak and Jones, 2015).

The recent increase in Broken Hill childhood blood Pb levels has stimulated further environmental contamination studies (e.g. Taylor et al., 2014c; Yang and Cattle, 2015) and a AUD$13 million investment from the NSW Government to '*rejuvenate the Broken Hill Environment Lead Program to address the issue of blood Pb levels in local children*' (Humphries, 2015). However, targeted remediation on sources is challenging because the primary source of contem porary environmental Pb in Broken Hill continues to remain in dispute — with arguments ranging from naturally occurring Pb, legacy contamination or contemporary emissions and depositions. For example, the misconception that one of the dominant sources of environmental lead contamination at Broken Hill was '*natural deposition*' was re circulated again in 2015 by Dr Rob Stokes, NSW Minister for Environment (at that time) (Humphries, 2015).

Recent assessments of soils and contemporary dusts have revealed two critical facts: (1) surface soil and dust Pb loading are predominantly derived from the ore body and (2) surface soil and dust Pb loading is unlikely to be related to natural weathering and dispersal of the lead rich ore from the gossan ore body (Kristensen and Taylor, 2016; Taylor et al., 2014c). As noted more than two decades ago by Gulson et al. (1994a,b) dust Pb is the primary pathway for childhood Pb exposures (cf. Lanphear et al., 1996, 2002; Mackay et al., 2013). Therefore, in order to undertake targeted and effective remediation to reduce childhood Pb levels, the precise sources and mechanisms of contemporary Pb contamination need to be resolved unequivocally. This study investigates sources of contemporary dust Pb deposition in Broken Hill using a multiple lines of evidence approach: spatial and temporal variations in dust Pb concentrations, its bioaccessibility, Pb isotopic compositions, particle morphology and chemical compositions.

2. Study area and methods

2.1. Study area

Broken Hill has a hot, arid climate with a mean annual precip itation of 260 mm (Stern et al., 2000; Bureau of Metrology, 2016a). Prevailing winds are predominantly from the south to north (Bureau of Metrology, 2016b). Currently, two mining companies operate in the city of Broken Hill: CBH Rasp Mine and Perilya Limited (Fig. 1). The reported atmospheric Pb emissions for CBH Rasp Mine and Perilya Limited in 2014 were 0.09 and 29 tonnes, respectively (NPI, 2015a, b). Atmospheric lead emissions from Perilya's operations during the period 2002–2014 were estimated to be 137.4 tonnes (Supplementary Table S1). Since 2011, the at mospheric Pb emissions from Perilya Limited's operations have averaged ~30 tonnes per year (Supplementary Table S1), ranking it as the 4th largest emitter of Pb in Australia (NPI, 2015c). Perilya Limited has two operations in Broken Hill — its northern and southern operations (Fig. 1). The southern mining operations (hereafter referred to as the mining operations) are currently the only active site, and emissions from this site form the focus of this investigation.

2.2. Sample collection

Dust Pb loading and its sources in the community were measured using six sampling sites distributed across the residential area of Broken Hill (Fig. 1). Dust monitoring sites belonging to the Broken Hill mining companies are located predominantly on the mining leases or close to their operations and do not monitor dust deposition in the residential areas (CBH Resources Limited, 2016; Perilya Limited, 2016). Dust gauge monitoring for this study was undertaken in accordance with the relevant Australian standard (Standards Australia, 2003). Sampling consisted of placing a 150 mm diameter glass funnel into a 4 L glass bottle ~2 m off the ground and mounted on a tripod. Samples were collected from each monitoring site every month for a year (Nov 2014 to Nov 2015) and were analysed for their metal content and Pb isotopic compositions at the National Measurement Institute (NMI), North Ryde, Sydney. Samples of remnant gossan (the source of the original ore) (n 3) were collected to assess morphological characteristics and chemi cal composition of natural, ancient weathered Pb bearing particles. In addition, three samples were collected from a local mine tailings dump as previous assessments have claimed tailings dumps were

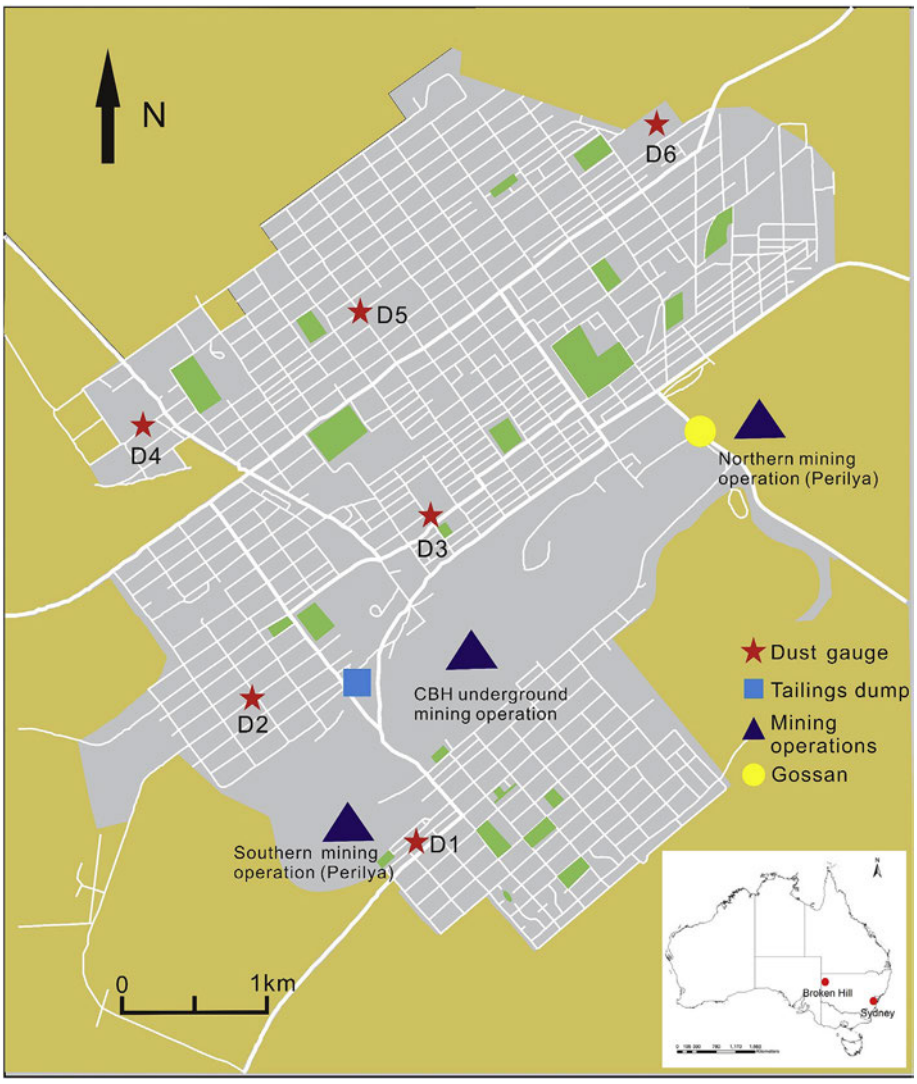


Fig. 1. Broken Hill (NSW, Australia) study area and sites for dust gauge, tailings dump and gossan samples.

contributing a considerable amount of Pb contamination to the Broken Hill environment (Woodward Clyde Pty Ltd, 1993, p. ES 2).

2.3. Samples preparation and methods

Following collection, the sample dust gauge bottles were rinsed out using 500 ml of Milli Q water on to pre weighed filters to capture particulates for analysis. After drying overnight at 105 °C followed by reweighing, the dry filters were digested using a two step sequential extraction. Step 1: 20 ml of 0.1 M HCl for 2 h at room temperature (to test for bioaccessible Pb) (Gulson et al., 1994a); centrifuged at 4000 rpm for 10 min with the supernatant decanted into a separate centrifuge tube. Bioaccessibility is used as a labo ratory proxy for bioavailability, which is determined via the use of laboratory animals. Step 2: The remaining solid residue was further digested using 3 ml of 16 M HNO_3 and 3 ml of 10 M HCl for 2 h at 105 °C (NMI, 2014). The supernatant from step 1 and 2 were ana lysed for bioaccessible and residual Pb concentrations, respectively. The total acid extractable Pb equals to the bioaccessible Pb (step 1) plus the residual Pb (step 2). Analysis for Pb concentration and its isotopic compositions were measured using an Agilent 7900 Inductively Coupled Plasma Mass Spectrometer (ICP MS) at NMI. Both methods at NMI are NATA (National Association of Testing Authorities) accredited. Lead isotopic composition data quality from NMI analyses has been established by Kristensen et al. (2016).

The metal content of five blank filters was determined from the analysis of 500 ml of Milli Q water that had been passed through each filter. The five blank filter samples returned <0.03 and < 0.1 μg/filter for bioaccessible and residual Pb analysis, respectively. National Measurement Institute in house reference materials AGAL 10 (Hawkesbury River Sediment, n 3) and AGAL 12 (bio soil, n 3) were processed with dust gauge samples. Relative standard deviations (RSDs) of AGAL 10 and AGAL 12 were 2.5% and 2.8% for bioaccessible Pb and 2.0% and 6.7% for residual Pb analysis, respectively. Mean recovery rates of AGAL 10 and AGAL 12 were 102% and 107% for total acid digestible Pb concentrations (step 1 + step 2). Mean recovery rates for sample matrix spikes were 99% and 96% for bioaccessible Pb (step 1) and the residual Pb analysis (step 2), respectively.

Dust gauge samples were diluted to 10 μg/L for Pb isotopic composition analysis. Concentration matched NIST SRM 981 (nat ural Pb isotope composition standard) bracketed each sample to correct for mass fractionation. The relative standard deviation (RSD) was 0.8% for $^{204}Pb/^{206}Pb$, 0.42% for $^{207}Pb/^{206}Pb$ and 0.40% for

$^{208}Pb/^{206}Pb$, respectively. Analytical uncertainty was 0.0005 for $^{204}Pb/^{206}Pb$, 0.004 for $^{207}Pb/^{206}Pb$ and 0.009 for $^{208}Pb/^{206}Pb$.

Dust particle morphology and chemical composition were analysed using a JEOL JSM 6480 scanning electron microscope (SEM) with an EX 94300 SDD energy dispersive X ray analyser (EDS). Carbon coating was carried out using a Quorum Q150T sputter coater. Three fields were selected randomly to identify dust Pb particles at 110 times magnification. Lead minerals were readily identified as bright particles due to their high atomic number in the backscatter electron imaging mode (Harding, 2002). The EDS data was processed using the ZAF Method Standardless Quantitative Analysis (van Borm and Adams, 1991).

3. Results and discussion

3.1. Dust Pb loading and bioaccessibility

The two sites closest to the mining operations (D1 and D2, Fig. 2) had the highest dust Pb loading of all monitoring sites with mean values of 255 μg/m^2/day and 248 μg/m^2/day, respectively (Fig. 2, Supplementary Table S2). Site D2, located north of the mining operations, had higher dust Pb loading in summer (mean 270 μg/m^2/day) than winter (93 μg/m^2/day) (Supplementary Table S2). By contrast, site D1, located on the southern side of the mining operations had higher dust Pb loading in winter (mean 217 μg/m^2/day) than summer (102 μg/m^2/day) (Supplementary Table S2). During summer, the dominant wind direction in Broken Hill is northwards, while during winter the dominant wind direction is reversed (Bureau of Metrology, 2016c, d). The other four dust monitoring sites located to the north of mining operations displayed similar seasonal Pb dust loading patterns to those recorded at site D2 (Supplementary Table S2). These prevailing wind patterns are reflected in the dust Pb loadings and their relative position to the mining operations.

There are no Australian guidelines for dust Pb deposition. However, the Queensland state government has set dust Pb at 100 μg/m^2/day as a trigger for environmental monitoring of Mount Isa Mines (Taylor et al., 2014a). This is the same value as listed in the German TA Luft (TA Luft, 2002), which has been used elsewhere as a benchmark value for assessing Pb deposition (Taylor, 2015). Further, the World Health Organization indicated that Pb dust deposition >250 μg/m^2/day will increase blood lead levels (WHO, 2000). Using this guideline as a benchmark, mean dust Pb loadings at site D1 (255 μg/m^2/day) and D2 (248 μg/m^2/day) exceed and approach acceptable international values (Fig. 2). Dust Pb loading generally decreased with distance away from the southern operations (Fig. 2).

The mean dust Pb bioaccessibility was 68% (range 23–92%) (Supplementary Table S3), which is consistent with a previous study of Broken Hill household vacuum dust (Gulson et al., 1994a). Total Pb loading correlated strongly with bioaccessible Pb concentrations (r^2 0.95, $p < 0.01$) (Fig. 3). Bioaccessible Pb concentration exceeded the dust Pb loading guideline of 100 μg/m^2/day at sites D1 (mean 181 μg/m^2/day) and D2 (mean 178 μg/m^2/day) with bioaccessibility decreasing with distance away from the mining operations (Fig. 2, Supplementary Table S3). Least significant difference (LSD) analysis (Supplementary Table S4) revealed the mean bioaccessibility values at the two closest sites (D1 and D2) were significantly ($p < 0.05$) greater compared to that at the furthest site, D6. Bioaccessibility at sites located at an 'intermediate' distance (D3, D4 and D5) from the mining operations, were not statistically different to sites closest or furthest away from the mining operations. As demonstrated by the spatial distribution of total dust Pb, dust bioaccessibility data suggests that children living closest to the mining operations are at greater risk of Pb exposure. Moreover, Yang and Cattle (2015) showed that soil Pb bioaccessibility generally decreased with distance from the ore body, which concurs with the data presented here.

3.2. Dust Pb isotopic compositions

In order to quantify the contribution of ore body Pb to dust Pb, the Pb isotopic composition mixing model devised by Larsen et al. (2012) was applied to the data:

$$x_s \sqrt{\frac{\left[(^{206}Pb/^{207}Pb)_s - (^{206}Pb/^{207}Pb)_b\right]^2 + \left[(^{208}Pb/^{207}Pb)_s - (^{208}Pb/^{207}Pb)_b\right]^2}{\left[(^{206}Pb/^{207}Pb)_o - (^{206}Pb/^{207}Pb)_b\right]^2 + \left[(^{208}Pb/^{207}Pb)_o - (^{208}Pb/^{207}Pb)_b\right]^2}} \times 100\ \%$$

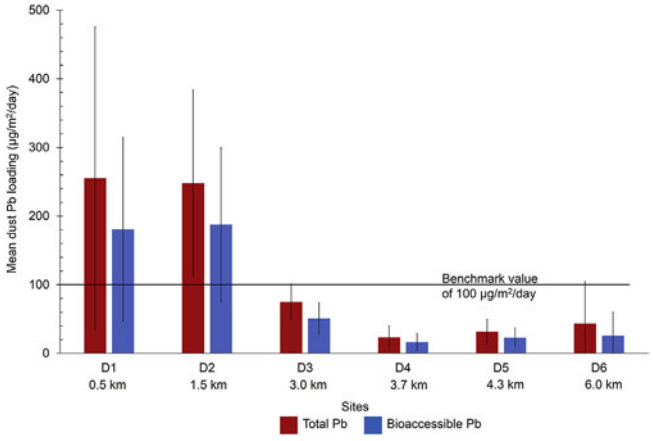


Fig. 2. Mean total and bioaccessible Pb loading of six dust gauge sites in Broken Hill (sites shown in Fig. 1). The error bars represent the standard deviation. The distance of each site away from the mining operations is also shown.

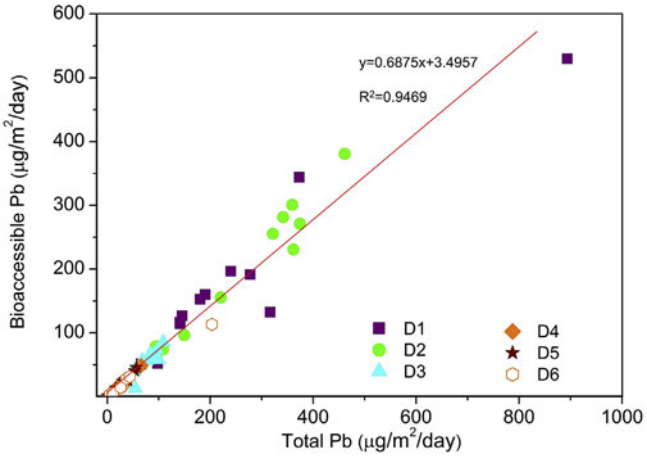


Fig. 3. Linear relationship between total dust Pb and bioaccessible Pb loading values.

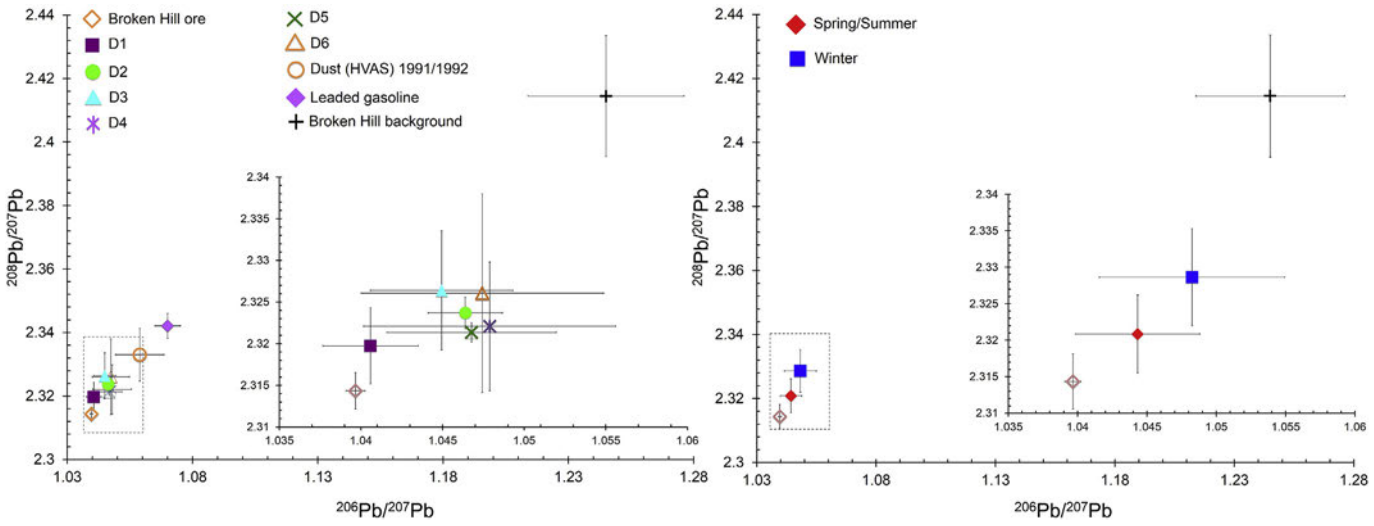


Fig. 4. Lead isotopic compositions of dust in Broken Hill. (a) Comparison of all sites, (b) comparison between spring/summer and winter samples. The averaged lead isotopic composition data of ore body in Broken Hill is from Cooper et al. (1969), Gulson (1986) and Townsend et al. (1998). The leaded gasoline and 1991/1992 dust Pb isotopic data are from Gulson et al. (1994a). The background soil values are from Kristensen and Taylor (2016). The error bars represent the standard deviations of the Pb isotopic compositions.

where x_s is the percent contribution of ore body Pb in the analysed samples; $(^{206}Pb/^{207}Pb)_s$ and $(^{208}Pb/^{207}Pb)_s$ are the isotopic compositions of Pb in sample; $(^{206}Pb/^{207}Pb)_o$ and $(^{208}Pb/^{207}Pb)_o$ are the Pb isotopic compositions of ore body; and $(^{206}Pb/^{207}Pb)_b$ and $(^{208}Pb/^{207}Pb)_b$ are from Broken Hill background soil (Kristensen and Taylor, 2016). Contemporary dust deposits have a Pb isotopic composition similar to the composition of the Broken Hill ore body (Fig. 4). Dust samples from the proximal site D1, contain ~99% Broken Hill ore, while distal dust samples (D6) contain a slightly lower proportion (~94%) of Broken Hill ore, suggesting mixing with other sources of Pb. Mixing model analysis also reveals seasonal differences in dust Pb isotopic compositions. In spring and summer, dust samples have a greater proportion of Pb derived from Broken Hill ore (~97%) than in winter (~94%). The data also corresponds to the dominant seasonal winds: southerlies in spring and summer (i.e. from the direction of the mining operations) and northerlies in winter, (towards the mining operations).

3.3. Morphology and geochemical compositions of Pb particles

Dust Pb particle surface morphology and mineral composition was assessed in dust gauge, gossan and tailings dump samples. Analysis of SEM images and EDS of Pb bearing particles showed that they could be categorised into four groups (Fig. 5):

i) Angular and well crystallized Pb and sulfur (S) bearing particles (interpreted as galena (PbS)—the dominant lead mineral being extracted at Broken Hill) have no apparent chemical and physical surface alteration. These particles also contain minor Fe, Mn, K, Mg, Ca, Al, Na, Cu and Zn concentrations.
ii) Subrounded galena (PbS) particles with minor Fe, Mn, K, Mg, Ca, Al, Na, Cu, Zn concentrations.
iii) Pb bearing particles with cavities, with minor Fe, P, Cl, Ca, Al, Na, Cu concentrations and no elemental S detected.
iv) Rounded and sub rounded Pb bearing particles with major weathering effects and high concentrations of Mn and Fe.

Dust Pb particle deposits are dominated by those from groups (i) and (ii). Angular and well crystallized galena particles were more commonly observed in dust collected at site D1, which was located adjacent to the mining operations. The size of galena particles from site D1 ranges from 20 to 50 μm, while galena particles from more distal sites are finer, at ~5 μm. Lead particles from tailings dump samples were classified as group (iii), while those from the gossan exhibited, as expected, extensive weathering and were classified as group (iv). Particle elemental composition analysis using EDS did not detect S in the tailings dump particles. Weathered gossan particles were characterized as having relatively abundant Fe and Mn and lower S compared with contemporary dust particles (Supplementary Table S5).

3.4. Sources of dust Pb particles

A study by Gulson et al. (1994a) found leaded gasoline was a significant contributor to Pb in air in Broken Hill during 1991/1992. However, the use of Pb additives in automotive gasoline was prohibited in Australia in 2002. Contemporary dust Pb isotopic compositions reveal a clear shift away from leaded gasoline sources, with Pb isotopic compositions now more similar to the Broken Hill ore body (Fig. 4). Moreover, Kristensen and Taylor (2016) found that other Pb sources including leaded paint and old batteries cannot reasonably account for the widespread Pb contamination across Broken Hill. However, stable Pb isotopic compositions on their own do not demonstrate unequivocally whether contemporary dust Pb depositions are derived from remobilized legacy emissions or whether they are from current emissions, natural sources or other anthropogenic activities. Analysis of Pb particle morphology combined with chemical composition data can reveal weathering processes that can assist with the interpretation of the sources of dust (Kristensen et al., 2015; Ettler et al., 2016).

Lead emissions from the former 28 Broken Hill Pb smelters operating between 1886 and 1897 (Woodward, 1965) were significant with an estimated emission rate of approximately 110 tonnes of Pb per week in 1893 (Thompson et al., 1893). By comparison, the total atmospheric Pb emissions from mining operations between 1998 and 2015 were 140 tonnes (NPI, 2015c). Although smelter emissions and depositions have significantly contributed to environmental Pb in Broken Hill, it remains unclear what contribution they have to contemporary dust Pb depositions around the city. Characteristic spherical metal(loid) bearing particles are emitted from Pb and Zn smelters, steelworks and power stations (Tye et al.,

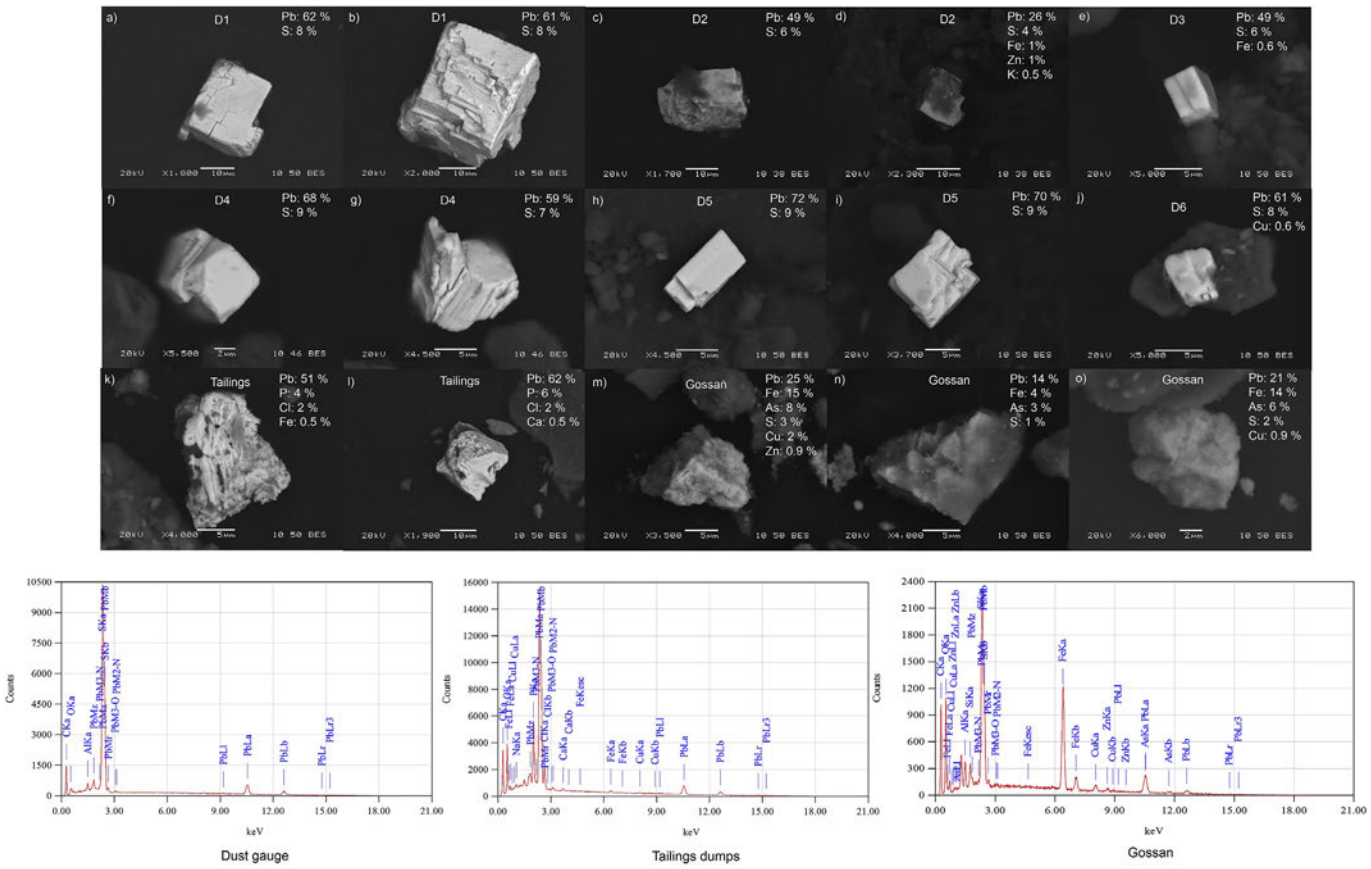


Fig. 5. Scanning electron micrographs taken using back-scattered electron mode (BSE) of Broken Hill Pb bearing particles. Energy-dispersive X-ray spectroscopy (EDS) results of dust gauge samples, tailings and gossan samples are also shown. The concentrations of elements are given as relative weight percentage.

2006; Csavina et al., 2014). Such particles are easily distinguished from geogenic grains due to their characteristic morphology (Csavina et al., 2011, 2014). Spherical Fe oxide particles have been widely reported from historical and active smelting communities in the world (Tye et al., 2006; Csavina et al., 2014; Ettler et al., 2016). At Mount Isa, an Australian Pb and other metal mining and smelting community, spherical Fe oxides contain approximately 11% Pb (Csavina et al., 2014). However, no spherical particles were observed in Broken Hill dust, suggesting that legacy Pb from smelting operations are not contributing to contemporary dust Pb exposures.

Other sources of environmental Pb include unconsolidated tailing deposits, which were subject to redistribution around the city prior to major remediation efforts in the 1990s (Supplementary Fig. S6). Since the 1890s, unweathered sulphide rich Pb and Zn ore has been mined and concentrated in Broken Hill (Blainey, 1968). Ore processing and concentrating using the froth flotation tech nique separates the valuable sulphide minerals from gangue (waste) minerals (Lynch, 1992). As a result, particles sourced from tailing dumps are likely to lack S compared to Pb and Zn from the ore body, providing an added opportunity for geochemical discrimination of contaminant sources.

Samples collected from the gossan were rounded/subrounded with high concentrations of Fe and Mn, suggesting these Pb parti cles have undergone significant long term weathering. Fresh galena crystal particles were present in all of the dust gauge sam ples, and decreased in particle size with distance from the mining operations. Given the softness of the mineral galena (Mohs hard ness 2.5), it is anticipated that atmospheric exposure is likely to induce chemical and physical alterations producing weathered surfaces and particle rounding (Kristensen et al., 2015; Davis et al., 2016). Under these assumptions, cuboid and sub rounded galena particles in contemporary dust particles suggest these depositions are derived from new sources and have experienced limited transport and weathering. The marked morphological and chemi cal differences in dust gauge (contemporary) samples versus those sampled from gossan/tailing dumps supports the contention that Pb rich dusts are sourced from current mining operations and not from legacy depositions that have been recycled. Galena is a dense mineral (7.57 g/cm^3) and the atmospheric transport of larger Pb particles is likely to be limited. For example, using the method detailed by Hinds (1999), cubic galena particles > 16 μm would travel < 1 km when exposed to the city's average wind speed of 3.5 m/s (9 a.m.) (Bureau of Metrology (2016a)). The diminishing size of galena particles with distance away from the active mining operations supports the contention that current mining operations are the primary source of contemporary Pb dust depositions. Furthermore, the video clip (Video 1) shows the transport of dusts from the lead and zinc ore pile at the head of the Perilya Mine at Broken Hill, NSW.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.04.024.

4. Study limitations

The assessment of particles using SEM was a semi quantitative technique. Further analysis of dust depositions using a quantita tive SEM system would enable quantification of the relative

portions of different grain morphologies and compositions (Williamson et al., 2013; Morrison et al., 2016). Dust sampling was non directional and additional relevant information could be complied by adding directional dust deposition sampling. In addi tion, the application of Micro Orifice Uniform Deposit Impactor (MOUDI) would allow size partitioning coupled with geochemical and SEM analysis of different aerosol fractions (e.g. Miranda et al., 2002; Csavina et al., 2011, 2014; Félix et al., 2015).

5. Conclusion

This assessment of contemporary dust deposits reveals the following relevant facts that are likely to be influential in deter mining blood Pb exposures in Broken Hill children:

- Dust Pb bioaccessibility ranges between 23 and 92% with a mean of 68%. This demonstrates the Broken Hill community, particularly those living close to the mining operations, are at risk of Pb exposure from contemporary dust depositions.
- Lead isotopic composition analysis indicates that contemporary Pb dust is sourced mainly from the Broken Hill ore body. Former sources of Pb including leaded gasoline emissions are no longer significant.
- Dust particle morphology and chemical composition corre sponds to characteristics associated with current physical min ing activities (e.g. crushing, grinding and loading).

The application of multiple lines of geochemical evidence demonstrates that it is possible to establish the relative importance of contemporary emissions and depositions against legacy sources. While it may seem 'obvious' to an outside observer that contami nation in mining towns are derived from the most likely source, a weight of evidence is required to shift the status quo and stimulate, targeted remediation and abatement. Indeed, the NSW EPA have recently implemented a pollution reduction program for Perilya's southern mining operations which include reducing waste pollu tion sources to soils and waters and developing a waste manage ment plan for the entire mine site (NSW EPA, 2016). Assuming the changes to the mining operations are effective at markedly reducing Pb emissions, this may enable an opportunity for a 'nat ural experiment' of the subsequent changes in aerosol and dust Pb along with blood Pb outcomes.

Author contributions

The research for this study completed by both authors. Both authors have approved the final version of the manuscript.

Funding sources

C. Dong is funded via an International Macquarie University Research Excellence Scholarship (iMQRES No. 2014098) and received technical and practical support from the Broken Hill Environmental Lead Program (BHELP) as part of a Macquarie Uni versity–BHELP collaboration agreement. C. Dong also received laboratory and analytical support from the National Measurement Institute as part of a Macquarie University–National Measurement Institute PhD research collaboration agreement.

Notes

The authors declare no competing financial interest. M.P. Taylor is completing an independent 'Review of the New South Wales Environment Protection Authority's Management of Contaminated Sites' for the NSW Minister for the Environment and is also an advisor to the Broken Hill Environmental Lead Program. Chenyin Dong has no potential conflicts of interest to declare.

Acknowledgments

Dr. Janae Casvina is thanked for providing methods to evaluate travel distance of galena particles to be applied in Broken Hill. The authors are also grateful to Peter Oldsen and Frances Boreland (NSW EPA, Broken Hill Environmental Lead Program), Shiva Prasad, Dr. Andrew Evans, Dr. Michael Wu, Dr. Ping Di (National Mea surement Institute), Nicole Vella, Nadia Suarez Bosche and Sue Lindsay (Macquarie University Microscopy Unit) for sample collection and analysis. Professor Brian Gulson, Macquarie Univer sity, is thanked for his comments in relation to this manuscript. Mr Marek Rouillon and Dr Guan Wang are thanked for reviewing early drafts of the manuscript.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.04.024.

References

Australian Bureau of Statistics, 2000. The Australian Mining Industry: From Set-tlement to 2000. http://www.abs.gov.au/ausstats/abs%40.nsf/94713ad445ff1425ca25682000192af2/93136e734ff62aa2ca2569de00271b10!OpenDocument (Accessed 1 November 16).

Australian Government, 2015. Australian Industry Report 2015. Office of the Chief Economist, Department of Industry, Innovation and Science. http://www.industry.gov.au/Office-of-the-Chief-Economist/Publications/Documents/AIR2015.pdf (Accessed 13 September 16).

Blainey, G., 1968. The Rise of Broken Hill. Macmillan of Australia, Melbourne.

Boreland, F., Lyle, D.M., Wlodarczyk, J., Balding, W.A., Reddan, S., 2002. Lead dust in Broken Hill homes a potential hazard for young children? Aust. N. Z. J. Public Health 26, 203 207.

Bureau of Metrology, 2016a. Climate Statistics for Broken Hill. http://www.bom.gov.au/climate/averages/tables/cw_047007.shtml (Accessed 24 July 16).

Bureau of Metrology, 2016b. Wind Speed and Direction Rose at Broken Hill. http://www.bom.gov.au/cgi-bin/climate/cgi_bin_scripts/windrose_selector.cgi?period Annual&type 9&location 47007 (Accessed 24 July 16).

Bureau of Metrology, 2016c. Summer–Wind Speed and Direction Rose at Broken Hill. http://www.bom.gov.au/cgi-bin/climate/cgi_bin_scripts/windrose_selector.cgi?period Summer&type 9&location 47007&Submit Get+Rose (Accessed 24 July 16).

Bureau of Metrology, 2016d. Winter–Wind Speed and Direction Rose at Broken Hill. http://www.bom.gov.au/cgi-bin/climate/cgi_bin_scripts/windrose_selector.cgi?period Winter&type 9&location 47007&Submit Get+Rose (Accessed 24 July 16).

CBH Resources Limited, 2016. Environment Monitoring Overview. http://www.cbhresources.com.au/files/6713/4551/1116/Monitoring_Overview_and_Criteria.pdf (Accessed 19 August 2016).

Cooper, J.A., Reynolds, P.H., Richards, J.R., 1969. Double-spike calibration of the Broken Hill standard lead. Earth Planet. Sci. Lett. 6, 467 478.

Csavina, J., Landázuri, A., Wonaschütz, A., Rine, K., Rheinheimer, P., Barbaris, B., Conant, W., Sáez, A.E., Betterton, E.A., 2011. Metal and metalloid contaminants in atmospheric aerosols from mining operations. Water Air Soil Pollut. 221, 145 157.

Csavina, J., Taylor, M.P., Félix, O., Rine, K.P., Sáez, A.E., Betterton, E.A., 2014. Size-resolved dust and aerosol contaminants associated with copper and lead smelting emissions: implications for emission management and human health. Sci. Total Environ. 493, 750 756.

Davis, J.J., Morrison, A.L., Gulson, B.L., 2016. Uncovering pathways of metal contamination with microscopic techniques and lead isotopic tracing. Aust. J. Earth Sci. 63, 795 803.

Ericson, B., Caravanos, J., Keith, J., Taylor, M.P., Frostad, J., Fuller, R., Landrigan, P., 2016. The global burden of lead toxicity attributable to informal used lead-acid battery (ULAB) sites. Ann. Glob. Health 82, 686 699.

Ettler, V., Johan, Z., Kříbek, B., Veselovský, F., Mihaljevic, M., Vaněk, A., Penížek, V., Majer, V., Sracek, O., Mapani, B., Kamona, F., Nyambe, I., 2016. Composition and fate of mine- and smelter-derived particles in soils of humid subtropical and hot semi-arid areas. Sci. Total Environ. 563 564, 329 339.

Félix, O.I., Csavina, J., Field, J., Rine, K.P., Sáez, A.E., Betterton, E.A., 2015. Use of lead isotopes to identify sources of metal and metalloid contaminants in atmo-spheric aerosol from mining operations. Chemosphere 122, 219 226.

Gulson, B.L., 1986. Lead isotopes in mineral exploration. Elsevier, Amsterdam.

Gulson, B.L., Mizon, K.J., Law, A.J., Korsch, M.J., Davis, J.J., 1994a. Source and

pathways of lead in humans from the Broken Hill mining community an alternative use of exploration methods. Econ. Geol. 89, 889 908.
Gulson, B.L., Davis, J.J., Mizon, K.J., Korsch, M.J., Law, A.J., Howarth, D., 1994b. Lead bioavailability in the environment of children: blood lead levels in children can be elevated in a mining community. Arch. Environ. Health 49, 326 331.
Gulson, B.L., Mizon, K.J., Davis, J.J., Palmer, J.M., Vimpani, G., 2004. Identification of sources of lead in children in a primary zinc-lead smelter environment. Environ. Health Perspect. 112, 52 60.
Harding, D.P., 2002. Mineral identification using a scanning electron microscope. Min. Metall. Proc. 19, 215 219.
Hinds, W.C., 1999. Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles, second ed. Wiely, New York.
Humphries, K., 2015. NSW Government Commits More than $13 Million to Reduce Lead Levels at Broken Hill. Media Release: Kevin Humphries MP Minister for Natural Resources, Lands and Water Minister for Western NSW, 13th February 2015. http://www.epa.nsw.gov.au/resources/MinMedia/EPAMin150213.pdf (Accessed 5 January 2017).
Kristensen, L.J., Taylor, M.P., 2016. Unravelling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. Environ. Geochem. Health 38, 1015 1027.
Kristensen, L.J., Taylor, M.P., Morrison, A.L., 2015. Lead and zinc dust depositions from ore trains characterised using lead isotopic compositions. Environ. Sci. Process. Impacts 17, 631 637.
Kristensen, L.J., Taylor, M.P., Evans, A.J., 2016. Reply to Gulson's comments on 'Tracing changes in atmospheric sources of lead contamination using lead isotopic compositions in Australian red wine'. Chemosphere 154, 40 47.
Lanphear, B.P., 2015. The impact of toxins on the developing brain. Annu. Rev. Publi. Health 36, 211 230.
Lanphear, B.P., Weitzman, M., Winter, N.L., Eberly, S., Yakir, B., Emond, M., Matte, T.D., 1996. Lead-contaminated house dust and urban children's blood lead levels. Am. J. Public Health 86, 1416 1421.
Lanphear, B.P., Hornung, R., Ho, M., Howard, C.R., Eberly, S., Knauf, K., 2002. Environmental lead exposure during early childhood. J. Pediatr. 140, 40 47.
Larsen, M.M., Blusztajn, J.S., Andersen, O., Dahllof, I., 2012. Lead isotopes in marine surface sediments reveal historical use of leaded fuel. J. Environ. Monit. 14, 2893 2901.
Lesjak, M., Jones, T., 2015. Lead Health Report 2014-Children Less than 5 Years Old in Broken Hill. Population Health Unit, NSW Government, Western NSW & Far West Local Health District. http://www.fwlhd.health.nsw.gov.au/UserFiles/files/Directorates/Population%20Health/2014%20Lead%20Report.pdf (Accessed 13 September 16).
Luft, T.A., 2002. Technical Instructions on Air Quality Control. in: First General Administration Regulation Pertaining the Federal Immission Control Act. http://www.bmub.bund.de/fileadmin/bmu-import/files/pdfs/allgemein/application/pdf/taluft_engl.pdf (Accessed 10 March 15).
Lyle, D.M., Philips, A.R., Balding, W.A., Burke, H., Stokes, D., Corbett, S., Hall, J., 2006. Dealing with lead in Broken Hill Trends in blood lead levels in young children 1991 2003. Sci. Total Environ. 359, 111 119.
Lynch, A.J., 1992. Broken Hill Metallurgy A Story of Innovations in Processes, Equipment and Instruments. In: The AusIMM Annual Conference (Broken Hill).
Mackay, A.K., Taylor, M.P., Munksgaard, N.C., Hudson-Edwards, K.A., Burn-Nunes, L., 2013. Identification of environmental lead sources and pathways in mining and smelting town: Mount Isa, Australia. Environ. Pollut. 180, 304 311.
Miranda, R.M., Andrade, M.F., Worobiec, A., Grieken, R.V., 2002. Characterisation of aerosol particles in the Sao Paulo Metropolitan Area. Atmos. Environ. 36, 345 352.
Morrison, A.L., Swierczek, Z., Gulson, B.L., 2016. Visualisation and quantification of heavy metal accessibility in smelter slags: the influence of morphology on availability. Environ. Pollut. 210, 271 281.
National Measurement Institute (NMI), 2014. National Measurement Institute, Inorganic Section, Method NT2.49: Determination of Acid Extractable Elements in Soils, Sediments, Sludges and Solid Waste. Sdyney.
National Pollutant Inventory (NPI), 2015a. 2014/2015 Report for BROKEN HILL OPERATION PTY LTD, CBH Resources Rasp Mine Broken Hill, NSW. http://www.npi.gov.au/npidata/action/load/emission-by-individual-facility-result/criteria/state/NSW/year/2015/jurisdiction-facility/1333 (Accessed 19 August 16).
National Pollutant Inventory (NPI), 2015b. 2014/2015 Report for PERILYA BROKEN HILL LIMITED, Perilya Broken Hill Operations Broken Hill, NSW. http://www.npi.gov.au/npidata/action/load/emission-by-individual-facility-result/criteria/state/NSW/year/2015/jurisdiction-facility/125 (Accessed 19 August 16).
National Pollutant Inventory (NPI), 2015c. Search by Form. http://www.npi.gov.au/npidata/action/load/advance-search (Accessed 23 July 16).
New South Wales (NSW) EPA, 2016. Licence Variation of Environment Protection Licence No. 2688. http://www.epa.nsw.gov.au/prpoeoapp/ViewPOEONotice.aspx?DOCID -1&SYSUID 1&LICID 1545186 (Accessed 2 November 16).
Perilya Limited, 2016. Monthly Reports: Environmental Reporting. http://www.perilya.com.au/health safety environment/environment/reports (Accessed 24 July 16).
Pure Earth and Green Cross, 2016. The World's Worst Pollution Problems 2016: The Toxics Beneath Our Feet. http://worstpolluted.org/docs/WorldsWorst2016Spreads.pdf (Accessed 1 November 16).
Solomon, R.J., 1988. The Richest Lode: Broken Hill 1883-1988. Hale & Iremonger, Sydney, NSW.
Spear, M., Thomas, R., Sharader-Frechette, K., 2015. Commentary: flawed science delays smelter cleanup and worsens health. Acc. Res. 22, 41 60.
Standards Australia, 2003. Australian/New Zealand 3580.10.1:2003. Determinationof Particulate Matter – Deposited Matter – Gravimetric Method. http://infostore.saiglobal.com/store/details.aspx?ProductID.373364 (Accessed 23 July 2016).
Stern, H., de Hoedt, G., Ernst, J., 2000. Objective Classification of Australian Climates. Australian Bureau of Meteorology, Melbourne.
Sullivan, M., 2014. Tainted Earth: Smelters, Public Health and the Environment. Rutgers University Press, New Brunswick (US).
Sullivan, M., Green, D., 2016. Misled about lead: an assessment of online public health education material from Australia's lead mining and smelting towns. Environ. Health 15, 1. http://dx.doi.org/10.1186/s12940-015-0085-9.
Taylor, M.P., 2015. Atmospherically deposited trace metals from bulk mineral concentrate port operations. Sci. Total Environ. 515 516, 143 152.
Taylor, M.P., Schniering, C., 2010. The public minimization of the risks associated with environmental lead exposure and elevated blood lead levels in children, Mount Isa, Queensland, Australia. Arch. Environ. Occup. Health 65, 45 48.
Taylor, M.P., Davies, P.J., Kristensen, L.J., Csavina, J.L., 2014a. 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 Res. 14, 35 52.
Taylor, M.P., Winder, C., Lanphear, B.P., 2014b. Australia's leading public health body delays action on the revision of the public health goal for blood lead exposures. Environ. Int. 70, 113 117.
Taylor, M.P., Mould, S.A., Kristensen, L.J., Rouillon, M., 2014c. Environmental arsenic, cadmium and lead dust emissions from metal mine operations: implications for environmental management, monitoring and human health. Environ. Res. 135, 296 303.
Thompson, A.J., Hamlet, W.M., Thomas, J., 1893. Report of Board Appointed to Inquire into the Prevalence and Prevention of Lead Poisoning at the Broken Hill Silver-Lead Mines to the Honorable the Minister for Mines and Agriculture (Legislative Assembly, New South Wales).
Thornton, I., 1996. Impacts of mining on the environment; some local, regional and global issues. Appl. Geochem 11, 355 361.
Tong, S.L., Schirnding, Y., von, E., Prapamontol, T., 2000. Environmental lead exposure: a public health problem of global dimensions. Bull. World Health Organ 78, 1068 1077.
Townsend, T.A., Yu, Z., McGoldrick, P.A., Hutton, J., 1998. Precise lead isotope ratios in Australian galena samples by high resolution inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. 13, 809 813.
Tye, A.M., Hodgkinson, E.S., Rawlins, B.G., 2006. Microscopic and chemical studies of metal particulates in tree bark and attic dust: evidence for historical atmospheric smelter emissions, Humberside, UK. J. Environ. Monit. 8, 904 912.
van Borm, W.A., Adams, F.C., 1991. A standardless ZAF correction for semi-quantitative electron probe microanalysis of microscopical particles. X-Ray Spectrom. 20, 51 62.
Williamson, B.J., Rollinson, G., Pirrie, D., 2013. Automated Mineralogical Analysis of PM_{10}: New Parameters for Accessing PM Toxicity. Environ. Sci. Technol. 47, 5570 5577.
Woodward, O.H., 1965. A review of the Broken Hill lead-silver-zinc Industry. West Publishing Corporation Pty. Ltd, Sydney, NSW.
Woodward-Clyde Pty Limited, 1993. Evaluation of Environmental Lead at Broken Hill. Prepared for Environment Protection Authority. Project No. 3328. Sydney, NSW.
World Health Organization (WHO), 2000. Air Quality Guidelines for Europe, second ed. Regional Office for Europe, Copenhagen http://www.euro.who.int/__data/assets/pdf_file/0005/74732/E71922.pdf. (Accessed 2 November 16).
Yang, K., Cattle, S.R., 2015. Bioaccessibility of lead in urban soil of Broken Hill, Australia: a study based on in *vitro* digestion and the IEUBK model. Sci. Total Environ. 538, 922 933.

Science of the Total Environment 584–585 (2017) 505–514

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Geochemical sources, forms and phases of soil contamination in an industrial city

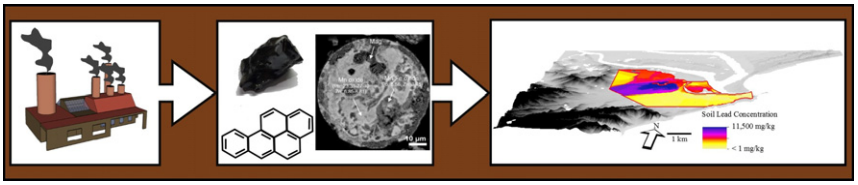
P.J. Harvey [a,*], M. Rouillon [b], C. Dong [b], V. Ettler [c], H.K. Handley [a], M.P. Taylor [b], E. Tyson [b], P. Tennant [b], V. Telfer [b], R. Trinh [b]

[a] Department of Earth and Planetary Sciences, Faculty of Science and Engineering, Macquarie University, Sydney, NSW 2109, Australia
[b] Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, Sydney, NSW 2109, Australia
[c] Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, Prague 2 128 43, Czech Republic

HIGHLIGHTS

- Ferrous and non ferrous metal smelting have caused an environmental contam ination legacy in the city environment.
- Children exposed to the soils in the city are vulnerable to metal(loid) and poly cyclic aromatic hydrocarbon exposure.
- Human health exposure risks should be considered when repurposing industrial cities for changing land uses.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 December 2016
Received in revised form 9 January 2017
Accepted 9 January 2017
Available online 24 January 2017

Editor: F.M. Tack

Keywords:
Soil
Metal(loids)
Lead isotopes
Bio-accessibility
Mineralogy of metal-bearing particles
Newcastle

ABSTRACT

This study examines current soil contamination in an Australian industrial city, Newcastle. Public (roadside verges and parks) and private (homes) surface soils (n = 170) contained metal(loid)s elevated above their re spective Australian Health Investigation Levels (HIL). Lead (Pb), the most common contaminant in the city, ex ceeds the HIL for residential soils (HIL A, 300 mg/kg) in 88% of private soils (median: 1140 mg/kg). In vitro Pb bio accessibility analysis of selected soils (n = 11) using simulated gastric fluid showed a high affinity for Pb solubilisation (maximum Pb concentration: 5190 mg/kg, equating to 45% Pb bio accessibility). Highly soluble Pb laden Fe and Mn oxides likely contribute to the bio accessibility of the Pb. Public and private space surface soils contain substantially less radiogenic Pb (range: $^{208}Pb/^{207}Pb$: 2.345 2.411, $^{206}Pb/^{207}Pb$: 1.068 1.312) than local background soil ($^{208}Pb/^{207}Pb$: 2.489, $^{206}Pb/^{207}Pb$: 1.198), indicating anthropogenic contamination from the less radiogenic Broken Hill type Pb ores ($^{208}Pb/^{207}Pb$: 2.319, $^{206}Pb/^{207}Pb$: 1.044). Source apportionment using Pb isotopic ratio quantification and soil mineralogy indicate the city's historic copper and steel industries contributed the majority of the soil contaminants through atmospheric deposition and use of slag waste as fill material. High temperature silicates and oxides combined with rounded particles in the soil are characteristic of smelter dust emissions. Additionally, a preliminary investigation of polycyclic aromatic hydrocarbons in soils, sometimes associated with ferrous metal smelting, coal processing or burning of fossil fuels, shows that these too pose a health exposure risk (calculated in comparison to benzo(*a*)pyrene: n = 12, max: 13.5 mg/kg, HIL: 3 mg/kg).

1. Introduction

Urban environmental contamination is an issue common to industri al cities throughout the world (Filippelli et al., 2015). Historically, em ployees would live close to their work, resulting in dense urban

* Corresponding author.
E-mail address: paul.harvey@mq.edu.au (P.J. Harvey).

http://dx.doi.org/10.1016/j.scitotenv.2017.01.053
0048-9697/

development around industrial operations. Due to the proximity of industrial operations to urban environments there is the potential for adverse impacts on human health arising from industrial emissions (Csavina et al., 2012; Dong et al., 2015; Ettler et al., 2009; Gulson et al., 1994; Gulson et al., 2004; Gulson et al., 2009; Morrison, 2003; Taylor et al., 2010; Taylor et al., 2013; Taylor et al., 2014a; Taylor et al., 2014b).

By 2050, the majority of the global population is expected to transition from rural to urban metropolitan living, increasing the risk associated with contaminated urban lands (United Nations (UN), 2015). The resulting environmental contamination burden from industrial cities is demonstrated in Detroit, USA, which has been considered one of the most contaminated cities in the USA (Lougheed, 2014). Sulfur dioxide, heavy metals, hydrocarbons and other organic contaminants that were emitted to the atmosphere during the city's automobile manufacturing era, accumulated in the urban soil environment and have been subsequently linked to a range of health impacts including

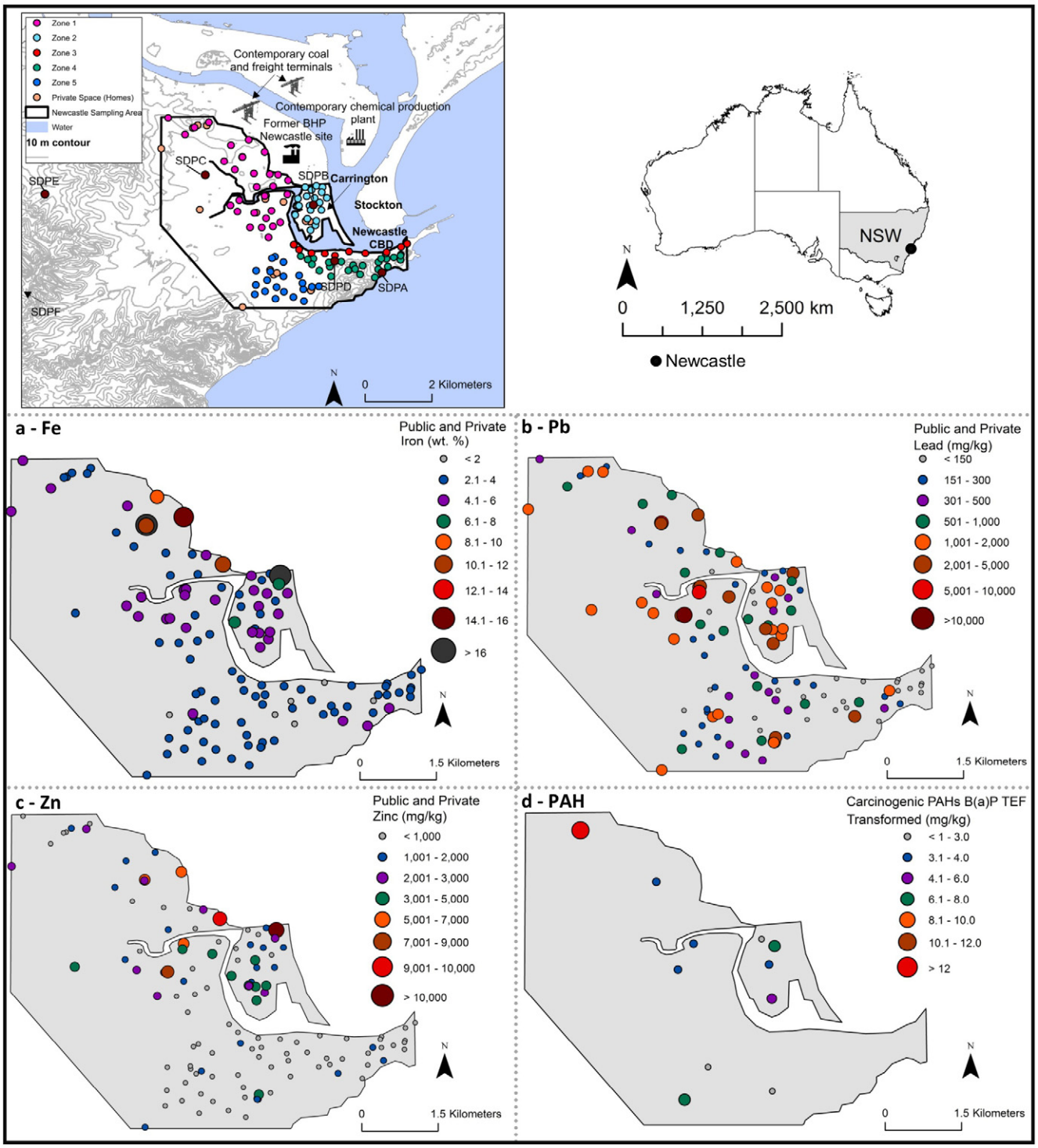


Fig. 1. Soil analyte concentrations within Newcastle (Australia) (panel a - iron, b - lead, c - zinc, d - TEF transformed PAHs). Sites marked SDP- are soil depth profiles.

chronic respiratory diseases and mental disabilities, particularly in infants and young adults (Canfield et al., 2003; Dong et al., 2015; Lougheed, 2014; Taylor et al., 2016). Although Detroit battles legacy environmental contamination issues, modern industrial processes can also contribute to the environmental contamination burden. More recently, the rapid and spontaneous expansion of China's manufacturing and industrial economy has resulted in an overlap of land use with urban residential areas. The emissions generated from industrial processes have been linked to substantial carcinogenic health effects in the city of Beijing (Chen et al., 2015). In order to address this problem, a better understanding of environmental contamination and the impacts on population health in urban industrial environments is required.

This study investigates an Australian industrial city, Newcastle, and the risk of exposure associated with environmental contaminants in the soils of the city. Newcastle, approximately 200 km north of Sydney (Fig. 1), was historically a manufacturing based city. However, the city has recently become a regional population center, with an economy moving towards services, arts and tourism (Newcastle City Council (NCC), 2013, 2015). Large scale industrial operations began in the mid 1800's with the Wallaroo Copper Company smelter (1868 to 1892) processing annually ~1300 tonnes of low grade Wallaroo Mine (South Australia) copper ore (NCC, 1997; SMH, 1871a; SMH, 1871b; The Mercury, 1867). During that time, a number of other operations were also established, including the Waratah Coal Company (SMH, 1871b), the English and Australian Copper Company (EACC) smelter in 1867 (SM, 1872) and the Sulphide Corporation Pb smelter at nearby Boolaroo in 1897 (Dames and Moore, 1994). The port and shipping facilities of Newcastle quickly became strategic industrial infrastructure as Pb sulfide ore was shipped through the Port of Newcastle to Boolaroo (NMH, 1902; Quorn Mercury, 1900a). In 1907 the Melbourne and Great Northern Smelter also joined the Cu smelting operations at Newcastle (MDM, 1907; SCT & WA, 1907). The Broken Hill Proprietary (BHP) Newcastle Steel Mill and subsidiaries were the industrial focus of Newcastle from 1915 until their closure in 1999 (Parliament of New South Wales, 1999). At peak operation, the facilities employed ~12,000 people (BHP Co. LTD, 1949; Parliament of New South Wales, 1999). The BHP operation became an industrial giant with the addition of, and partnership with, two other large scale manufacturers of steel products (BHP Co. LTD, 1949; NS, 1925; Parliament of New South Wales, 1999). Today, coal and freight shipping terminals and an ammonium nitrate facility dominate the industrial activities of the city.

Despite the industrial heritage of Newcastle, there has been no publicly accessible wide scale geochemical assessment of soils in the city area. This study investigates soil metal(loid)s and polycyclic aromatic hydrocarbons (PAHs) to help close this knowledge gap and highlight potential environmental contamination risks associated with living in an industrial city.

2. Methods

2.1. Soil sampling

2.1.1. Soil metal(loid) concentrations

Newcastle city was divided into five sampling areas (Fig. 1) to reflect the dominant land use types covering open spaces, retail and industrial (Zone 1), residential (Zone 2), rehabilitated industrial land along the foreshore now used for high density residential (Zone 3), Central Business District (CBD) (Zone 4) and low to medium density residential (Zone 5). Soils collected in public spaces (n = 103) were sampled from roadside verges, parklands and other accessible locations. Soils collected from private spaces (n = 67 from 23 homes) were obtained through the Macquarie University VegeSafe soil metal testing program (Rouillon et al., 2016), where Newcastle community members submitted samples for analysis. Samples were also received from outside of the specified target area but were included here to provide additional detail to the investigation. Public space samples were collected at the surface (0 2 cm) in accordance with the standard methods (Taylor et al., 2010). A number of control sites (n = 6) with pits dug to a defined depth of 40 cm irrespective of soil horizons were sampled throughout the city to determine local background soil concentrations.

2.1.2. Slag deposits

A slag waste deposit was identified outcropping on a beach adjacent to a children's playground in Stockton (Fig. 1). Large chunks of a black glass like slag and a ferrous slag material were collected using a rock hammer to separate them from the consolidated mass. This deposit has been documented in the local media as one of many civil works sites in the city where BHP derived material was used as stabilization fill (NMH, 1948a; NMH, 1948b; NMH, 1949a; NMH, 1949b; NS, 1926; NS, 1948).

2.1.3. Soil polycyclic aromatic hydrocarbon concentrations

Coal, ferrous metal smelting and fossil fuels present significant sources of environmental PAH contamination (Albuquerque et al., 2016; Odabasi et al., 2010; Yang et al., 2016). To further compliment the metal(loid) analysis, a preliminary investigation of soil PAH concentrations was conducted. Soil samples for PAH analysis were collected from 12 locations around the city (Fig. 1d). Soils were collected in clean glass bottles with a Teflon lid and stored at <4 °C until analysis.

2.2. Laboratory analysis

2.2.1. Soil metal(loid) concentrations

Soil samples (n = 170) were oven dried at 40 °C for 72 h, then sieved to <180 μm. This fraction was selected for analysis because the research evidence shows that finer soil fractions are susceptible to resuspension and subsequent ingestion or inhalation (Horowitz, 1991; Youn et al., 2016). Approximately 10 g of the <180 μm sample was packed in 35 mm open ended PANalytical XRF cups using 3.6 μm Chemplex Mylar X ray film for analysis. An Olympus Delta Premium XRF Analyzer (pXRF) fitted with a 50 kV, 4 W Ta anode X ray tube and a silicon drift detector was used for the measurement of Ti, Cr, Mn, Fe, Cu, Zn, As, Cd and Pb concentrations in surface and subsurface soils. Analysis was conducted at Macquarie University. Recommended operational procedures were followed, including: daily measurements of an energy calibration check, measurements of a silicate (SiO_2) blank at the beginning and end of analysis to ensure no instrument contamination had occurred, and measurements of NIST certified reference materials (CRMs) conducted every 25 samples to monitor instrument performance (Table 1). Soil samples and CRMs were placed on the measurement window and analyzed using the proprietary soil mode at 60 s per measurement condition (180 s total measurement). A matrix matched calibration was applied to optimize the pXRF in the measurement of metal contaminated silicate based soils (Rouillon and Taylor, 2016).

Instrument detection limits, analytical precision, sample homogeneity and recoveries of each element are presented in Table 1. Analytical precision was determined by the relative standard deviation (RSD) of

Table 1
Summary of the limits of detection, analytical precision, sample homogeneity and recoveries for pXRF.

	Ti	Cr	Mn	Fe	Cu	Zn	As	Cd	Pb
pXRF									
Limit of detection	[c]	8	9	[c]	4	5	3	2	3
Analytical precision[a] (%)	<1	3	<1	<1	2	<1	7	9	2
Analytical precision[b] (%)	<1	1	<1	<1	1	<1	7	12	<1
Sample homogeneity (%)	2	5	1	<1	2	<1	7	10	1
Mean CRM recovery (%)	101	102	102	100	108	99	106	103	99

[a] Relative standard deviation of reference material suite.
[b] Relative standard deviation of soil samples.
[c] Limits of reporting were not calculated for Ti and Fe as no CRM values between 3 and 10 times the expected manufacturer detection limit were present in the CRM suite.

samples (n = 18) analyzed in triplicate (Table 1), while soil (n = 7) homogeneity (RSD) was measured by triplicate preparation and analysis.

2.2.2. In vitro Pb bio accessibility

Spatially diverse soil samples with a range of total Pb concentrations (n = 12) were digested using the US EPA (2012) method for in vitro Pb bio accessibility on the <180 μm soil fraction (Horowitz, 1991; Youn et al., 2016). Soil (~1 g) was digested in 100 ml 0.4 M glycine in de ionized water adjusted to pH 1.5 using hydrochloric acid (HCl, Reagent Grade, Sigma Aldrich) and analyzed for total Pb on the National Measurement Institute's (North Ryde, Sydney) Agilent 7900 ICP MS, with a limit of detection (LOR) of 0.5 mg/kg. All blanks were <0.5 mg/kg and laboratory control spikes were between 90 and 130%. Relative percent difference for replicate analysis (n = 2) was <20%. Sample duplicate analysis (n = 1) had an RSD < 20%.

2.2.3. Soil Pb isotopic compositions

To understand potential sources of soil metal contaminants, Pb isotopic compositions were determined for soils with a range of concentrations and locations, slag samples and reference ore specimens (Broken Hill and Wallaroo mine galena) (n = 18). Broken Hill galena was used as an end member due to its prolific use in commercial and industrial commodities (Gulson et al., 2004). Wallaroo galena was used as a reference specimen as the copper ore processed at the Wallaroo Copper Company smelter was often co associated with galena deposits as impurities in the host orebody. Samples were extracted using an aqua regia (HNO_3/HCl) digestion to mobilize the labile Pb bound to the soil matrix (Ayuso et al., 2013; Civitillo et al., 2016; Das et al., 2016; Gallego et al., 2016). Following digestion, the samples was centrifuged and the supernatant filtered using a 0.45 μm Minisart syringe filter. Soils were analyzed on an Agilent 7900 ICP MS at the National Measurement Institute following the method and instrument conditions detailed previously in Kristensen and Taylor (2016). Measurement values were collected for ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb and then corrected for variation based on blank values and the effect of ^{202}Hg on ^{204}Pb. Samples were bracketed during analysis with NIST 981 SRM (certified values: ^{206}Pb/^{204}Pb: 16.94, ^{206}Pb/^{207}Pb: 1.09, ^{208}Pb/^{207}Pb: 2.37). This method for Pb isotope ratio quantification reports ^{204}Pb/^{206}Pb: 0.0590 ± 0.0005, ^{207}Pb/^{206}Pb: 0.915 ± 0.004 and ^{208}Pb/^{206}Pb: 2.168 ± 0.009 as a maximum uncertainty for NIST 981 (Kristensen et al., 2016).

2.2.4. Soil mineralogy

To explore the mineralogy of contaminants in public and private soils (n = 9), heavy mineral separation was conducted on the <180 μm sieved fraction for soils from a range of metal(loid) concentrations and locations around the city, following established methods (Ettler et al., 2016).

The phase composition of the samples (n = 9) was assessed by X ray powder diffraction analysis (XRPD) using a PANalytical X'Pert Pro diffractometer with an X'Celerator detector (PANalytical, the Netherlands) (analytical conditions: CuKα radiation at 40 kV and 30 mA, 2theta range 2 80°, step 0.02°, counting time 150 s per step). The XRPD pattern was analyzed using X'Pert HighScore Plus 3.0 software coupled to the Crystallography Open Database (COD) (Gražulis et al., 2012). Relative abundances of phases were estimated from XRPD patterns using the relative intensity ratio (RIR) method.

Heavy mineral fractions, prepared as polished sections, were examined under a Leica DM LP polarizing microscope (Leica, Germany) followed by an automated scanning electron microscope (TIMA 3LM, TESCAN Integrated Mineral Analyzer, Czech Republic) operating at 25 keV using a 'dot mapping' mode method (dot spacing of 2 μm). The integrated images were then used to identify metal(loid) bearing particles and their distribution.

Particles, from two representative samples from private land with the highest metal(loid) content, were examined using a scanning electron microscope (SEM; TESCAN VEGA3 XM, Czech Republic operating at 20 kV) equipped with an energy dispersion spectrometer (EDS; Quantax 200 X Flash 5010, Bruker, Germany).

2.2.5. Soil polycyclic aromatic hydrocarbon concentrations

Approximately 1 g of the <180 μm fraction was mixed with anhydrous sodium sulfate (Na_2O_4S, Reagent Grade, Sigma Aldrich). The sample was then extracted in 1:1 dichloromethane (CH_2Cl_2, Reagent Grade, Sigma Aldrich) and acetone (C_3H_6O, Reagent Grade, Sigma Aldrich) and then concentrated prior to analysis on an Agilent 5975 gas chromatography mass selective detector (GC MSD) at the National Measurement Institute, North Ryde. The instrument was operated in selected ion monitoring mode for 15 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(*a*)anthracene, chrysene, benzo(*b*)&(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3 *cd*)pyrene, dibenzo(*a*,*h*)anthracene and benzo(*g*,*h*,*i*)perylene). All PAHs have a LOR of 0.5 mg/kg except for

Table 2
Newcastle city (Australia) soil element concentrations (mg/kg) (pXRF derived) for public spaces in addition to median soil element concentrations for each sampling zone. Complete dataset is presented in Supplementary data 2.

	Ti	Cr	Mn	Fe[a]	Cu	Zn	As	Cd	Pb
Private spaces									
n detected	67	67	67	67	67	67	67	11	67
Minimum	2520	54	120	1.31	44	140	8	3	42
25th percentile	4090	96	600	2.38	130	740	21	4	570
Median	5180	128	790	3.36	180	1190	35	5	1140
75th percentile	6210	179	1240	4.50	300	2070	63	6	1770
Maximum	12,200	2400	3600	16.0	1040	8570	283	9	1.16[a]
Mean	5160	190	1020	4.00	252	1690	56	5	1630
NEPM (2013) HIL-A	No value	100 (VI)	3000	No value	7000	8000	100	20	300
n > guideline	–	[b]	2	–	0	1	8	0	59
% > guideline	–	[b]	4%	–	0	2%	12%	0	88%
Public spaces									
n detected	103	100	100	103	103	103	103	13	103
Minimum	1670	38	180	1.36	34	96	5	3	14
25th percentile	3870	76	600	2.43	70	270	12	4	120
Median	4660	92	920	3.00	110	550	22	6	280
75th percentile	5390	140	1540	4.11	240	1230	44	11	617
Maximum	14,760	710	4490	17.1	1170	1.2[a]	380	16	4650
Mean	4850	120	1230	3.67	180	1120	37	7	550
NEPM (2013) HIL-A	No value	100 (VI)	3000	No value	7000	8000	100	20	300
n > guideline	–	[b]	8	–	0	2	5	0	45
% > guideline	–	[b]	8%	–	0%	2%	5%	0%	44%
Median per zone (public spaces)									
Zone 1 (n = 29)	4650	140	1450	3.99%	170	980	34	6	500
Zone 2 (n = 19)	5130	140	1810	4.34%	330	1860	44	6	900
Zone 3 (n = 10)	4490	85	750	2.75%	100	340	12	<LOD	170
Zone 4 (n = 25)	5120	92	670	2.65%	74	270	15	3	130
Zone 5 (n = 20)	4240	77	730	2.56%	78	410	16	<LOD	230

– Cannot be calculated due to the absence of a NEPM (2013) HIL.
[a] Concertation presented as wt%.
[b] Indicates that the soil NEPM (2013) HIL is based on element species rather than total concentration, this analysis was not conducted in this study and cannot be calculated. LOD indicates analytical limit of detection.

Table 3
Soil toxicity equivalence factor (TEF) transformed PAH concentrations for Newcastle city (Australia) surface soil samples.

Sample	x co-ordinate	y co-ordinate	TEF PAH 1	TEF PAH 2	TEF PAH 3	TEF PAH 4	TEF PAH 5	TEF PAH 6	TEF PAH 7	∑ TEF PAH
Zone 5 S1	151.765942	-32.935172	0.08	0.0068	0.14	1.0	0.0061	***	0.0076	1.2
Zone 5 S4	151.751481	-32.936583	0.35	0.035	0.69	5.2	0.029	0.57	0.034	**6.9**
Zone 5 S5	151.755347	-32.931136	0.15	0.015	0.31	2.2	0.014	***	0.016	2.7
Zone 2 S1	151.765858	-32.91974	0.24	0.021	0.45	3.3	0.02	***	0.024	**4.1**
Zone 2 S2	151.765405	-32.914048	0.20	0.020	0.42	2.7	0.019	***	0.022	**3.4**
Zone 2 S2**	151.765405	-32.914048	0.23	0.022	0.45	3.2	0.020	***	0.024	**3.9**
Zone 2 S3	151.764169	-32.909803	0.061	0.006	0.15	0.96	0.0072	***	0.0089	1.2
Zone 2 S4	151.766314	-32.910977	0.40	0.038	0.73	5.4	0.031	0.70	0.035	**7.3**
Zone 1 S5	151.746816	-32.900268	0.20	0.020	0.44	2.9	0.020	***	0.025	**3.6**
Zone 1 S2	151.750378	-32.914897	0.18	0.020	0.43	2.8	0.018	***	0.020	**3.5**
Zone 1 S4	151.752958	-32.910561	0.17	0.018	0.37	2.7	0.016	***	0.020	**3.3**
Zone 1 S7	151.734307	-32.891691	0.73	0.075	1.4	9.8	0.061	1.4	0.076	**13.5**

TEF PAH: 1 - Benz(*a*)anthracene, 2 – Chrysene, 3 - Benzo(*b*)&(*k*)fluoranthene, 4 - Benzo(*a*)pyrene, 5 - Indeno(1,2,3-*cd*)pyrene, 6 - Dibenzo(*a*,*h*)anthracene, 7 - Benzo(*g*,*h*,*i*)perylene.
All concentrations in mg/kg.
Concentrations in bold exceed the NEPM (2013) HIL for TEF transformed PAH (3 mg/kg).
Cells denoted with *** cannot be calculated as the non-transformed data was <LOR.
Sample marked with ** is a field duplicate.

benzo(*b*)&(*k*)fluoranthene which has an LOR of 1 mg/kg. Laboratory blanks contained <LOR for each analyte and laboratory control spikes were 94 130% for all analytes.

2.3. Data analysis

Inorganic elemental concentrations were benchmarked against Australian Health Investigation Levels for residential soils (HIL A) (NEPM, 2013, Table 2). The NEPM (2013) identifies eight carcino genic PAHs categories (reported here as seven PAHs categories as benzo(*b*)&(*k*)fluoranthene were not separated in the analysis method): benz(*a*)anthracene, chrysene, benzo(*b*)&(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3 *cd*)pyrene, dibenzo(*a*,*h*)anthracene and benzo(*g*,*h*,*i*)perylene). The toxicity of these eight PAHs are weighted using a toxicity equivalence factor (TEF) relative to the most toxic PAH benzo(*a*)pyrene, the HIL for the sum of these weighted PAHs is 3 mg/kg (Table 3).

3. Results and discussion

3.1. Soil metal(loid) concentrations

Newcastle was divided into five soil sampling zones to characterize different land uses across the city (Fig. 1). Within these zones, public and private space surface soils were analyzed. A summary of surface soil metal(loid) concentrations is presented in Fig. 1 and Table 2, with the complete data set provided in Supplementary data.

Public space surface soils The greatest concentrations of Fe, Pb and Zn were detected in the Zone 1 and Zone 2 sampling areas (Fig. 1, Table 2). Soil Fe concentrations were >17 wt% in soils of the Zone 2 sam pling area (Fig. 1, Table 2). Soil Pb concentrations were detected at a maximum of 4650 mg/kg (median: 280 mg/kg, n = 103) with the greatest median Pb concentrations in Zone 2 (median: 900 mg/kg, n = 19) followed by Zone 1 (median: 500 mg/kg, n = 29). Zinc concen trations were detected at a maximum of 1.2 wt% in Zone 1 (Fig. 1). The Zone 2 sampling area had the greatest median concentration of soil Zn (1860 mg/kg) (Fig. 1, Table 2). All elements of interest (Table 2), except Ti, had the highest median concentration in Zones 1 and 2. Titanium (n = 103; median: 4830 mg/kg; max: 14,760 mg/kg) is predominantly a geogenic element and had no clear spatial concentration pattern, however, concentration spikes were detected across the city.

Private (residential) space surface soils Surface soil samples collect ed from private gardens were markedly more contaminated than those in public spaces (Table 2). Soil Fe was detected with a maximum of 16 wt% in Zone 1 with a median across all sample zones of 3.36 wt% (n = 67). Soil Pb was detected up to a maximum concentration of 1.16 wt% (Zone 1, Fig. 1) (median: 1140 mg/kg, n = 67). The maximum Zn concentration detected (8570 mg/kg) was in Zone 1 (Fig. 1; Table 2). Private soils contained a median Zn concentration of 1190 mg/kg. Over 90% of homes exceeded the 300 mg/kg Australian soil Pb HIL A (NEPM, 2013), with As, Mn and Zn exceeding their respective HIL A values at 30%, 9% and 4% of homes (Table 2). Soil samples were not collected from private spaces in Zone 3 and 4 where high density housing and ground surface cover limited access to soil.

Soil metal(loid) concentrations from depth profiles in Newcastle are presented in Fig. 2 and in Supplementary data 1. Subsurface soils col lected from depth profiles within the urban areas (profiles a d, Fig. 1) showed that metal(loid) concentrations did not necessarily decrease with depth (Fig. 2, panels a d). Soil metal(loid) concentrations remain at ~100 mg/kg for Mn, Pb and Zn at 30 cm in depth profile a, while all other depth profiles (b c, Fig. 2) have concentrations > 100 mg/kg for all metal(loid)s. Soil depth profile b had Pb concentrations > HIL A of 300 mg/kg (NEPM, 2013); until >10 cm depth. Soil depth profile c showed an increase in soil metal(loid) concentration to depth, with Mn concentrations (1430 mg/kg) at 30 cm depth double surface values (700 mg/kg) (Fig. 2). Soil Pb concentrations in profile 3 also remained above the HIL A (300 mg/kg; NEPM, 2013) at 30 cm depth. Other met al(loid)s not presented in Fig. 2, but reported in Supplementary data 1, show that concentrations also increase with depth (e.g. Fe: 2.29 wt% at surface; 3.79 wt% at 30 cm depth) implying that profile c likely occupies a brownfield site now repurposed as a parkland. By contrast two addi tional soil depth profiles from remnant bushland (Figs. 1 and 2, e f) showed a clear decrease in metal(loid) concentrations with depth. These data are comparable to uncontaminated soil concentrations at depth from similar studies of industrial cities (e.g. Rouillon et al., 2013, Mn: ~100 mg/kg; Pb: <5 mg/kg; Zn: ~30 mg/kg). The data show that surface soil metal(loid)s from Newcastle have been enriched significantly by anthropogenic sources.

3.2. Potential source(s) of inorganic soil contaminants

It is well documented that Cu smelter waste, and more recently, steel smelter waste was used prolifically around the Newcastle city area as landfill and stabilization material (NMH, 1948a; NMH, 1948b; NMH, 1949b; NS, 1926; NMH, 1925; SA, 1951; SMH, 1948; The Australasian, 1905; TNC, 1950). Much of this material may have contained Broken Hill Pb ore due to the movement of this ore through the Newcastle Ports from BHP to the Sulphide Company smelter (later the Pasminco Cockle Creek Smelter) at Boolaroo (Petersburg Times, 1901; PPR, 1904; Quorn Mercury, 1900). The Sulphide Company also contributed large volumes of smelter waste for capital works (Gulson et al., 2004; Morrison, 2003; Morrison and Gulson, 2007; Morrison et al., 2016).

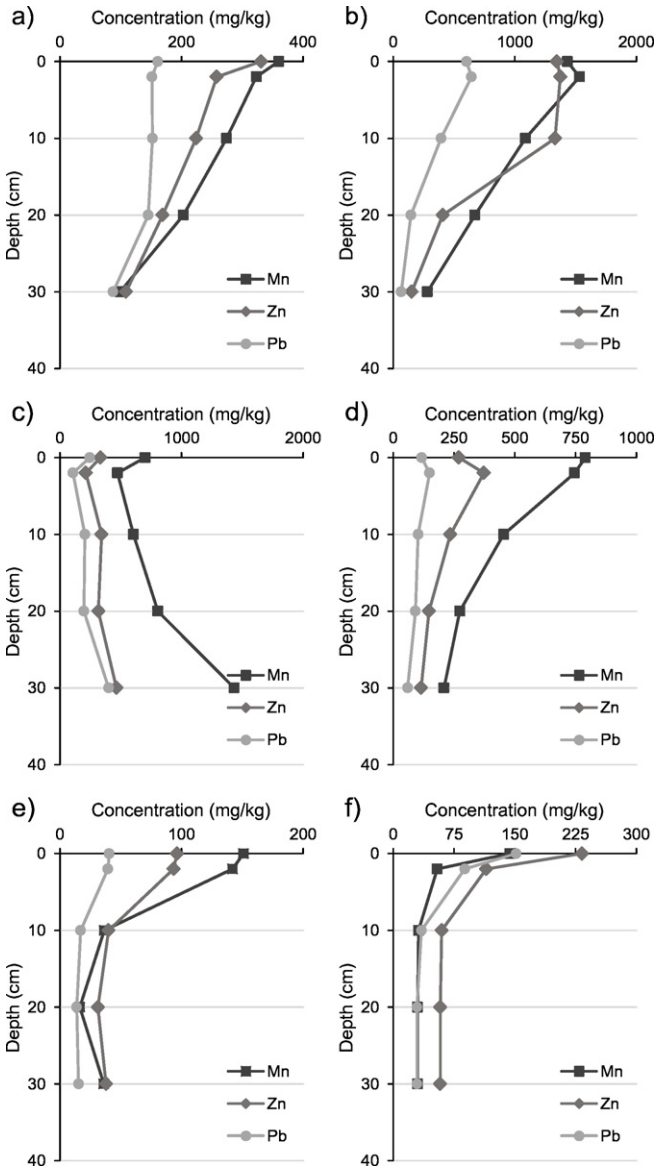


Fig. 2. Soil depth profiles from urban areas (a–d) and remnant bushland (e–f) in Newcastle city (Australia) displaying Mn, Pb and Zn soil concentrations. Complete data and site locations are provided in Supplementary data 1.

This study's bulk mineralogical investigation of soils showed that high temperature silicates (clinopyroxenes, olivines and glass) typically originating from smelting industry, as well as smelter derived oxides (spinels) were present in the majority of the samples (Supplementary data 4). All the samples contained geogenic/pedogenic heavy minerals such as zircon, Ti , Fe and Al bearing oxides in addition to traces of quartz and other geogenic minerals. No metal(loid) bearing phases were detected by XRPD indicating that contaminants are bound in trace phases in the soil materials (Supplementary data 4).

Fe and Mn oxides were the most common metal bearing phases in soils, with Fe oxides containing high Pb levels (up to 27.3 wt% PbO) (Fig. 3b, c, e, f). The occurrence of smelter derived slag like particles, possibly windblown from slag dumps (Fig. 3a, c, e, f, i) and rounded par ticles characteristic of quenched melt droplets from the smelter emis sions (Fig. 3b) implies they are derived from smelting emissions. Metal bearing droplets in slag particles corresponded to Cu sulfides; slag silicates and glass also containing Cu and Zn are characteristic of Cu smelting waste materials (Ettler et al., 2009; Ettler et al., 2016). By contrast, mine derived sulfides (commonly identified with weathering rims) were relatively rare in the studied soils (Fig. 3d). Lead phosphates (Fig. 3f, h, i), arsenates (Fig. 3f) and sulfates (Fig. 3h) were common. Some of these form solid solutions (mimetite pyromorphite; Fig. 3h) or are associated to similar phases (anglesite barite) (Fig. 3h). Given that these phases are relatively insoluble, the Pb release from these compounds in aqueous environments would be minimal. Rare particles of Sn oxides were also observed (Fig. 3f) with weathering rims enriched in metal(loids) including Pb, Sb and Zn. Interestingly, metals (mainly Pb and Zn) were bound in Fe and Mn oxides formed as weathering products on particles (e.g. Fig. 3b, c), indicating contaminants can be absorbed from surrounding soil during the formation of secondary Fe Mn oxides.

Lead isotopic compositions were used in this study to delineate po tential contaminant sources. The Pb isotopic compositions of soils and reference samples (galena and slag) are presented in Fig. 4 and Supple mentary data 3. Surface soils from public and private spaces (n = 8) have similar loosely clustered Pb isotopic compositions (range: $^{208}Pb/^{207}Pb$: 2.345 2.411, $^{206}Pb/^{207}Pb$: 1.068 1.312). Lead isotopic compositions of soils collected from depth profiles (n = 3) within the urban area (profiles b, c, d; Fig. 1) fall within the range of Pb isotopic compositions of surface soils in public and private spaces (range: $^{208}Pb/^{207}Pb$: 2.370 2.406, $^{206}Pb/^{207}Pb$: 1.093 1.234). Lead isotopic compositions from soil collected from the depth profile in the remnant bushland (profile e; Fig. 1; n = 1) are more radiogenic and outside of the range of urban surface soils ($^{208}Pb/^{207}Pb$: 2.489, $^{206}Pb/^{207}Pb$: 1.198) (Fig. 4, Supplementary data 3). Lead isotopic compositions for the two slag samples reveal divergent Pb isotopic compositions. A black glassy material similar to non ferrous smelter slag as identified in other studies (Morrison and Gulson, 2007; Piatak et al., 2015) was less radiogenic than surface soils ($^{208}Pb/^{207}Pb$: 2.319, $^{206}Pb/^{207}Pb$: 1.044) (Fig. 4, Supplementary data 3). A second slag deposit that was more similar to ferrous smelter slag as identified in other studies (Piatak et al., 2015) contained more radiogenic Pb than surface and depth profile soils ($^{208}Pb/^{207}Pb$: 2.543, $^{206}Pb/^{207}Pb$: 1.318) (Fig. 4, Sup plementary data 3). The Wallaroo Mine copper ore that was smelted at the site prior to Newcastle BHP was co associated with galena Pb ore ($^{208}Pb/^{207}Pb$: 2.640, $^{206}Pb/^{207}Pb$: 1.477), which has more radiogenic Pb isotopic compositions compared to bushland depth profile soil ($^{208}Pb/^{207}Pb$: 2.489, $^{206}Pb/^{207}Pb$: 1.198) and slag (Fig. 4, Supplementary data 3). Consequently, we used Wallaroo galena Pb isotopic composi tions as an end member for source apportionment analysis. Although the Pb bearing Cu ore associated with the Wallaroo Mine was smelted in large volumes during the early industrial era of Newcastle it appears to have had little influence on soil Pb isotopic compositions (Fig. 4, Sup plementary data 3). The other Pb isotopic composition end member used is the less radiogenic Broken Hill ore ($^{208}Pb/^{207}Pb$: 2.319, $^{206}Pb/^{207}Pb$: 1.044) (Fig. 4, Supplementary data 3).

The Pb isotopic compositions (Fig. 4, Supplementary data 3) showed an enrichment of public and private space soils (Fig. 4) by the distinct Broken Hill Pb isotope signature ($^{208}Pb/^{207}Pb$: 2.319, $^{206}Pb/^{207}Pb$: 1.044). Enrichment of public and private soils less radiogenic Pb sources suggests an introduction of Broken Hill type ore bearing material (e.g. black glassy slag waste and fill material) into the Newcastle city envi ronment. Leaded petrol and paint are also potential contributors to Pb in the surface soils of the urban environment (Datko Williams et al., 2014; Kristensen, 2015; Laidlaw et al., 2012; Mielke et al., 1983; Mielke and Reagan, 1998; Mitchell et al., 2014; Zahran et al., 2013). The Pb isotopic ratios of the soils derived from ICP MS do not allow dis crimination between these tightly clustered sources (Fig. 4). However, despite this limitation, the data show clearly that Pb sources match closely the Broken Hill ore signature in urban soils.

3.3. Soil polycyclic aromatic hydrocarbon concentrations

Soil PAH concentrations are presented in Fig. 1 and Supplementary data 2. Soil samples (n = 12) contained 12 of the 15 target PAH

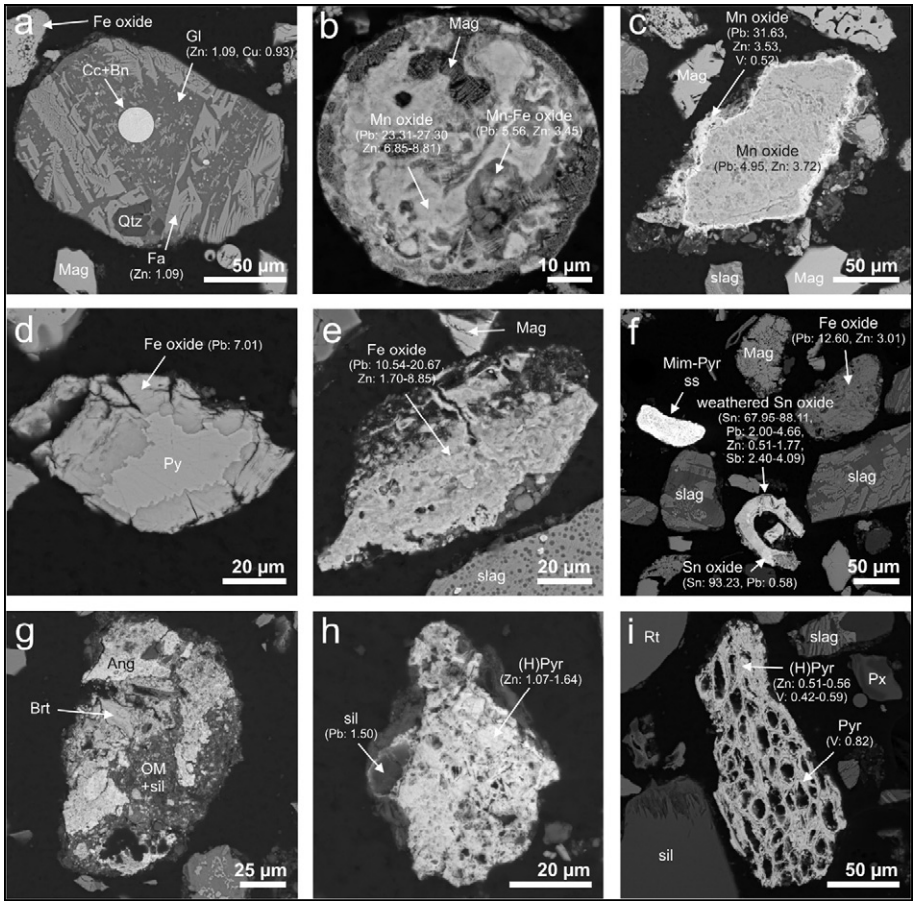


Fig. 3. Scanning electron micrographs in back-scattered electrons (BSE) of representative metal(loid)-bearing particles from two samples (PRS3D and PRS4C) from Newcastle city soils (Australia). Complete data available in Supplementary data 4. a) Smelter slag particle composed of Fe-olivine (fayalite), metal-bearing glass and symplectitic inclusions of chalcocite and bornite (PRS3D); b) Slag-like particle originating probably from smelter dust emissions composed of magnetite sub-micrometric dendrites and newly-formed Mn- and Mn-Fe oxides resulting from alteration process in soil (PRS4C); c) Mn oxide particle particularly rich in metals associated with slag particles and magnetite grains (PRS3D); d) Weathered pyrite grain with Fe-oxide rim (PRS3D); e) Metal-bearing Fe oxide associated with slag and magnetite particles (PRS3D); f) Mimetite-pyromorphite solid solution (ss) associated to weathered Sn-oxide and Fe-oxides particles, slag and magnetite grains (PRS3D); g) Complex intergrowth of barite and anglesite with organic matter and unidentified silicate material (PRS3D); h) (hydroxyl)pyromorphite grain associate with unidentified Pb-bearing silicate (probably slag glass) (PRS3D); i) Sponge-like particle composed of hydroxylpyromorphite and pyromorphite associated to rutile and smelter-derived silicates (slag) (PRS4C). The metal(loid) concentrations obtained by EDS are expressed in wt% of oxides. Abbreviations: Ang – anglesite ($PbSO_4$), Bn – bornite (Cu_5FeS_4), Brt – barite ($BaSO_4$), Cc – chalcocite (Cu_2S), Fa – fayalite (Fe_2SiO_4), Gl – glass (slag), (H)Pyr – hydroxypyromorphite ($Pb_5(PO_4)_3OH$), Mag – magnetite (Fe_3O_4), Mim - mimetite ($Pb_5(AsO_4)_3Cl$), OM – organic matter; Px – pyroxene ($(Ca,Fe,Mg)_2Si_2O_6$), Py – pyrite (FeS_2), Pyr – pyromorphite ($Pb_5(PO_4)_3Cl$), Qtz – quartz (SiO_2), Sil – unidentified silicate; Rt – rutile (TiO_2).

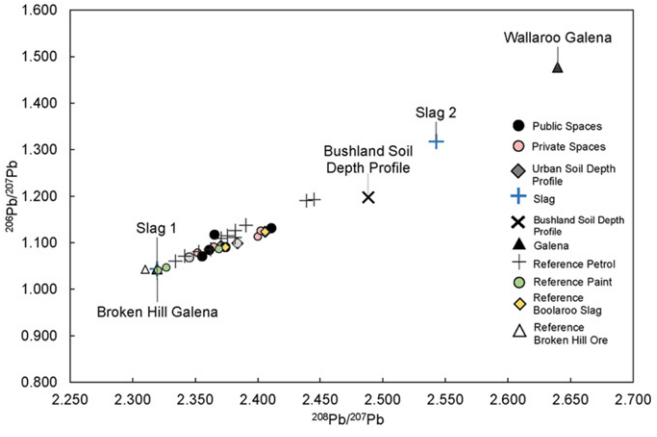


Fig. 4. Lead isotopic compositions of Newcastle city (Australia) soils and slag and galena from Broken Hill and Wallaroo Mines analyzed in this study. Standard deviation from repeat analysis (10 analyses) of one sample: $^{208}Pb/^{207}Pb$: 0.004, $^{206}Pb/^{207}Pb$: 0.004. Comparison is made to reference Pb isotopic compositions from the nearby Sulphide Corporation's Boolaroo smelter slag (Gulson et al., 2004), Broken Hill ore galena (Gulson, 1984), petrol and paint values (Gulson et al., 1982; Laidlaw et al., 2014).

compounds (Supplementary data 2). The carcinogenic compound benzo(*a*)pyrene was detected in all samples with the maximum concentration in Zone 1 (9.8 mg/kg; Fig. 1). Nine samples exceeded the Australian HIL A guideline (3 mg/kg) for benzo(*a*)pyrene TEF transformed PAHs (Table 3, Fig. 1, max 13.5 mg/kg). The maximum TEF transformed PAH concentration (13.5 mg/kg) was detected in Zone 1 sampling area.

3.4. Potential health impacts of soil contamination

Soils in Newcastle are contaminated by a range of metal(loid)s and PAHs. While there is strong evidence to link the soil metal(loid) concentrations to the legacy industrial activities of the city, the source of PAHs in Newcastle is unclear. Steel manufacturing (Khaparde et al., 2016; Song et al., 2015; Yang et al., 2002), coal transport (Huang et al., 2013; Wang et al., 2016), and incomplete combustion of motor vehicle emissions (Jedrychowski et al., 2015; Perer et al., 2006) are known to contribute PAHs to the soil environment. Regardless of the source, recent studies have demonstrated a link between prenatal and early life exposure to PAHs (Huang et al., 2013) and a range of cancers (Lemieux et al., 2015; Mordukhovich et al., 2016; Perer et al., 2006; Zhang et al., 2016).

Exposure to PAHs in the Newcastle soil environment, combined with the metal(loid) contaminants is likely to generate a significant burden of disease.

Blood Pb (and other metals) analysis of the Newcastle population would be one determinant of exposure to contaminated soils in Newcastle. Unfortunately, no such data exists. Given the paucity of blood Pb (and other metals) data, surrogate indicators are used here to predict the potential health impacts of Pb contaminated soils in the city. Our in vitro bio accessibility analysis (n = 11) shows that the Pb found in soils would be subject to absorption following ingestion of soils from the study area (Table 4). This is not surprising given that the Pb bearing Fe and Mn oxides identified in Fig. 3b and c are known to be susceptible to dissolution under acidic conditions. Moreover, the in vitro bio accessible Pb concentrations indicate a potential burden of disease associated with Newcastle's soil Pb concentrations, which could be better quantified with a childhood blood Pb survey in Newcastle city linked to participant's home soil and dust metal analysis.

3.5. Managing environmental contaminants in Newcastle city

Some information is available to landowners about the potential risk of environmental contamination in Newcastle, but it is not extensive and it is often site specific. In addition to sites being listed on the NSW Environment Protection Authority's (NSW EPA) list of notified contaminated sites (NSW EPA, 2016) some properties in Carrington have a certificate issued under section 149 of the *Environmental Planning and Assessment Act 1979* (NSW) advising purchasers:

> Land history information indicates that the subject land may be within an area which was once low lying and may have been filled. Limited investigation indicates that the filling material may contain ballast and industrial slag which contains some heavy metals including lead. The Council does not hold information which allows it to say whether or not the subject land contains such filling material and purchasers should make their own enquiries in this respect. If the land does contain such filling material this should be taken into account in the use and the development of the property. Soil sampling and remediation may be required for the further development of the land.
>
> [Newcastle City Council (NCC) (1997)]

To address the absence of site specific contamination information, soil metal screening programs such as VegeSafe (Rouillon et al., 2016) could be employed across the city to help inform homeowners of extant soil metal(loid) contamination on their property and the potential associated risks. Such information can be used by homeowners to initiate mitigation strategies, including: engagement of professional trained contractors to remediate soils where appropriate; using raised garden beds for food growing; removing and replacing soils in areas regularly visited by children and pets.

3.6. Industry, smelting and development in global urban cities environmental implications

This study demonstrates the extensive environmental contamination legacy that can be created by a long history of manufacturing, processing and smelting along with inappropriate waste disposal in urban environments. In 2011, it was estimated that around 30% of the global feedstock for ferrous ore processing was discarded generating ~550 million tons of waste slag (Van Oss, 2011). The waste material produced from manufacturing industries, typically rich in a range of environmental contaminants, is often discarded haphazardly in the environment, leading to problematic brownfield sites, requiring costly environmental clean up (Gallego et al., 2016).

4. Conclusions

This study details a significant potential health risk associated with environmental metal(loid) and PAH contamination of soils in the industrial city of Newcastle, Australia. Surface soils collected from public (roadside verges and parks) and private (homes) spaces (n = 170) show that a range of metal(loid)s are present in the soils above their relevant Australian Health Investigation Level (HIL) concentrations. Lead was the most common contaminant detected in the city soils with a median concentration of 1140 mg/kg in private space soils. Deep soil metal(loid) concentrations across the city were also elevated indicating contamination was laterally and vertically pervasive. In vitro bio accessibility analysis of Pb in soils (maximum Pb concentration: 5190 mg/kg; 45% Pb bio accessibility) revealed these were readily available to the gastric system. Soil Pb isotopic compositions (range: $^{208}Pb/^{207}Pb$: 2.345 2.411, $^{206}Pb/^{207}Pb$: 1.068 1.312) show that the anthropogenic contamination was sourced from a low radiogenic source, with a Broken Hill type Pb orebody ($^{208}Pb/^{207}Pb$: 2.319, $^{206}Pb/^{207}Pb$: 1.044) being the most likely origin. Examination of soil mineralogy, particularly the rounded quenched droplet particles extracted during heavy mineral separation (Fig. 3), indicates that Pb and soil metal(loid) contaminants are derived predominantly from smelter emissions and industrial waste slag. An additional burden of contamination in the city soils comes from elevated levels of PAH compounds, typically associated with coal, ferrous metal smelting and fossil fuels, with 75% of samples (n = 12) analyzed exceeding the Australian HIL A guideline for benzo(*a*)pyrene TEF transformed PAHs.

Source assessment of the environmental contamination indicates that historic and legacy Cu and steel smelting industries in the city have contributed substantially to the contamination of soils. This study highlights the health risks faced by communities residing in industrial locations and demonstrates the 'need to know' so that individuals can protect themselves from unnecessary and potentially toxic exposures.

Table 4
In-vitro bio-accessible soil Pb concentrations.

Sample	In-vitro bio-accessible Pb (mg/kg)	Total Pb (mg/kg)	% bio-accessible[a]
PRS10B	5000	7640	65
PRS7A	732	2830	26
PRS3D	1670	3420	49
Zone 1 S7	1730	1550	112
Zone 2 S17	1410	2770	51
PRS8C	282	1060	27
Zone 1 S20	972	2060	47
Zone 1 S9	607	4650	13
PRS4C	5190	11,570	45
Zone 2 S4	1350	2550	53
Zone 2 S4[b]	1340	2550	52
NIST2586 (500 mg/kg)	156		31
BLK	<0.5		-
CAL-24 (10 ppm)	10		-

NIST2586 is a Pb paint contaminated soil used to assess the extraction efficiency of the in-vitro bio-accessibility method.
BLK = analysis blank.
CAL-24 = 10 ppm 12-element standard reference material used during IPC-MS analysis.
- not applicable.
[a] Calculated from pXRF total.
[b] Denotes field duplicate sample.

Acknowledgements

P.J. Harvey is funded by a Macquarie University Research Excellence Scholarship (MQRES) (2012195) associated with an Australian Research Council Future Fellowship awarded to H.K. Handley

(FT120100440). M. Rouillon is funded by an Australian Postgraduate Award. C. Dong is funded by a Macquarie University Research Excellence Scholarship (iMQRES No. 2014098). Support from the Czech Science Foundation (project no. 13 17501S) is greatly acknowledged. Ernest Ameyaw is thanked for fieldwork and laboratory assistance. The authors thank Tony Morrison and Brian Gulson (Macquarie University) for comments on data interpretation. We would like to thank our colleagues from Charles University and the Geological Institute of the Czech Academy of Science, who helped with the data acquisition and treatment: Petr Drahota (XRPD), Tomáš Hrstka (TIMA) and Zuzana Korbelová (SEM/EDS).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.01.053.

References

Albuquerque, M., Coutinho, M., Borrego, C., 2016. Long-term monitoring and seasonal analysis of polycyclic aromatic hyrdocarbons (PAHs) measured over a decade in the ambient air of Porto, Portugal. Sci. Total Environ. 543, 439–448.

Ayuso, R.A., Foley, N.K., Seal II, R.R., Bove, M., Civitillo, D., Cosenza, A., Grezzi, G., 2013. Lead isotope evidence for metal dispersal at the Callahan Cu–Zn–Pb mine: Goose Pond tidal estuary, Maine, USA. J. Geochem. Explor. 126, 1–22.

BHP Co. LTD, 1949. Progress: Outlining the Main Factors in the Establishment and Growth of the Newcastle Steel Works, and Giving Details of the Operations Required in Iron and Steel Manufacture. The Broken Hill Co. LTD, Melbourne.

Canfield, R.L., Henderson, C.R., Cory-Slechta, D.A., Cox, C., Jusko, T.A., Lanphear, B.P., 2003. Intellectual impairment in children with blood lead concentrations below 10 μg per deciliter. N. Engl. J. Med. 348, 1517–1526.

Chen, H., Teng, Y., Lu, S., Wang, Y., Wang, J., 2015. Contamination features and health risk of soil heavy metals in China. Sci. Total Environ. 512, 143–153.

Civitillo, D., Ayuso, R.A., Lima, A., Albanese, S., Esposito, R., Cannatelli, C., De Vivo, B., 2016. Potentially harmful elements and lead isotopes distribution in a heavily anthropized suburban area: the Casoria case study (Italy). Environ. Earth Sci. 75, 1325.

Csavina, J., Field, J., Taylor, M.P., Gao, S., Landázuri, A., Betterton, E.A., Saez, A.E., 2012. A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations. Sci. Total Environ. 433, 58–73.

Dames and Moore, 1994. Review and Summary of Available Data Soil Lead Distribution around Boolaroo Smelter for Pasminco Metals – Sulphide PTY LTD. Dames and Moore.

Das, A., Krishna, K., Kumar, R., Das, A., Sengupta, S., Ghosh, J.G., 2016. Tracing lead contamination in foods in the city of Kolkata, India. Environ. Sci. Pollut. Res. 23, 22454–22466.

Datko-Williams, L., Wilkie, A., Richmond-Bryant, J., 2014. Analysis of U.S. soil lead (Pb) studies from 1970 to 2012. Sci. Total Environ. 468, 854–863.

Dong, C., Taylor, M.P., Kristensen, L.J., Zahran, S., 2015. Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes. Environ. Pollut. 207, 345–356.

Ettler, V., Johan, Z., Kříbek, B., Šebek, O., Mihaljevič, M., 2009. Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. Appl. Geochem. 24, 1–15.

Ettler, V., Johan, Z., Kříbek, B., Veselovský, F., Mihaljevič, M., Vaněk, A., Penížek, V., Majer, V., Sracek, O., Mapani, B., Kamona, F., Nyambe, I., 2016. Composition and fate of mine- and smelter-derived particles in soils of humid subtropical and hot semi-arid areas. Sci. Total Environ. 563, 329–339.

Filippelli, G.M., Risch, M., Laidlaw, M.A., Nichols, D.E., Crewe, J., 2015. Geochemical legacies and the future health of cities: a tale of two neurotoxins in urban soils. Elementa 3, 59.

Gallego, J.R., Rodríguez-Valdés, E., Esquinas, N., Fernández-Braña, A., Afif, E., 2016. Insights into a 20-ha multi-contaminated brownfield megasite: an environmental forensics approach. Sci. Total Environ. 563, 683–692.

Gražulis, S., Daškevič, A., Merkys, A., Chateigner, D., Lutterotti, L., Quirós, M., Serebryanaya, N.R., Moeck, P., Downs, R.T., Le Bail, A., 2012. Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration. Nucleic Acids Res. 40, D420–D427.

Gulson, B.L., 1984. Uranium-lead and lead-lead investigations of minerals from the Broken Hill lodes and mine sequence rocks. Econ. Geol. 79, 476–490.

Gulson, B.L., Mizon, K.J., Korsch, M.J., 1982. Fingerprinting the source of lead in Sydney air using lead isotopes. Publication of Commonwealth Scientific & Indus Res Org, Australia.

Gulson, B.L., Mizon, K.J., Law, A.J., Korsch, M.J., Davis, J.J., Howarth, D., 1994. Source and pathways of lead in humans from the Broken Hill mining community; an alternative use of exploration methods. Econ. Geol. 89, 889–908.

Gulson, B.L., Mizon, K.J., Davis, J.D., Palmer, J.M., Vimpani, G., 2004. Identification of sources of lead in children in a primary zinc-lead smelter environment. Environ. Health Perspect. 112, 52–60.

Gulson, B., Korsch, M., Matisons, M., Douglas, C., Gillam, L., McLaughlin, V., 2009. Wind-blown lead carbonate as the main source of lead in blood of children from a seaside community: an example of local birds as “canaries in the mine”. Environ. Health Perspect. 117, 148–154.

Horowitz, A.J., 1991. A primer on sediment-trace element chemistry. second ed. Lewis, Chelsea, Michigan.

Huang, H.B., Chen, G.W., Wang, C.J., Lin, Y.Y., Liou, S.H., Wang, S.K., 2013. Exposure to heavy metals and polycyclic aromatic hydrocarbons and DNA damage in Taiwanese traffic conductors. Cancer Epidemiol. Biomark. Prev. 22, 102–108.

Jedrychowski, W.A., Perera, F.P., Maugeri, U., Majewska, R., Mroz, E., Flak, E., Camann, D., Sowa, A., Jacek, R., 2015. Long term effects of prenatal and postnatal airborne PAH exposures on ventilatory lung function of non-asthmatic preadolescent children. Prospective birth cohort study in Krakow. Sci. Total Environ. 502, 502–509.

Khaparde, V.V., Bhanarkar, A.D., Majumdar, D., Rao, C.V.C., 2016. Characterization of polycyclic aromatic hydrocarbons in fugitive PM10 emissions from an integrated iron and steel plant. Sci. Total Environ. 562, 155–163.

Kristensen, L.J., 2015. Quantification of atmospheric lead emissions from 70 years of leaded petrol consumption in Australia. Atmos. Environ. 111, 195–201.

Kristensen, L.J., Taylor, M.P., 2016. Unravelling a ‘miner's myth’ that environmental contamination in mining towns is naturally occurring. Environ. Geochem. Health 38, 1015–1027.

Kristensen, L.J., Taylor, M.P., Evans, A.J., 2016. Reply to Gulson's comments on ‘tracing changes in atmospheric sources of lead contamination using lead isotopic compositions in australian red wine’. Chemosphere 165, 579–584.

Laidlaw, M.A.S., Zahran, S., Mielke, H.W., Taylor, M.P., Filippelli, G.M., 2012. Re-suspension of lead contaminated urban soil as a dominant source of atmospheric lead in Birmingham, Chicago, Detroit and Pittsburgh, USA. Atmos. Environ. 49, 302–310.

Laidlaw, M.A.S., Zahran, S., Pingitore, N., Clague, J., Devlin, G., Taylor, M.P., 2014. Identification of lead sources in residential environments: Sydney Australia. Environ. Pollut. 184, 238–246.

Lemieux, C.L., Long, A.S., Lambert, I.B., Lundstedt, S., Tysklind, M., White, P.A., 2015. Cancer risk assessment of polycyclic aromatic hydrocarbon contaminated soils determined using bioassay-derived levels of benzo[a]pyrene equivalents. Environ. Sci. Technol. 49, 1797–1805.

Lougheed, T., 2014. Arising from the ashes? Environmental health in Detroit. Environ. Health Perspect. 122, A324–A331.

MDM, 1907. Our Newcastle Letter. Maitland Daily Mercury Tuesday 23 July 1907. Available at:. http://trove.nla.gov.au/newspaper/article/124428751 (accessed 09 January 2017).

Mielke, H.W., Reagan, P.L., 1998. Soil is an important pathway of human lead exposure. Environ. Health Perspect. 106, 217–229.

Mielke, H.W., Anderson, J.C., Berry, K.J., Mielke, P.W., Chaney, R.L., Leech, M., 1983. Lead concentrations in inner-city soils as a factor in the child lead problem. Am. J. Public Health 73, 1366–1369.

Mitchell, R.G., Spliethoff, H.M., Ribaudo, L.N., Lopp, D.M., Shayler, H.A., Marquez-Bravo, L.G., Lambert, V.T., Ferenz, G.S., Russell-Anelli, J.M., Stone, E.B., McBride, M.B., 2014. Lead (Pb) and other metals in New York City community garden soils: factors influencing contaminant distributions. Environ. Pollut. 187, 162–169.

Mordukhovich, I., Beyea, J., Herring, A.H., Hatch, M., Stellman, S.D., Teitelbaum, S.L., Richardson, D.B., Millikan, R.C., Engel, L.S., Shantakumar, S., Steck, S.E., Neugut, A.I., Rossner, P., Santella, R.M., Gammon, M.D., 2016. Polymorphisms in DNA repair genes, traffic-related polycyclic aromatic hydrocarbon exposure and breast cancer incidence. Int. J. Cancer 139, 310–321.

Morrison, A.L., 2003. An assessment of the effectiveness of lead pollution reduction strategies in North Lake Macquarie, NSW, Australia. Sci. Total Environ. 303, 125–138.

Morrison, A.L., Gulson, B.L., 2007. Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. Sci. Total Environ. 382, 30–42.

Morrison, A.L., Swierczek, Z., Gulson, B.L., 2016. Visualisation and quantification of heavy metal accessibility in smelter slags: the influence of morphology on availability. Environ. Pollut. 210, 271–281.

National Environment Protection Measure (NEPM), 2013. National Environment Protection Measure 1999 Schedule B1. Federal Register of Legislative Instruments, Australia.

Newcastle City Council (NCC), 1997. Information sheet industrial filling used in Carrington. Newcastle City Council. Available at:. http://www.newcastle.nsw.gov.au/getattachment/Business/Regulations/Health-safety/Contaminated-Land/Carrington_contaminated_land.pdf.aspx?lang=en-AU (accessed 09 January 2017).

Newcastle City Council (NCC), 2013. Newcastle 2030: Our Vision for a Smart, Liveable and Sustainable City – Newcastle Community Strategic Plan (Revised 2013). The City of Newcastle. Available at:. http://www.newcastle.nsw.gov.au/Council/Our-Responsibilities/Newcastle-2030-Vision-Strategic-Plan (accessed 09 January 2017).

Newcastle City Council (NCC), 2015. Local Planning Strategy - Background Report. The City of Newcastle. Available at:. http://www.newcastle.nsw.gov.au/Newcastle/media/Documents/Strategies,%20Plans%20and%20Policies/Strategies/Local-Planning-Strategy-Background-Report-2015.pdf (accessed 09 January 2017).

NMH, 1902. Sulphide Corporation a Prosperous Year. Solution of a Great Problem. Newcastle Morning Herald Saturday 22 February 1902. Available at:. http://nla.gov.au/nla.news-article135339351 (accessed 09 January 2017).

NMH, 1925. Carrington Council Meeting. Newcastle Morning Herald and Miners' Advocate (Thursday 30 July 1925. Available at: http://trove.nla.gov.au/newspaper/article/137830721?searchTerm=carrington%20council%20meeting&searchLimits=dateFrom=1925-01-01|||dateTo=1925-12-31 accessed 09 January 2017).

NMH, 1948a. Slag Ruins Beach, Says Club Captain. Newcastle Morning Herald Friday 20 August 1948. Available at:. http://nla.gov.au/nla.news-article140356359 (accessed 09 January 2017).

NMH, 1948b. Council Dumped 800 Tons Slag. Newcastle Morning Herald Monday 21 June 1948. Available at:. http://nla.gov.au/nla.news-article134334745 (accessed 09 January 2017).
NMH, 1949a. Rapid Slag Dumping at Stockton. Newcastle Morning Herald Thursday 24 March 1949. Available at:. http://trove.nla.gov.au/newspaper/article/134339600?searchTerm=Rapid%20Slag%20Dumping%20at%20Stockton&searchLimits= (assessed 09 January 2017).
NMH, 1949b. Dumps Scoured for Stone to Fight Erosion. Newcastle Morning Herald and Miners' Advocate Tuesday 5 April 1949. Available at:. http://trove.nla.gov.au/newspaper/article/134343452?searchTerm=Dumps%20scoured%20for%20stone%20to%20fight%20erosion&searchLimits= (accessed 09 January 2017).
NS, 1925. Faith and Courage in Newcastle Industries. Newcastle Sun Tuesday 3 November 1925. Available at:. http://trove.nla.gov.au/newspaper/article/163367941?searchTerm=Faith%20and%20Courage%20in%20Newcastle%20Industries&searchLimits= (accessed 09 January 2017).
NS, 1926. Slag for Road, Stockton Council's Decision, Fullerton Rd Work. Newcastle Sun Wednesday 10 February 1926. Available at:. http://trove.nla.gov.au/newspaper/article/163396050?searchTerm=Slag%20for%20Road%20Stockton%20Council%E2%80%99s%20Decision&searchLimits= (accessed 09 January 2017).
NS, 1948. B.H.P. Gift Slag Being Dumped At Stockton. Newcastle Sun Friday 30 July 1948. Available at:. http://nla.gov.au/nla.news-article158263500 (accessed 09 January 2017).
NSW EPA, 2016. List of NSW Contaminated Sites Notified to EPA. (Available at). http://www.epa.nsw.gov.au/clm/publiclist.htm (accessed 04 January 2017).
Odabasi, M., Bayram, A., Elbir, T., Seyfioglu, R., Dumanoglu, Y., Ornektekin, S., 2010. Investigation of soil concentrations of persistent organic pollutants, trace elements, and anions due to iron-steel plant emissions in an industrial region in Turkey. Water Air Soil Pollut. 213, 375–388.
Parliament of New South Wales, 1999. BHP Newcastle Steelworks Closure. Legislative Assembly Hansard 22 September 1999. Available at:. http://23.101.218.132/prod/web/common.nsf/V3HHBDay?open&key=19990922 (accessed 09 January 2017).
Perer, A.F.P., Rauh, V., Whyatt, R.M., Tsai, W.-Y., Tang, D., Diaz, D., Hoepner, L., Barr, D., Tu, Y.-H., Camann, D., Kinney, P., 2006. Effect of prenatal exposure to airborne polycyclic aromatic hydrocarbons on neurodevelopment in the first 3 years of life among inner-city children. Environ. Health Perspect. 114, 1287–1292.
Petersburg Times, 1901. Port Pirie Shipping Departures October 27. Petersburg Times Friday 4 October 1901. Available at:. http://trove.nla.gov.au/newspaper/article/124969874?searchTerm=Port%20Pirie%20Shipping%20Departures&searchLimits= (accessed 09 January 2017).
Piatak, N.M., Parsons, M.B., Seal II, R.R., 2015. Characteristics and environmental aspects of slag: a review. Appl. Geochem. 57, 236–266.
PPR, 1904. Sailed Shipping Report 5th July. Port Pirie Recorder and North Western Mail (Wednesday 6 July 1904. Available at: http://trove.nla.gov.au/newspaper/article/95260908?searchTerm=Shipping%20Port%20Pirie&searchLimits=l-decade=190|||l-year=1904|||l-month=7 accessed 09 January 2017).
Quorn Mercury, 1900a. Port Pirie Shipping Departures. Quorn Mercury Friday 2 November 1900. Available at:. http://nla.gov.au/nla.news-article213625784 (accessed 09 January 2017).
Rouillon, M., Taylor, M.P., 2016. Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research? Environ. Pollut. 214, 255–264.
Rouillon, M., Gore, D.B., Taylor, M.P., 2013. The nature and distribution of Cu, Zn, Hg, and Pb in urban soils of a regional city: Lithgow, Australia. Appl. Geochem. 36, 83–91.
Rouillon, M., Harvey, P.J., Kristense, L.J., George, S.G., Taylor, M.P., 2016. VegeSafe: A community science program measuring soil-metal contamination, evaluating risk and providing advice for safe gardening. Environ. Pollut. http://dx.doi.org/10.1016/j.envpol.2016.11.024.
SA, 1951. Railway Laws Under Fire – Road Slag Delivery. Singleton Argus Friday 22 June 1951. Available at:. http://trove.nla.gov.au/newspaper/article/82758348?searchTerm=Railway%20Laws%20Under%20Fire&searchLimits= (accessed 09 January 2017).
SCT&WA, 1907. Newcastle. South Coast Times and Wollongong Argus Saturday 27 April 1907. Available at:. http://trove.nla.gov.au/newspaper/article/141921919?searchTerm=Melbourne%20and%20Great%20Northern%20Newcastle&searchLimits= (accessed 09 January 2017).
SM, 1872. Opening of the English and Australian Copper Company's Works New Lambton Newcastle. Sydney Mail and New South Wales Advertiser Saturday 22 June 1872. Available at:. http://trove.nla.gov.au/newspaper/article/13259327 (accessed 09 January 2017).
SMH, 1871a. Hunter River Copper Works: Port Waratah. Sydney Morning Herald Thursday 14 September 1871. Available at:. http://trove.nla.gov.au/newspaper/article/18757249 (accessed 09 January 2017).
SMH, 1871b. Copper Smelting Works at Waratah. Sydney Morning Herald Friday 6 October 1871. Available at:. http://trove.nla.gov.au/newspaper/article/13246089 (accessed 09 January 2017).
SMH, 1948. Newcastle Seeks McGirr's Aid. Sydney Morning Herald Tuesday 20 July 1948. Available at:. http://trove.nla.gov.au/newspaper/article/18078411?searchTerm=Newcastle%20Seeks%20McGirr%E2%80%99s%20Aid&searchLimits= (accessed 09 January 2017).
Song, N., Ma, J., Yu, Y., Yang, Z., Li, Y., 2015. New observations on PAH pollution in old heavy industry cities in northeastern China. Environ. Pollut. 205, 415–423.
Taylor, M.P., Mackay, A.K., Hudson-Edwards, K.A., Holz, E., 2010. Soil Cd, Cu, Pb and Zn contaminants around Mount Isa City, Queensland, Australia: potential sources and risks to human health. Appl. Geochem. 25, 841–855.
Taylor, M.P., Camenzuli, D., Kristensen, L.J., Forbes, M., Zahran, S., 2013. Environmental lead exposure risks associated with children's outdoor playgrounds. Environ. Pollut. 178, 447–454.
Taylor, M.P., Davies, P.J., Kristensen, L.J., Csavina, J.L., 2014a. 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 Res. 14, 35–52.
Taylor, M.P., Mould, S.A., Kristensen, L.J., Rouillon, M., 2014b. Environmental arsenic, cadmium and lead dust emissions from metal mine operations: implications for environmental management, monitoring and human health. Environ. Res. 135, 296–303.
Taylor, M.P., Forbes, M.K., Opeskin, B., Parr, N., Lanphear, B.P., 2016. The relationship between atmospheric lead emissions and aggressive crime: an ecological study. Environ. Health 15, 23.
The Australasian, 1905. Broken Hill Proprietary Company Manufacturing of Spelter Works at Newcastle. The Australasian Saturday 22 April 1905. Available at:. http://trove.nla.gov.au/newspaper/article/139804665?searchTerm=Broken%20Hill%20Proprietary%20Company%20Manufacturing%20of%20Spelter%20Works%20at%20Newcastle&searchLimits= (accessed 09 January 2017).
The Mercury, 1867. Hunter River Copper Works. The Mercury Thursday 12 September 1867. Available at:. http://trove.nla.gov.au/newspaper/article/8847971 (accessed 09 January 2017).
TNC, 1950. Bitumening of Highway by April. The Northern Champion Wednesday 15 February 1950. Available at:. http://trove.nla.gov.au/newspaper/article/162461085?searchTerm=Bitumening%20of%20Highway%20by%20April&searchLimits= (accessed 09 January 2017).
United Nations (UN), 2015. World Urbanization Prospects: The 2014 Revision (ST/ESA/SER.A/366). Department of Economic and Social Affairs, Population Division Available at:. https://esa.un.org/unpd/wup/Publications/Files/WUP2014-Report.pdf (accessed 9 January 2017).
United States Environmental Protection Authority (US EPA), 2012,. Standard Operating Procedure for an In-vitro Bio-accessibility Assay for Lead in Soil.
Van Oss, H.G., 2011. Slag, Iron and Steel: U.S. Geological Survey, Minerals Yearbook. vol. 1 pp. 69.1–69.9.
Wang, X., Thai, P.K., Li, Y., Li, Q., Wainwright, D., Hawker, D.W., Mueller, J.F., 2016. Changes in atmospheric concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls between the 1990s and 2010s in an Australian city and the role of bushfires as a source. Environ. Pollut. 213, 223–231.
Yang, H.-H., Lai, S.-O., Hsieh, L.-T., Hsueh, H.-J., Chi, T.-W., 2002. Profiles of PAH emission from steel and iron industries. Chemosphere 48, 1061–1074.
Yang, J., Yu, F., Yu, Y., Zhang, J., Wang, R., Srinivasulu, M., Vasenev, V., 2016. Characterization, source apportionement, and risk assessment of polycyclic aromatic hydrocarbons in urban soil in Nanjing, China. J. Soils Sediments http://dx.doi.org/10.1007/s11368-016-1585-0.
Youn, J.-S., Csavina, J., Rine, K.P., Shingler, T., Taylor, M.P., Sáez, A.E., Betterton, E.A., Sorooshian, A., 2016. Hygroscopic properties and respiratory system deposition behavior of particulate matter emitted by mining and smelting operations. Environ. Sci. Technol. 50, 11706–11713.
Zahran, S., Mielke, H.W., McElmurry, S.P., Filippelli, G.M., Laidlaw, M.A.S., Taylor, M.P., 2013. Determining the relative importance of soil sample locations to predict risk of child lead exposure. Environ. Int. 60, 7–14.
Zhang, J., Wang, P., Li, J., Mendola, P., Sherman, S., Ying, Q., 2016. Estimating population exposure to ambient polycyclic aromatic hydrocarbon in the United States – part II: source apportionment and cancer risk assessment. Environ. Int. 97, 163–170.

Chapter 4: Blood Pb and its response to environmental Pb

Chapter Four presents the following paper:

- Paper Three: A 25-year record of childhood blood lead exposure and its relationship to environmental sources. **Dong, C.,** Taylor, M. P.
  Draft for submission to *Environmental Research*

In Chapter Three, the research showed that not only was total dust Pb loading (μg/m^2/day) elevated in Broken Hill, but that it was also highly bioaccessible (at an average of 68% of total dust Pb), especially for the area adjacent to the active mining operations. In addition, elevated total Pb and bioaccessibility have also been observed in Broken Hill soil (Yang and Cattle, 2015). Research in the 1990s contended that soil and dust Pb ingestion was responsible for the elevated blood Pb concentrations in Broken Hill children (Gulson et al., 1994a). Furthermore, an analysis of Pb isotopic composition in Broken Hill showed that childhood blood Pb was more strongly correlated to dust fall than soil (Gulson et al., 1995). A recent study of Broken Hill and the environmental Pb problem asserted that the primary contributor to elevated childhood blood Pb could be explained by soil Pb through the Integrated Exposure Uptake Biokinetic (IEUBK) model (Yang and Cattle, 2015). However, the Broken Hill dataset, including over 24,000 blood Pb tests and 10,000 environmental Pb data covering the last 25 years, has yet to be examined in order to investigate a dose response relationship between blood Pb and environmental Pb. Thus, this chapter examines children's blood Pb and its response to soil and dust Pb contamination through multivariate regression analysis using the Broken Hill dataset. This study differs from the studies conducted in the 1990s (Gulson et al., 1994a,b) and that undertaken by Yang and Cattle (2015) in that the sample size is much larger, involves actual measures of exposures in children and incorporates a suite of relevant covariates, including age, sex, ethnicity, age of house and socio-economic status, that are known to influence blood Pb outcomes.

References

Gulson, B. L., Davis, J. J., Mizon, K. J., Korsch, M. J., Bawden-Smith, J., 1995. Sources of lead in soils and dust and the use of dust fallout as a sampling medium. Science of the Total Environment 166, 245-262.

Gulson, B. L., Davis, J. J., Mizon, K. J., Korsch, M. J., Law, A. J., Howarth, D., 1994a. Lead Bioavailability in the Environment of Children: Blood Lead Levels in Children Can Be Elevated in a Mining Community. Archives of Environmental Health 49, 326-331.

Gulson, B. L., Howarth, D., Mizon, K. J., Law, A. J., Korsch, M. J., Davis, J. J., 1994b. Sources of lead in humans from Broken Hill mining community. Environmental Geochemistry and Health 16, 19-25.

Yang and Cattle, 2015. Bioaccessibility of lead in urban soil of Broken Hill, Australia: A study based on in vitro digestion and the IEUBK model. Environmental Pollution 538, 922-933.

A 25-year record of childhood blood lead exposure and its relationship to environmental sources

Chenyin Dong[a,*], Mark Patrick Taylor[a, b]

[a] Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, North Ryde, Sydney, NSW 2109, Australia

[b] Energy and Environmental Contaminants Research Centre, Macquarie University, North Ryde, Sydney, NSW 2109, Australia

*** Corresponding Author**

Phone: +61 9850 4221; email: chenyin.dong@hdr.mq.edu.au

Abstract

Broken Hill, the oldest silver (Ag)–zinc (Zn)–lead (Pb) mining community in Australia, has an ongoing and legacy problem of Pb exposure that dates back to as early as 1893. This study aims to identify potential pathways of blood Pb (PbB) in Broken Hill with the aim of identifying children with high environmental Pb exposure risk for future remediation programs. This study examines PbB levels of children <5 years old, along with corresponding soil, petri-dish dust and ceiling dust Pb concentrations at homes over 25 year period from 1991–2015. Regression analysis was used to identify potential factors driving blood Pb exposures as well as the relationship between environmental Pb sources and children's PbB.

The results show that age, sex, ethnicity, socio-economic status and age of housing were statistically significant independent predictors (p<0.01) of PbB. More specifically, Aboriginal children (PbB 7.4 μg/dL, 95% CI: 6.7–7.4) in Broken Hill are more vulnerable to environmental Pb exposure compared to non-Aboriginal children (PbB 6.2 μg/dL, 95% CI: 6.2–6.3) for all years during the period of 1991-2015. Children at the age of 24–36 months had a higher PbB exposure risk compared with other age groups. Blood Pb concentrations increased significantly (p<0.01) with decreased socio-economic status and for children living in houses built before 1940 (p<0.01). A 100 mg/kg increase in soil Pb was associated with a 0.12 μg/dL increase in childhood PbB for the entire Broken Hill area. In addition, PbB concentrations increased with greater indoor petri-dish dust Pb loadings (i.e. 0.08 μg/dL per 100 μg/m^2/30 days). Blood Pb was significantly correlated with both soil Pb and indoor petri-dish dust Pb loadings, confirming that these are the most probable sources of PbB exposure in Broken Hill. In terms of moving forward and mitigating harmful early life Pb exposures, the data show that children aged 24–36 months, and Aboriginal children should be prioritised for practical intervention practices. Such interventions should include household soil remediation, dust cleaning using wet mopping and wiping techniques, vacuuming of carpets and furnishings and sealing of older homes to minimise dust penetration.

Keywords

Blood lead; soil; dust; Aboriginality; age of house; socio-economic status

1. Introduction

Anthropogenic lead (Pb) enters the environment through a range of sources such as mining and smelting, the use of batteries, pigments and ceramics, combustion of fossil fuels (e.g. coal, leaded gasoline), the use of mineral fertilisers, sewage sludge application and the use of lead water pipes (Komárek et al., 2008; Pieper et al., 2017). Consequently, the prevalence of Pb in residential environments has meant that Pb poisoning has continued to be a common public health problem, especially among young children (Needlemen, 2004; Flora et al., 2012). Young children are more vulnerable to Pb exposure due to their frequent hand-to-mouth activity, higher absorption rates (when compared to adults) and their developing central nervous system (Needleman, 2004). The adverse health impacts of Pb poisoning on children are well known and include intellectual impairment (e.g. Lanphear et al., 2005; Jusko et al., 2008; Liu et al., 2013; Alvare-Ortega et al., 2017), cognitive deficits as well as behavioural functions (e.g. Liu et al., 2014; Skerfving et al., 2015; Choi et al., 2016; Huang et al., 2016; Rodrigues et al., 2016) and low birth weight/length (McMichael et al., 1986; Zhu et al., 2010; Zhang et al., 2015). Such impacts are still observed at low levels of children blood Pb (PbB) concentrations (Bellinger et al., 1992; Schwartz, 1994; Lanphear et al., 2005; Zhu et al., 2010; NTP, 2012; Xie et al., 2013; Skerfving et al., 2015; Earl et al., 2016). Hence, in order to reduce children's PbB exposure risk, the association between environmental Pb (e.g. water, soil, dust) and PbB has been examined widely outside of Australia (e.g. Lanphear et al., 1998; Mielke et al., 2007; Dixon et al., 2009; Levallois et al., 2014; Bello et al., 2016; Hanna-Attisha et al., 2016). While these association analyses can identify the main pathways of childhood PbB, they can also provide target environmental Pb values to achieve particular childhood PbB outcomes. For example, Dixon et al. (2009) suggested that lowering the floor dust Pb standard below 40 μg/ft^2 (~431 μg/m^2) would better protect children from elevated PbB. The US Department of Housing and Urban Development recently lowered the acceptable clearance Pb dust values following remedial works to 10 μg/ft^2 (~110 μg/m^2) in 2017 (US HUD, 2017). With regard to soil Pb, Mielke et al. (2007) found that PbB was likely to exceed 5 μg/dL when soil Pb concentrations were greater than 300 mg/kg. In addition to the association between environmental Pb and PbB, childhood PbB is also influenced by other factors including age, sex, ethnicity, housing condition and socio-economic status (e.g. Mielke et al., 1997; Bellinger, 2008; Zahran et al., 2011; White et al., 2016).

In Australia, there has been relatively limited research examining children's PbB and its response to environmental Pb. The majority of Australian childhood PbB studies mainly focus on Port Pirie, a zinc (Zn) and Pb smelting community (e.g. Wilson et al., 1986; McMichael et al., 1988; Baghurst et al., 1992; Tong et al., 1996; Burns et al., 1999; Earl et al., 2016), and

were largely completed before the year 2000. In other Australian communities, there are relatively few studies applying city-wide data to estimate the relationship between environmental Pb and PbB (e.g. Willmore et al., 2006). Most Australian studies have used small cohorts of participants to estimate the relationship between environmental Pb and PbB (e.g. Fett et al., 1992; Young et al., 1992; Boreland et al., 2006; Gulson and Taylor, 2017). For example, Boreland et al. (2006) used interior dust Pb from the homes of 74 preschool aged children (4–5 years) and their PbB samples to identify a relationship between both sets of data. Recently, Gulson and Taylor (2017) applied soil/dust Pb and PbB data (2001–2006) from 100 houses and 108 children located in Sydney and estimated the relationship between PbB and environmental Pb. The association between PbB and environmental Pb has also been examined using Integrated Exposure Uptake Biokinetic (IEUBK) modelling in Australia (e.g. Yang and Cattle, 2015; Laidlaw et al., 2017). Hence, an opportunity exists to estimate the relationship between environmental Pb and PbB in Australia using a long-term city-wide dataset.

Broken Hill, located in far west New South Wales (NSW), Australia, has the world's largest Ag-Pb-Zn ore deposit (Solomon, 1988). The ore deposit was discovered in 1883 and has since been mined uninterrupted (Kristensen and Taylor, 2016). The ore processing operations have left a legacy of widespread Pb contamination in the adjoining residential community, with occupational and community Pb poisoning being reported as early as 1893 (Thompson et al., 1893). In 1991, systematic investigation of childhood PbB levels commenced, at which time 86% of children had PbB levels ≥10 μg/dL (the upper acceptable PbB value from 1993 to 2015) (Lyle et al., 2006), thereafter childhood PbB in Broken Hill decreased continuously from 1991 to 2010. However, the proportion of children with a PbB >10 μg/dL increased from 12.6% in 2010 to 21% in 2012 and remained at ~20% after 2012 (Lesjak and Jones, 2016). The recent increase of PbB concentrations may be due, in part, to a recent increase of participation in the annual PbB monitoring programs, resulting in a more accurate assessment of exposures in children.

In order to identify potential sources of PbB, environmental Pb samples, including soil and indoor dust, were collected in parallel to an NSW Health PbB investigation program that has run from 1991–present. However, up until now, the full dataset comprising the PbB and environmental Pb data has yet to be examined in an integrated manner. Therefore, the aim of this study is to identify the linkages between environmental sources, pathways, and childhood PbB levels. In order to achieve this aim, we first investigate the dose response relationship

between PbB and Pb concentrations in soil, petri-dish dust and ceiling dust, respectively. Second, we investigate potential impacts of other variables (i.e. age, sex, ethnicity, housing condition and socio-economic status) on childhood PbB to identify those children most vulnerable to environmental Pb exposure. This study begins to address the paucity of research using a large dataset to establish a relationship between environmental Pb and blood Pb in Australia.

2. Data and Methods

2.1 Data

2.1.1 Blood Pb

The blood Pb dataset (1991–2015) was obtained from Broken Hill Child & Family Health Centre. Data access and its subsequent analysis were subject to ethics approval from NSW Health and Macquarie University. From 1991 to 2015, there were 25,385 PbB test results recorded for children aged 0-5 years old. However, some of the test results were duplicated in the dataset and consequently were removed. The cleaned dataset contains 24,108 PbB test records. Before 2008, venous blood sampling was used to test Broken Hill children's PbB concentrations, while after this date the finger-prick (capillary) method was applied (Lesjak and Jones, 2016).

In this study, PbB was analysed as a continuous variable (μg/dL), while associated metadata was also analysed comprising information on the residence of each child, date of blood sample collection, age, sex (male=1; female=0), and ethnicity (Aboriginal=1; non-Aboriginal=0).

2.1.2 Environmental Pb samples

The available Broken Hill data contains 10,160 residential soil Pb samples collected between 1994 and 2015, from 1940 Broken Hill properties. Wherever possible, multiple samples were collected from different sites around each house from a depth of 0–5 cm (Western NSW Public Health, 1994). Indoor house dust was collected in two ways at Broken Hill. Indoor dust Pb deposition (μg/m^2/30 days) was measured at 106 houses predominantly between 1996 and 1998, using 85 mm diameter polystyrene petri-dishes using established methods (Gulson et al. 1995a). Ceiling dust (n=80 houses) collected during 1996–1998 was sieved to <150 μm prior to analysis for Pb concentration. The laboratory analysis of petri-dish dust and ceiling dust followed the methods used in the studies Boreland et al. (2002) and Gulson et al. (1994a), respectively.

Previous Pb isotopic composition analyses showed that household soil and dust but not water were the most significant sources of Pb in blood (Gulson et al., 1994a). Therefore, this study focuses on the relationships between Pb in soil and dust childhood PbB outcomes.

2.1.3 Age of house

The ages of houses located in Broken Hill were obtained from the New South Wales Environment Protection Authority (NSW EPA). In Broken Hill, age of house data were recorded as an ordinal number (i.e. pre-1914, 1915-1939, 1940-1970 and post-1970). Rouillon et al. (2017) demonstrated that soil Pb concentrations of homes built before 1935 in Sydney, Australia, were likely to exceed the Australian residential soil Pb guideline of 300 mg/kg due to the accumulation of leaded petrol emissions and the deterioration of Pb-based paints (NEPM, 2013). In New Orleans, USA, census tracts with a majority of houses built before 1940 also had higher PbB levels (Mielke et al., 1997). Furthermore, a national study conducted in the United States has shown that there is a greater Pb hazard in houses built before the 1940s (68% houses with Pb hazard issues) (Jacobs et al., 2002). To evaluate the potential influence of house age on PbB data in this study, the age of Broken Hill houses was placed in one of two categories (before 1940=1; post 1940=0). The pre/post-1940 division provided best possible statistical signal of Pb-based paint exposure risk in Broken Hill. In addition to the increased risk of Pb-based paint in older Broken Hill homes, it is also likely older houses have been subject to significant dust loading over time. Their poor structure means that they are likely to be affected by dust penetration and the accumulation of Pb from atmospheric and soil sources. The age of house information was merged with PbB and environmental Pb data according to the address of the house.

2.1.4 Socio-economic status

Statistical area data relating socio-economic metrics for Broken Hill was extracted from the Australian Bureau of Statistics website. Index of Relative Socio-Economic Advantage and Disadvantage (IRSAD) data for 52 ‘Statistical Areas Level 1 (hereafter SA1)’ across Broken Hill was used for this assessment. The SA1 level is the most granular unit for the release of census data. The IRSAD data ranks areas on a scale from most disadvantaged (low index score) to advantaged (high index score) using the variables of income, education, employment, occupation, housing and other indicators of relative advantage and disadvantage (ABS, 2013). Blood Pb and environmental Pb data in this study were matched to their corresponding SA1 areas prior to analysis.

2.2 Data analysis

Statistical analyses were undertaken using Stata 12. Multivariate regression analysis was undertaken to evaluate the relationship between children's age, sex, ethnicity, socio-economic status and PbB outcomes.

The relationship between soil Pb and PbB was estimated in two ways. First, blood and environmental Pb data were geocoded and matched to their corresponding SA1 areas by year of analysis during the period of 1991-2015. Geometric mean values of soil Pb and PbB from the corresponding SA1 areas were used to estimate the association between soil Pb and PbB data. Second, multivariate regression analysis including demographic parameters was conducted at the house level, i.e. PbB of each house for a particular year was regressed against the mean soil Pb of the same house in the same year between 1991 and 2015.

Regarding the limited petri-dish dust and ceiling dust samples (hereafter referred to as dust) collected during the period of 1996 to 1998, the PbB of children in corresponding homes from the same period was regressed against the mean dust Pb of the same house.

3. Results

3.1 Blood Pb

Table 1 shows that the geometric mean PbB of Aboriginal children (7.4 μg/dL) was higher than non-Aboriginal children (6.2 μg/dL) (*t*-test; $p<0.001$) for all years, 1991–2015. Children <12 months of age had the lowest PbB concentrations (2.7 μg/dL) compared to other age groups, with PbB values peaking at 9.7 μg/dL in children aged 24–36 months (Table 1). Broken Hill boys under five years of age had higher PbB (6.2 μg/dL) than girls of a similar age (5.5 μg/dL) (*t*-test; $p<0.001$) (Table 1). Children living in older houses (pre-1940) had higher PbB (6.9 μg/dL) when compared to those living in houses built post-1940 (5.8 μg/dL).

Table 1. Characteristics of study participants with weighted percentage 1991-2015.

Variables	Number of observations (%)	PbB levels (μg/dL) GM (95% CI)
Total	24,076 (100)	6.39 (6.32, 6.47)
Sex		
Male	12,717 (53)	6.89 (6.77, 6.99)
Female	11,034 (46)	6.09 (5.99, 6.19)
Age (months)		
0-12	6561 (27)	2.70 (2.65, 2.75)
12-24	5216 (22)	8.20 (8.04, 8.37)
24-36	4502 (19)	9.70 (9.50, 9.91)
36-48	3939 (16)	9.18 (8.98, 9.39)
48-60	3858 (16)	8.36 (8.17, 8.55)
Ethnicity		
Aboriginality	3521 (15)	7.37 (6.69, 7.40)
Non-Aboriginality	20,555 (85)	6.24 (6.16, 6.32)
Age of House		
pre-1940	12,603 (52)	6.94 (6.83, 7.06)
after 1940	9326 (39)	5.83 (5.73, 5.94)

Multivariate regression analyses show that PbB in Broken Hill children is significantly correlated to demographic parameters, such as age, sex, ethnicity, age of house and socio-economic status (Table 2). In particular, a non-linear association between child age and PbB was found, which is consistent with previous studies (e.g. Baghurst et al., 1992; Willmore et al., 2006; Searle et al., 2014). Assessment of blood Pb exposures against socio-economic values shows that exposures are inversely related (Table 2).

Table 2. Multivariate regression analysis of PbB including demographic parameters.

PbB (μg/dL)	Coefficients
Sex	1.161***
	(0.0997)
Aboriginality	1.887***
	(0.140)
Age	7.028***
	(0.117)
Age^2	-1.151***
	(0.0246)
SES	-0.0156***
	(0.000930)
House age	1.206***
	(0.103)
Constant	14.68***
	(0.860)
Observations	21,646
R-squared	0.220

Note: *** p<0.01.

3.2 Soil Pb and PbB

Figure 1 showed that geometric mean soil Pb associated with the corresponding PbB at the SA1 area level in Broken Hill (r=0.22, p<0.01) (Figure 1). An increase in soil Pb concentration from 100 to 1000 mg/kg resulted in a 1.9 μg/dL increase in PbB.

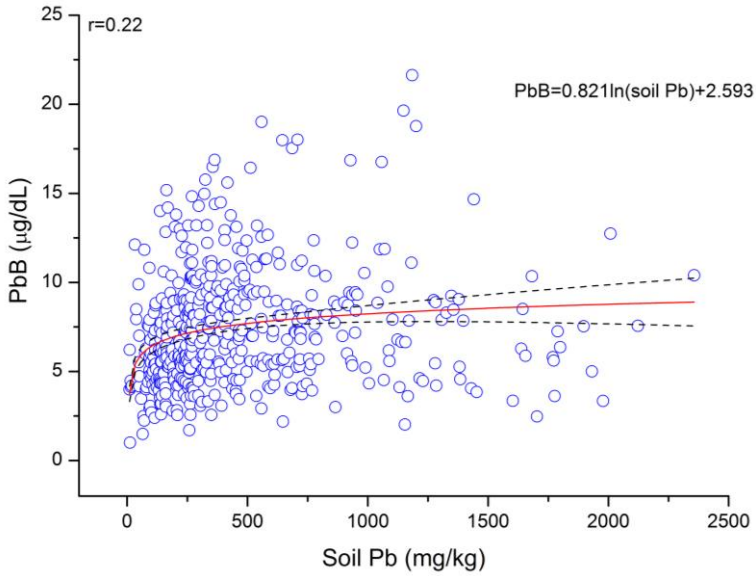


Figure 1. Scatter plot of geometric soil Pb against geometric PbB at the SA1 level for all years, 1994–2015 (n=499). The solid line represents the non-linear regression model, with the outer dashed lines being the 95% confidence interval boundaries.

The relationship between soil Pb and PbB at the house level were investigated along with relevant demographic factors (age, sex, ethnicity, socio-economic status and age of house) (Table 3). Table 3 shows that PbB of Broken Hill is not only significantly correlated with soil Pb, but also with other variables such as age, sex, Aboriginality, age of house, and socio-economic status (Table 3), which makes untangling the actual cause of elevated PbB difficult. This model shows that a soil Pb increase of 100 mg/kg is associated with a 0.12 μg/dL increase in PbB for the whole Broken Hill area (geometric mean soil Pb for the 6265 individual household samples was 502 mg/kg). That means 1.1 μg/dL increase in PbB when soil Pb concentration increase from 100 to 1000 mg/kg, which is also comparable with the increase of 1.9 μg/dL based on the geometric soil Pb and geometric PbB analysis (Figure 1). The gradient of soil Pb versus PbB is also consistent with that established in Sydney (0.17 μg/dL per 100 mg/kg) (Gulson and Taylor, 2017).

Table 3. Relationships between PbB and soil Pb including demographic parameters.

PbB (μg/dL)	Coefficients
Soil Pb (mg/kg)	0.0012***
	(0.000)
Sex	0.9788***
	(0.183)
Aboriginality	2.0353***
	(0.302)
Age	7.7895***
	(0.218)
Age^2	-1.3188***
	(0.045)
SES	-0.0164***
	(0.002)
House age	0.8825***
	(0.196)
Constant	15.7878***
	(1.715)
Observations	6,265
R-squared	0.246

Note: *** p<0.01. Sex: male=1; female=0. Aboriginality: Aboriginal=1; non-Aboriginal=0. House age: before 1940=1; post 1940=0. Age^2: square of child age. SES: Index of Relative Socio-Economic Advantage and Disadvantage (IRSAD).

3.3 Dust Pb and PbB

Unlike the soil–PbB data for which there were 6265 observations, the relationship between the paired dust and PbB dataset is based on a much smaller subset of observations (n=99 and n=98, respectively for petri-dish dust and ceiling dust, Table 4).

Table 4. Characteristics of the paired dust and PbB dataset from 1996-1998.

	Paired Petri-dish dust		Paired ceiling dust	
Variables	observations (%)	PbB (μg/dL) GM (95% CI)	Number of observations (%)	PbB (μg/dL) GM (95% CI)
Total	99 (100)	11.36 (9.92, 12.99)	98	8.32 (7.05, 9.82)
Sex				
Male	56 (57)	12.66 (10.59, 15.13)	53 (55)	9.94 (8.06, 12.25)
Female	43 (43)	9.86 (8.03, 12.11)	44 (45)	6.94 (5.36, 8.98)
Ethnicity				
Aboriginality	13 (13)	15.08 (10.65, 21.37)	6 (6)	19.73 (9.49, 40.98)
Non-Aboriginality	86 (87)	10.88 (9.40, 12.59)	92 (94)	7.86 (6.66, 9.29)
Age of House				
pre-1940	59 (66)	10.85 (9.02, 13.07)	58 (39)	8.54 (6.71, 10.86)
after 1940	31 (34)	12.46 (9.92, 15.63)	37 (61)	7.80 (6.16, 9.87)

Notes: GM: Geometric mean value of PbB (95% confidence interval).

Multivariate regression analysis showed that PbB increases with indoor petri-dish dust Pb loadings (i.e. 0.08 μg/dL per 100 $\mu g/m^2$/30 days), while ceiling dust Pb did not correlate with

PbB concentrations (Table 5). Gulson and Taylor (2017) recently reported Sydney data that showed an increase in petri-dish dust Pb loadings of approximately 100 μg/m^2/30 days would increase PbB by about 1.5 μg/dL.

Table 5. Multivariate regression analysis: association between dust Pb (i.e. petri-dish dust and ceiling dust) and PbB.

PbB	Petri-dish dust (μg/m^2/30 days)	Ceiling dust (mg/kg)
Dust Pb	0.0008**	-0.0002
	(0.0003)	(0.0002)
Sex	2.5686*	2.0257*
	(1.2939)	(1.1598)
Aboriginality	2.3771	10.3731***
	(1.9529)	(2.3868)
Age	8.6540***	7.7885***
	(1.4143)	(1.3823)
Age^2	-1.5460***	-1.4952***
	(0.2878)	(0.2928)
SES	-0.0108	-0.0591***
	(0.0138)	(0.0177)
House age	-1.3457	1.7063
	(1.4187)	(1.1882)
Constant	12.6240	56.4656***
	(12.8537)	(16.9415)
Observations	90	93
R-squared	0.4075	0.5397

Notes: *** p<0.01, ** p<0.05, * p<0.1. Sex: male=1; female=0. Aboriginality: Aboriginal=1; non-Aboriginal=0. House age: before 1940=1; post 1940=0. Age^2: square of child age. SES: Index of Relative Socio-Economic Advantage and Disadvantage (IRSAD).

4. Discussion

4.1 Age, socio-economic status and race influencing children's PbB outcomes

This study reveals that children's PbB is significantly correlated to a wide variety of demographic factors including age, sex, ethnicity, socio-economic status and the age of the house where the child lives. Other studies have found similar complexity in attempting to unravel the causal factors driving childhood blood lead exposure (e.g. Baghurst et al., 1992; Brody et al., 1994; Son et al., 2009; Liu et al., 2012; Jeong et al., 2014; Keller et al., 2017; Sadler et al., 2017). Blood Pb concentrations in Broken Hill children peaked at the age of 24–36 months and slightly decreased after 36 months (Table 1 and Figure 2). The Broken Hill findings are consistent with data from Australia's only other long-term PbB monitoring of children in the Pb smelting city of Port Pirie (SA Health, 2017). In Port Pirie, childhood PbB increased rapidly up to the age of 24 months and decreased slowly thereafter (Figure 2; Baghurst et al., 1992; Searle et al., 2014). In another (former) Australian Pb smelting community, North Lake Macquarie, childhood PbB was also significantly higher for children aged 12–36 months (ranging 10.0–10.8 μg/dL), when compared to other age groups (Figure 2;

Willmore et al., 2006). Additionally, children in Mount Isa, another Australian mining and smelting community, also had higher PbB at the age of 12-35 months (Queensland Government, 2011). Similar relationships between PbB and child age are also observed outside Australia, for example, children's PbB in Cincinnati and Rochester, USA also peaked at 24 months of age and then slowly declined (Hornung et al., 2009). Above all, these results indicate that children's PbB is normally expected to peak at 18 to 24 months of age (Zahran et al., 2011), though PbB continues to increase with age beyond 24–36 months for some cases (e.g. Rabito, 1998). Higher PbB concentrations in children aged around 24 months is linked to a range of developmental factors. As children grow, their motor capacity and interactions with their surrounding environment increases (Cohen Hubal et al., 2000; Simon, et al., 2007), resulting in more exploratory behaviours, including hand to mouth activity thereby increasing their opportunity for self-contamination via ingestion of soil/dust (cf. von Lindern et al., 2016). As children age from 3 to 4 years and their hand-mouth-activity decreases so does exposure via ingestion (von Lindern et al., 2016).

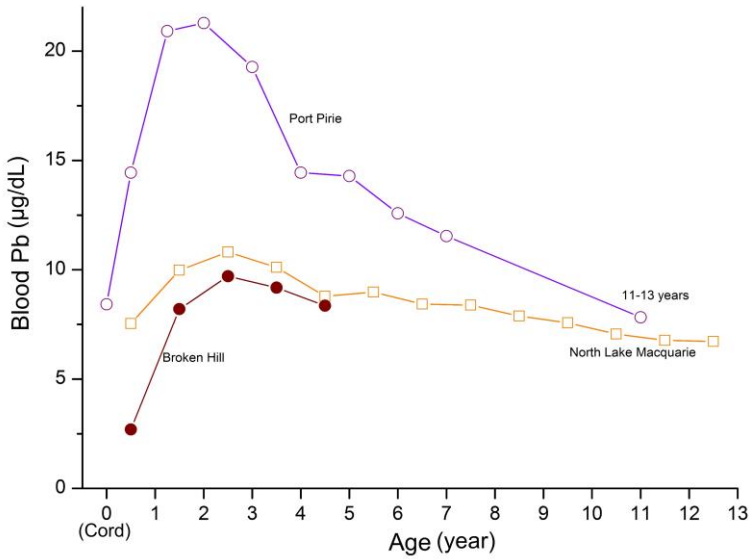


Figure 2. PbB concentrations by age of children from the Australian lead industry impacted communities of Broken Hill, Port Pirie and Lake Macquarie. The PbB data of Port Pirie and Lake Macquarie were extracted from Searle et al., (2014) and Willmore et al., (2006), respectively. The PbB data from Broken Hill and North Lake Macquarie are the geometric mean values of age groups (<1 year, 1–2, 2–3…12–13 year), while the Port Pirie data is estimated by age rather than age groups (Searle et al., 2014).

Multivariate regression analysis indicates that lower socio-economic status is linked to higher PbB concentrations in Broken Hill children, which is consistent with a range of other previous international studies (e.g. Mahaffey et al., 1982; Malcoe et al., 2002; Morales et al., 2005; Hana-Attisha et al., 2016). The influence of socio-economic status on environmental Pb exposure is complex and multifactorial (Pelc et al., 2016). In particular, socio-economic status influences the familial awareness of environmental health risks, living conditions and

childhood behaviours (Evans and Kantrowitz, 2002; Pelc et al., 2016), which in turns alters the response to known or perceived contamination risks in the home environment (Evans and Kantrowitz, 2002). In the case of Broken Hill, a relationship between socio-economic status and household exposure risk (i.e. household soil Pb) is evident in the fact that lower socio-economic status of SA1 areas is associated with higher household soil Pb concentrations (Supplementary Figure S1). A similar relationship between socio-economic status and soil Pb has been observed elsewhere (Campanella and Mielke, 2008; Aelion et al., 2013).

Ethnicity is also significantly associated with a clear disparity in children's PbB concentrations. Studies of children from Mount Isa, a Pb mining and smelting city in Australia (Queensland Government, 2011) showed that Aboriginal children had a geometric mean PbB of 5.4 μg/dL (95% CI: 4.5, 6.5), while non-Aboriginal children had a geometric mean PbB of 4.0 μg/dL (95% CI: 3.68, 4.32). Similarly, the 2015 Broken Hill annual PbB report (Lesjak and Jones, 2016) showed that the percentage of Aboriginal children exceeding the current NHMRC benchmark of 5 μg/dL was 79%, compared to only 35% for non-Aboriginal children. This discrepancy of higher PbB concentration is a persistent problem, with long term data from this study (1991–2015) revealing that Aboriginal children had a higher PbB geometric mean of 7.4 μg/dL compared with non-Aboriginal children who had a geometric mean of 6.2 μg/dL (Table 1). The mechanisms responsible for this disparity remain poorly understood, particularly in Australia, where there has been limited investigation of this phenomenon. Outside of Australia, ethnicity has been examined in more detail with respect to Pb exposure (e.g. Lanphear et al., 1996; Malcoe et al., 2002; Jones et al., 2009; Ngueta, 2014; White et al., 2016). Although subtle biological differences (e.g. DMT 1 and Vitamin D receptor Fok1 Polymorphism) have been implicated as possible causal factors for driving racial disparities in children's PbB outcomes (Ngueta, 2014), White et al. (2016) have suggested that such disparities exist as a result of varying socio-economic statuses. Socioeconomic deprivation is contributing to racial/ethnic disparities in childhood Pb poisoning (Krieger et al., 2005). Moody et al. (2016) determined that this PbB disparity between children of different race can be negated when the children have similar socio-economic statuses. Homes of Aboriginal children in Broken Hill were found to have a lower socio-economic status compared to non-aboriginal children's homes (Supplementary Table S2; Supplementary Document S3), which may partly explain why Aboriginal children in Broken Hill have had persistently higher Pb exposure over the last two decades (Lesjak and Jones, 2016).

In older homes, Pb-based paint can also be a significant source of PbB exposure (Staes et al., 1994; Gulson et al., 1995a; Markus and McBratney, 1996; Potula et al., 2001; Laidlaw and Taylor et al., 2011; Rouillon et al., 2017). Prior to 1970, Pb-based paint contained up to 50 wt% Pb and was gradually reduced to <1.0 wt% and <0.1 wt% Pb by 1970 and 1997, respectively (Australian Government, 2014). A study of Sydney garden soils by Rouillon et al. (2017) found that the majority (85%) of painted houses built pre-1914 had one or more soil samples with Pb concentrations in excess of the Australian health investigation level of 300 mg/kg (NEPM, 2013), while only 43% of painted houses built between 1955–1975 exceeded this benchmark. Similarly, older painted homes in Broken Hill are likely to have elevated soil Pb concentrations partly due to paint sources (Gulson et al., 1996). In this study, houses built before the 1940s had higher mean soil Pb (884 mg/kg) compared to those houses built after the 1940s (475 mg/kg) (Supplementary Table S2). Higher Pb hazard in houses built before the 1940s is also observed in the United States (68% houses with Pb hazard issues) (Jacobs et al., 2002). A further complicating factor is that older houses are typically also characterised by a lower socio-economic status (Supplementary Table S2).

4.2 Relationships between environmental Pb and PbB

The association between PbB and different environmental media including water, soil, indoor petri-dish dust, ceiling dust, vacuum dust and surface wipes dust have been well documented (e.g. Lanphear et al., 1995, 1998; Hanna-Attisha et al., 2016; Safruk et al., 2017; Gulson and Taylor, 2017). Examination of the association between environmental Pb and blood Pb in Broken Hill has previously been assessed using Pb isotopic compositions (Gulson et al., 1995b) and the IEUBK model (Yang and Cattle, 2015). Gulson et al. (1994a) found that Pb isotopic compositions of PbB were aligned closely to the composition of soil and dust, while Yang and Cattle's (2015) analysis concluded soil Pb concentrations were a reliable predictor of PbB. This study advances previous analyses by assessing two decades of environmental data alongside other variables (i.e. age, sex, ethnicity, age of house and socio-economic status) to determine the relative contributions of different source(s) and their relationship to PbB outcomes.

The analyses show that soil Pb and childhood PbB at the same residence are associated with a 0.12 μg/dL increase in PbB per 100 mg/kg increase of soil Pb. The exposure pathway from soil in young children is likely to occur via ingestion through touching contaminated soil, and then transferring it to the mouth by hand, nail biting, finger sucking, or other hand to mouth

activities including the mouthing of contaminated objects and food (California Office of Environmental Health Hazard Assessment, 2011; von Lindern et al., 2016).

Soil Pb has been shown to influence indoor dust Pb concentrations (e.g. Laidlaw et al., 2005; Layton and Beamer, 2009; Laidlaw et al., 2014), with it being transported inside homes via soil resuspension (Laidlaw et al., 2005, 2014) and via shoes and family pets (Hunt et al., 2006). In the 1990s, household soil Pb concentrations were correlated strongly with petri-dish dust Pb deposition in Broken Hill (Supplementary Figure S4), which is consistent with Boreland et al's (2002) study. This association implies that that Broken Hill soil Pb concentrations influence PbB levels by contributing to indoor dust Pb, and not simply as a direct result of soil Pb ingestion.

In line with existing literature, the relationship between soil Pb and Broken Hill PbB shifts according to the age of child. For children aged 12–48 months the increase in PbB is more strongly related to soil Pb (0.15–0.16 μg/dL per 100 mg/kg of soil Pb) compared to age groups 0–12 months (<0.001 μg/dL per 100 mg/kg of soil Pb) and 48–60 months (0.09 μg/dL per 100 mg/kg of soil Pb) (Supplementary Figure S5). The shifting gradients of soil Pb versus PbB is consistent with the pattern of PbB exposure risk, i.e. children <12 months are unlikely to be able to access directly contaminated soil due to their limited motor capacity, while after 12 months, children's motor capacity increases rapidly as does their hand-mouth-activity. As children age beyond 3 to 4 years, the extent of soil Pb exposure from hand-mouth-activity decreases (von Lindern et al., 2016), as is reflected in the Broken Hill data.

Indoor dust is also considered to be a primary source of elevated PbB (Dixon et al., 2009), through hand to mouth activities and even inhalation (e.g. Lanphear et al., 1998; Roberts et al., 2009). Diverse indoor dust samples including those from vacuums, surface wipes, petri-dishes and ceilings have been used to evaluate indoor dust Pb exposure risks (Lanphear et al., 1995; Davis and Gulson, 2005; Dixon et al., 2009; Gulson and Taylor, 2017). In this study, petri-dish and ceiling dust samples were analysed to determine their potential relationship and exposure significance to childhood PbB. The results show that PbB increases with indoor petri-dish dust Pb (0.08 μg/dL per 100 μg/m^2/30 days) in Broken Hill. Boreland et al. (2006) also found that PbB was associated with indoor petri-dish dust Pb concentration (0.37 μg/dL per 100 μg/m^2/30 days). Compared with other indoor dust samples (e.g. vacuum dust and surface wipes dust) petri-dish dust Pb can provide a measure of integrated recent exposure over a specific period (30 days in this study) (Gulson and Taylor, 2017). By contrast, the results show that ceiling dust is less representative of the current indoor exposure risk

compared to petri-dish dust in Broken Hill. This is not surprising given that ceiling dust is not directly accessible to children. However, many older homes have cracks and gaps in ceiling joins allowing contaminated dust to leak into living spaces adding to the burden of dust Pb exposure (Davis and Gulson, 2005). Such conditions are not uncommon in Broken Hill where old, poorly renovated homes co-exist with a hot, dry and dusty climate (Supplementary Figure S6). Furthermore, the use of ceiling dust as a correlate of recent PbBs is more problematic because it is a composite of contamination over an extended, unknown period (Davis and Gulson, 2005). By contrast, petri-dish dust Pb represents recently deposited materials and is more likely to be related to any associated PbB exposure (Gulson and Taylor, 2017).

5. Study limitations

Even though PbB outcomes over the last 25 years have shown a decreasing trend (Lesjak and Jones, 2016), a significant proportion of the population have continued to present with values above the national standard at the time of assessment (Figure 3). Although this study cast light on the sources and causes of long-term childhood PbB exposure, it does not necessarily reflect the contemporary situation, which is characterised by lower PbB and reduced exposures (Figure 3). A limitation of the analyses in this study is that matching environmental data (soil Pb, petri-dish dust Pb and ceiling dust Pb) was not collected from all of the homes of children tested for their PbB. Further, there markedly fewer houses involved in the assessment of residential petri-dish dust Pb (108 houses) and ceiling dust Pb (80 houses) than soil Pb data (1940 houses). Although the effect of these sources on PbB were modelled individually, a lack of all of these data types (soil Pb, petri-dish Pb and ceiling dust Pb) at sufficient homes meant that it was not possible to estimate the relative contribution from these sources on the individual PbB outcomes. Furthermore, this study demonstrated that PbB concentrations were significantly associated with a range of demographic factors including age, sex, ethnicity, age of house and socio-economic status. Unfortunately, data on other potentially relevant human-related mechanisms are not available because physiological and behavioural parameters such as nutrition, personal hygiene and mouthing behaviours were not historically assessed as part of the childhood PbB screening program at Broken Hill.

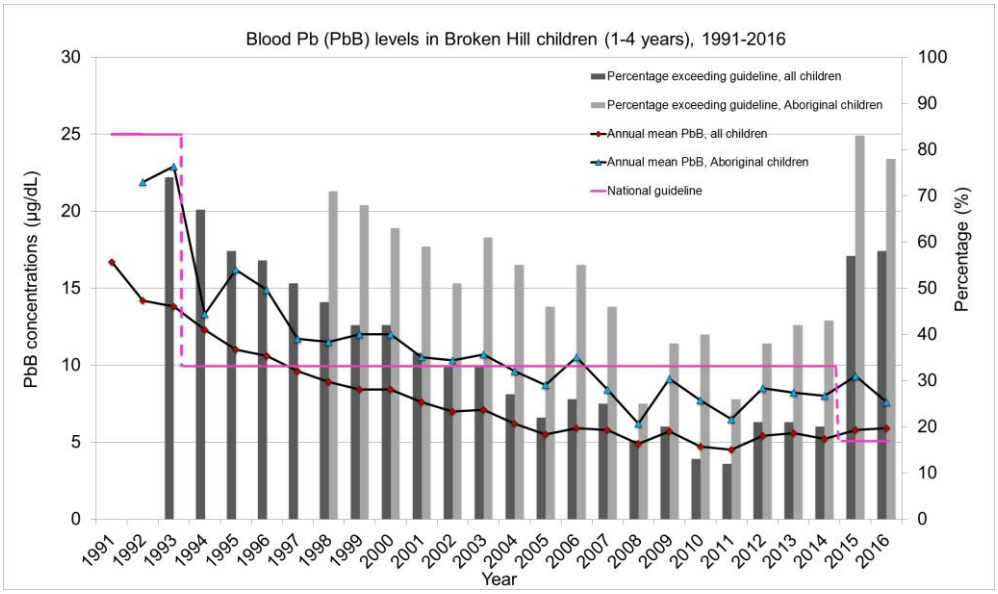


Figure 3. Blood Pb (PbB) concentrations of children aged between 1 and 4 years and percentage exceeding the national guideline of PbB at that time over the period 1991-2016. The data were extracted from Broken Hill PbB annual reports (Lesjak and Jones, 2015; Western NSW Health, 2017).

6. Lead exposure management

Consistent with previous studies (e.g. Lanphear et al., 1998; Boreland et al., 2002; Mielke et al., 2007), this research confirmed that both household soil Pb and indoor dust Pb were significant sources of Pb exposure for children in Broken Hill. Further, the association between soil Pb (mg/kg) and indoor dust Pb loading (µg/m^2/day) in Broken Hill suggests that household soil Pb contamination was played an important role in determining household Pb exposure in Broken Hill. Therefore, reducing exposure resulted from household soil lead contamination includes two aspects: first, capping contaminated soil can be applied to Broken Hill community. Previous studies have demonstrated that capping contaminated soil is economic and effective to reduce Pb exposure (Mielke et al., 2011; Ericson et al., 2018; Yang and Cattle, 2017). Second, to reduce exposure raised from tracked-in contaminated soil, wet mopping and HEPA (high efficiency particulate air) vacuuming of carpets would be required. This study shows that older Broken Hill houses have elevated Pb exposure, which also may be a function of Pb-based paint contamination and the inadequate sealing of ceilings, which are prone to accumulated Pb contaminated leaking dust into living spaces. Therefore, appropriate renovation and sealing of older homes will help to minimise Pb-based paint exposure and dust penetration from internal and external sources. Indeed, a limited number of Broken Hill household interventions involving internal cleaning and capping of contaminated soil were conducted in in the 1990s (Lyle, 2001; Lyle et al., 2006; Boreland et al., 2009), which were effective at reducing the risk at the time (Boreland et al., 2006).

In addition to household interventions, a suite of other actions were implemented to help reduce Broken Hill Pb exposures. These include: the capping of tailing dumps, which was completed by the end of the 1990s (Broken Hill Environmental Lead Program, 2016), capping and remediation of some contaminated open space areas, and the use of a low Pb crushed rock capping (known locally as 'cracker dust') on numerous unmade footpaths across the city in 2005–2006 (Yang and Cattle, 2017).

Given that the majority of the environmental data used in this study was collected more than a decade ago (dust measures in 1996–1998; 94% of soil Pb data before 2004) it might be prudent to establish the sources of Pb driving exposures in the current period. Such knowledge would assist the NSW Government's 2015 AUD$13 million investment to "rejuvenate the Broken Hill Environment Lead program to address the issue of blood lead levels in local children" (Humphries, 2015). Specifically, such data would assist in establishing relevant maximum environmental guideline values to help bring all children's PbB levels below 5 μg/dL (the current guideline of PbB).

7. Conclusions

This study reveals that a wide range of demographic factors (i.e. age, sex, ethnicity, age of house and socio-economic status) appear to be influencing child PbB levels. The data shows that Aboriginal children are clearly more vulnerable to Pb exposure, which may be linked, in part, to their lower socio-economic status in Broken Hill. To control children's exposure risk, intervention should occur before the period of 12–36 months, since children's motor capacity and hand to mouth interactions with their surrounding environment peaks during this timeframe. When taking into account the demographic factors, the regression analysis further confirms, not unsurprisingly, that soil Pb and indoor dust Pb both contribute to PbB. Indoor dust Pb exposure was better evaluated via petri-dish dust deposition collection compared to other indoor dust samples (i.e. ceiling dust). The association between PbB and household soil Pb and indoor dust Pb loadings reinforces the proposal that prevention of childhood Pb exposure must include soil remediation, dust cleaning and sealing of older homes to minimise dust penetration. Regarding atmospheric Pb emissions sourced from current mining activities in Broken Hill, further study is needed to determine the relative contribution of current mining emissions to contemporary PbB exposure compared to residual soil Pb contamination.

Conflicts of interests

The authors declare no competing financial interests. M.P. Taylor has completed an independent Review of the New South Wales Environment Protection Authority's Management of Contaminated Sites for the NSW Minister for the Environment (available at: http://www.epa.nsw.gov.au/resources/epa/Contaminated-Sites-Review-2016.pdf) and is also an advisor to the Broken Hill Environmental Lead Program.

Acknowledgements

C. Dong is funded via an International Macquarie University Research Excellence Scholarship (iMQRES No. 2014098). He received technical and practical support from the Broken Hill Environmental Lead Program (BHELP) as part of a Macquarie University–BHELP collaboration agreement. The authors are grateful to Peter Oldsen, Frances Boreland (NSW EPA, Broken Hill Environmental Lead Program) and Dr Margaret Lesjak (NSW Health Far West Local Health District) for their help in accessing the relevant environmental and human health data. We acknowledge the Child and Family Health Centre at Broken Hill for their support in collecting the PbB and residential soil Pb data. Dr Marek Rouillon, Bret Ericson and emeritus Professor Gulson Brian of Macquarie University are thanked for comments on draft versions of the manuscript.

References

Aelion, C. M., Davis, H. T., Lawson, A. B., Cai, B., McDermott, S., 2013. Associations between soil lead concentrations and populations by race/ethnicity and income-to-poverty ratio in urban and rural areas. Environmental Geochemistry and Health 35, 1-12.

Alvarez-Ortega, N., Caballero-Gallardo, K., Olivero-Verbel, J., 2017. Low blood lead levels impair intellectual and hematological function in children from Cartagena, Caribbean coast of Colombia. Journal of Trace Elements in Medicine and Biology 44, 233-240.

Australian Bureau of Statistics (ABS), 2013. Technical Paper – Socio-Economic Indexes for Areas (SEIFA) 2011. http://www.ausstats.abs.gov.au/Ausstats/subscriber.nsf/0/22CEDA8038AF7A0DCA257B3B00116E34/$File/2033.0.55.001%20seifa%202011%20technical%20paper.pdf (accessed 03.06.2017).

Australian Government, 2014. Lead in House Paint. http://www.environment.gov.au/protection/chemicals-management/lead/lead-in-house-paint (accessed 11.06.17).

Baghurst, P. A., Tong, S. L., McMichael, A. J., Robertson, E. F., Wigg, N. R., Vimpani, G. V., 1992. Determinants of blood lead concentrations to age 5 years in a birth cohort study of children living in the lead smelting city of Port Pirie and surrounding areas. Archives of Environmental Health 47, 203-210.

Bellinger, D. C., 2008. Lead neurotoxicity and socioeconomic status: Conceptual and analytical issues. NeuroToxicology 29, 828-832.

Bellinger, D. C., Stiles, K. M., Needleman, H. L., 1992. Low-Level Lead Exposure, Intelligence and Academic Achievement: A Long-term Follow-up Study. Pediatrics 90, 855-861.

Bello, O., Naidu, R., Rahman, M. M., Liu, Y., Dong, Z., 2016. Lead concentration in the blood of the general population living near a lead-zinc mine site, Nigeria: Exposure pathways. Science of the Total Environment 542, 908-914.

Boreland, F., Lesjak, M., Lyle, D., 2009. Evaluation of home lead remediation in an Australian mining community. Science of the Total Environment 408, 202-208.

Boreland, F., Lyle, D. M., Wlodarczyk, J., Balding, W. A., Reddan, S., 2002. Lead dust in Broken Hill homes — a potential hazard for young children? Australian and New Zealand Journal of Public Health 26, 203-207.

Boreland, F., Lyle, D. M., Wlodarczyk, J., Balding, W. A., 2006. Lead Dust in Broken Hill Homes: Relationship between House Dust and Children's Blood Lead Levels. Environmental Health 6, 15-24.

Brody, D. J., Pirkle, J. L., Kramer, R. A., Flegal, K. M., Matte, T. D., Gunter, E. W., Paschal, D. C., 1994. Blood Lead Levels in the US Population—Phase 1 of the Third National Health and Nutrition Examination Survey (NHANES III, 1988 to 1991). JAMA 272, 277-283.

Broken Hill Environmental Lead Program, 2016. STEERING COMMITTEE ANNUAL

REPORT 2015-2016. http://leadsmart.nsw.gov.au/wp-content/uploads/2017/03/DOC17-125421-02-Attachment-B-Broken-Hill-Environmental-Lead-Program-BHELP-Steering-Committee-Annual-Report-2015-2016.pdf (accessed 03.07.17).

Burns, J. M., Baghurst, P. A., Sawyer, M. G., McMichael, A. J., Tong, S., 1999. Lifetime Low-Level Exposure to Environmental Lead and Children's Emotional and Behavioral Development at Ages 11–13 Years: The Port Pirie Cohort Study. American Journal of Epidemiology 149, 740-749.

California Office of Environmental Health Hazard Assessment, 2008. Proposition 65 Interpretive Guideline No. 2011-001: Guideline for hand-to-mouth transfer of lead through exposure to consumer products. https://oehha.ca.gov/media/downloads/crnr/2011handtomouthpb.pdf (accessed 30.10.17).

Campanella, R., Mielke, H. W., 2008. Human geography of New Orleans' high-lead geochemical setting. Environmental Geochemistry and Health 30, 531-540.

Choi, W., Kwon, H., Lim, M. H., Lim, J., Ha, M., 2016. Blood lead, parental marital status and the risk of attention-deficit/hyperactivity disorder in elementary school children: A longitudinal study. Psychiatry Research 236, 42-46.

Cohen Hubal, E. A., Sheldon, L., Burke, J. M., McCurdy, T. R., Berry, M. R., Rigas, M. L., Zartarian, V. G., Freeman, N. C. G., 2000. Children's exposure assessment: a review of factors influencing children's exposure, and the data available to characterize and assess that exposure. Environmental Health Perspectives 108, 475-486.

Davis, J. J., Gulson, B. L., 2005. Ceiling (attic) dust: A "museum" of contamination and potential hazard. Environmental Research 99, 177-194.

Dixon, S. L., Gaitens, J. M., Jacobs, D. E., Strauss, W., Nagaraja, J., Pivetz, T., Wilson, J. W., Ashley, P. J., 2009. Exposure of U.S. Children to Residential Dust Lead, 1999–2004: II. The Contribution of Lead-Contaminated Dust to Children's Blood Lead Levels. Environmental Health Perspectives 117, 468-474.

Earl, R., Burns, N., Nettelbeck, T., Baghurst, P. 2016. Low-level environmental lead exposure still negatively associated with children's cognitive abilities. Australian Journal of Psychology 68, 98-106.

Ericson, B., Duong, T. T., Keith, J., Nguyen, T. C., Havens, D., Daniell, W., Karr, C. J., Hai, D. N., Tung, L. V., Ha, T. T. N., Wilson, B., Hanrahan, D., Croteau, G., Taylor, M. P., 2018. Improving human health outcomes with a low-cost intervention to reduce exposures from lead acid battery recycling: Dong Mai, Vietnam. Environmental Research 161, 181-187.

Evans, G. W., Kantrowitz, E., 2002. SOCIOECONOMIC STATUS AND HEALTH: The Potential Role of Environmental Risk Exposure. Annual Review of Public Health 23, 303-331.

Fett, M. J., Mira, M., Smith, J., Alperstein, G., Causer, J., Brokenshire, T., Gulson, B., Cannata, S., 1992. Community prevalence survey of children's blood lead levels and environmental lead contamination in inner Sydney. Medical Journal of Australia 157, 441-445.

Flora, G., Gupta, D., Tiwari, A., 2012. Toxicity of lead: A review with recent updates.

Interdisciplinary Toxicology 5, 47-58.

Gulson, B. L., Davis, J. J., Bawden-Smith, J., 1995a. Paint as a source of recontamination of houses in urban environments and its role in maintaining elevated blood leads in children. Science of the Total Environment 164, 221-235.

Gulson, B. L., Davis, J. J., Mizon, K. J., Korsch, M. J., Bawden-Smith, J., 1995b. Sources of lead in soil and dust and the use of dust fallout as a sampling medium. Science of the Total Environment 166, 245-262.

Gulson, B. L., Mizon, K. J., Korsch, M. J., Howarth, D., 1996. Non-orebody sources are significant contributors to blood lead of some children with low to moderate lead exposure in a major lead mining community. Science of the Total Environment 181, 223-230.

Gulson, B. L., Mizon, K. J., Law, A. J., Korsch, M, J., Davis, J. J., 1994a. Source and Pathways of Lead in Humans from the Broken Hill Mining Community – An Alternative Use of Exploration Methods. Economic Geology 89, 889 – 908.

Gulson, B. L., Howarth, D., Mizon, K. J., Law, A. J., Korsch, M. J., Daivs, J. J., 1994b. Source of lead in humans from Broken Hill mining community. Environmental Geochemistry and Health 16, 19-25.

Gulson, B. L., Taylor, A., 2017. A simple lead dust fall method predicts children's blood lead level: New evidence from Australia. Environmental Research 159, 76-81.

Hanna-Attisha, M., LaChance, J., Sadler, R. C., Schnepp, A. C., 2016. Elevated Blood Lead Levels in Children Associated With the Flint Drinking Water Crisis: A Spatial Analysis of Risk and Public Health Response. American Journal of Public Health 106, 283-290.

Hornung, R. W., Lanphear, B. P., Dietrich, K. N., 2009. Age of Greatest Susceptibility to Childhood Lead Exposure: A New Statistical Approach. Environmental Health Perspectives 117, 1309-1312.

Huang, S., Hu, H., Sanchez, B. N., Peterson, K. E., Ettinger, A. S., Lamadrid-Figueroa, H., Schnaas, L., Mercado-García, A., Wright, R. O., Basu, N., Cantonwine, D. E., Hernández-Avila, M., Téllez-Rojo, M. M., 2016. Childhood Blood Lead Levels and Symptoms of Attention Deficit Hyperactivity Disorder (ADHD): A Cross-Sectional Study of Mexican Children. Environmental Health Perspectives 124, 868-874.

Humphries, K. 2015. NSW Government commits more than $13 million to reduce lead levels at Broken Hill. Media release: Kevin Humphries MP Minister for Natural Resources, Lands and Water Minister for Western NSW, 13th February 2015. http://www.epa.nsw.gov.au/resources/MinMedia/EPAMin150213.pdf (accessed 05.01.2017).

Hunt, A., Johnson, D. L., Griffith, D. A., 2006. Mass transfer of soil indoors by track-in on footwear. Science of the Total Environment 370, 360-371.

Jacobs, D. E., Clickner, R. P., Zhou, J. Y., Viet, S. M., Marker, D. A., Rogers, J. W., Zeldin, D. C., Broene, P., Friedman, W., 2002. The prevalence of lead-based paint hazards in U.S. housing. Environmental Health Perspectives 110, A599-A606.

Jeong, S. W., Lee, C. K., Suh, C. H., Kim, K. H., Son, B. C., Kim, J. H., Lee, J. T., Lee, S.

W., Park, Y. B., Lee, J. W., Yu, S. D., Moon, C. S., Kim, D. H., Lee, S. Y., 2014. Blood lead concentration and related factors in Korea from the 2008 National Survey for Environmental Pollutants in Human Body. International Journal of Hygiene and Environmental Health 217, 871-877.

Jones, R. L., Homa, D. M., Meyer, P. A., Brody, D. J., Caldwell, K. L., Pirkle, J. L., Brown, M. J., 2009. Trends in Blood Lead Levels and Blood Lead Testing Among US Children Aged 1 to 5 Years, 1988-2004. Pediatrics 123, e376-e385.

Jusko, T. A., Henderson, C. R., Lanphear, B. P., Cory-Slechta, D. A., Parsons, P. J., Canfield, R. L., 2008. Blood Lead Concentrations < 10 μg/dL and Child Intelligence at 6 Years of Age. Environmental Health Perspectives 116, 243-248.

Keller, B., Faciano, A., Tsega, A., Ehrlich, J., 2017. Epidemiologic Characteristics of Children with Blood Lead Levels ≥45 μg/dL. Journal of Pediatrics 180, 229-234.

Komárek, M., Ettlěr, V., Chrastný, V., Mihaljevič, M., 2008. Lead isotopes in environmental sciences: A review. Environment International 34, 562-577.

Krieger, N., Chen, J. T., Waterman, P. D., Rehkopf, D. H., Subramanian, S. V., 2005. Painting a Turer Picture of US Socioeconomic and Racial/Ethnic Health Inequalities: The Public Health Disparities Geocoding Project. American Journal of Public Health 95, 312-323.

Kristensen, L. J., Taylor, M. P., 2016. Unraveling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. Environmental Geochemistry and Health 38, 1015-1027.

Laidlaw, M. P., Mielke, H. W., Filippelli, G. M., Johnson, D. L., Gonzales, C. R., 2005. Seasonality and children's PbB levels: developing a predictive model using climatic variables and PbB data from Indianapolis, Indiana, Syracuse, New York, and New Orleans, Louisiana (USA). Environmental Health Perspectives 113, 793-800.

Laidlaw, M. P., Mohmmad, S. M., Gulson, B. L., Taylor, M. P., Kristensen, L. J., Birch, G., 2017. Estimates of potential childhood lead exposure from contaminated soil using the US EPA IEUBK Model in Sydney, Australia. Environmental Research 156, 781-790.

Laidlaw, M. A. S., Taylor, M. P., 2011. Review: Potential for childhood lead poisoning in the inner cities of Australia due to exposure to lead in soil dust. Environmental Pollution 159, 1-9.

Laidlaw, M. A. S., Zahran, S., Pingitore, N., Clague, J., Devlin, G., Taylor, M. P., 2014. Identification of lead sources in residential environments: Sydney Australia. Environmental Pollution 184, 238-246.

Lanphear, B. P., Emond, M., Jacobs, D. E., Weitzman, M., Tanner, M., Winter, N. L., Yakir, B., Eberly, S., 1995. A Side-by-Side Comparison of Dust Collection Methods for Sampling Lead-Contaminated House Dust. Environmental Research 68, 114-123.

Lanphear, B. P., Hornung, R., Khoury, J., Yolton, K., Baghurst, P., Bellinger, D. C., Canfield, R. L., Dietrich, K. N., Born, R., Greene, T., Rothenberg, S. J., Needleman, H. L., Schnaas, L., Wasserman, G., Graziano, J., Roberts, R., 2005. Low-Level Environmental Lead Exposure and Children's Intellectual Function: An International Pooled Analysis. Environmental Health Perspectives 113, 894-899.

Lanphear, B. P., Matte, T. D., Rogers, J., Clickner, R. P., Dietz, B., Bornschein, R. L., Succop, P., Mahaffey, K. R., Dixon, S., Galke, W., Rabinowitz, M., Farfel, M., Rohde, C., Schwartz, J., Ashley, P., Jacobs, D. E., 1998. The contribution of lead-contaminated house dust and residential soil to children's blood lead levels: A pooled analysis of 12 epidemiologic studies. Environmental Research 79, 51-68.

Lanphear, B. P., Weitzman, M., Eberly, S., 1996. Racial Differences in Urban Children's Environmental Exposures to Lead. American Journal of Public Health 86, 1460-1463.

Layton, D. W., Beamer, P. I., 2009. Migration of Contaminated Soil and Airborne Particulates to Indoor Dust. Environmental Science & Technology 43, 8199-8205.

Lesjak, M., Jones, T., 2016. Lead Health Report 2015 – Children less than 5 years old in Broken Hill. Population Health Unit, NSW Government, Western NSW & Far West Local Health District. http://leadsmart.nsw.gov.au/wp-content/uploads/2016/12/Broken-Hill-Lead-Health-Report-2015-children-aged-0%E2%80%934.pdf (accessed 26.07.17).

Lesjak, M., Jones, T., 2015. Lead Health Report 2014 – Children less than 5 years old in Broken Hill. Population Health Unit, NSW Government, Western NSW & Far West Local Health District. http://leadsmart.nsw.gov.au/wp-content/uploads/2016/12/Broken-Hill-Lead-Health-Report-2014-children-aged-0%E2%80%934.pdf (accessed 26.07.17).

Levallois, P., St-Laurent, J., Gauvin, D., Courteau, M., Prevost, M., Campagna, C., Lemieux, F., Nour, S., D'Amour, M., Rasmussen, P. E., 2014. The impact of of drinking water, indoor dust and paint on blood lead levels of children aged 1–5 years in Montréal (Québec, Canada). Journal of Exposure Science and Environmental Epidemiology 24, 185-191.

Liu, J., Ai, Y., McCauley, L., Pinto-Martin, J., Yan, C., Shen, X., Needleman, H., 2012. Blood lead levels and associated sociodemographic factors among preschool children in the South Eastern region of China. Paediatric and Perinatal Epidemiology 26, 61-69.

Liu, J., Liu, X., Wang, W., McCauley, L., Pinto-Martin, J., Wang, Y., Li, L., Yan, C., Rogan, W. J., 2014. Blood Lead Concentrations and Children's Behavioral and Emotional Problems A Cohort Study. JAMA Pediatrics 168, 737-745.

Liu, J., Wang, Y., Yan, C., Liu, X., 2013. Impact of Low Blood Lead Concentrations on IQ and School Performance in Chinese Children. PloS ONE 8, e65230. https://doi.org/10.1371/journal.pone.0065230

Lyle, D. M., 2001. NSW LEAD MANAGEMENT PROGRAM IN BROKEN HILL. NSW Public Health Bulletin 12, 165-167.

Lyle, D. M., Phillips, A. R., Balding, W. A., Burke, H., Stokes, D., Corbett, S., Hall, J., 2006. Dealing with lead in Broken Hill−Trends in blood lead levels in young children 1991−2003. Science of the Total Environment 359, 111-119.

Mahaffey, K. R., Annest, J. L., Roberts, J., Murphy, R. S., 1982. National Estimates of Blood Lead Levels: United States, 1976–1980 — Association with Selected Demographic and Socioeconomic Factors. New England Journal of Medicine 307, 573-579.

Malcoe, L. H., Lynch, R. A., Keger, M. C., Skaggs, V. J., 2002. Lead sources, behaviors, and socioeconomic factors in relation to blood lead of native american and white children: a community-based assessment of a former mining area. Environmental Health Perspectives

110, 221-231.

Markus, J.A., McBratney, A.B., 1996. An urban soil study: heavy metals in Glebe, Australia. Aust. J. Soil Res. 34, 453-465.

McMichael, A. J., Baghurst, P. A., Wigg, N. R., Vimpani, G. V., Robertson, E. F., Roberts, R. J., 1988. Port Pirie Cohort Study: Environmental Exposure to Lead and Children's Abilities at the Age of Four Years. New England Journal of Medicine 319, 468-475.

McMichael, A. J., Vimpani, G. V., Robertson, E. F., Baghurst, P. A., Clark, P. D., 1986. The Port Pirie cohort study: maternal blood lead and pregnancy outcome. Journal of Epidemiology and Community Health 40, 18-25.

Mielke, H. W., Covington, T. P., Mielke, P. W., Wolman, F. J., Powell, E. T., Gonzales, C. R., 2011. Soil intervention as a strategy for lead exposure prevention: The New Orleans lead-safe childcare playground project. Environmental Pollution 159, 2071-2077.

Mielke, H. W., Gugas, D., Mielke, P. W., Smith, K. S., Smith, S. L., Gonzales, C. R., 1997. Associations between Soil Lead and Childhood Blood Lead in Urban New Orleans and Rural Lafourche Parish of Louisiana. Environmental Health Perspectives 105, 950-954.

Mielke, H. W., Gonzales, C. R., Powell, E., Jartun, M., Mielke, P. W., 2007. Nonlinear association between soil lead and PbB of children in metropolitan New Orleans, Louisiana: 2000-2005. Science of the Total Environment 388, 43-53.

Moody, H., Darden, J. T., Pigozzi, B. W., 2016. The Racial Gap in Childhood Blood Lead Levels Related to Socioeconomic Position of Residence in Metropolitan Detroit. Sociology of Race and Ethnicity 2, 200-218.

Morals, L. S., Gutierrez, P., Escarce, J. J., 2005. Demographic and Socioeconomic Factors Associated with Blood Lead Levels among Mexican-American Children and Adolescents in the United States. Public Health Report 120, 448-454.

National Environmental Protection Measure (NEPM), 2013. Schedule B1: Guideline on Investigation for Soil and Groundwater. http://www.nepc.gov.au/system/files/resources/93ae0e77-e697-e494-656f-afaaf9fb4277/files/schedule-b1-guideline-investigation-levels-soil-and-groundwater-sep10.pdf. (accessed 24.10.17)

National Toxicology Program (NTP), 2012. NTP MONOGRAPH ON HEALTH EFFECTS OF LOW-LEVEL LEAD. https://ntp.niehs.nih.gov/ntp/ohat/lead/final/monographhealtheffectslowlevellead_newissn_508.pdf (accessed 19.12.17).

Needleman, H. L., 2004. LEAD POISONING. Annual Review of Medicine 55, 209-222.

Ngueta, G., 2014. Racial disparities in children's blood lead levels: Possible implication of divalent metal transporter 1. Medical Hypotheses 82, 71-73.

Pelc, W., Pawlas, N., Dobrakowski, M., Kasperczyk, S., 2016. Environmental and socioeconomic factors contributing to elevated blood lead levels in children from an industrial area of Upper Silesia. Environmental Toxicology and Chemistry 35, 2597-2603.

Pieper, K. J., Tang, M., Edwards, M. A., 2017. Flint Water Crisis Caused By Interrupted

Corrosion Control: Investigating “Ground Zero” Home. Environmental Science & Technology 51, 2007-2014.

Potula, V., Hegarty-Steck, M., Hu, H., 2001. Blood Lead Levels in Relation to Paint and Dust Lead Levels: The Lead-Safe Cambridge Program. American Journal of Public Health 91, 1973-1974.

Queensland Government, 2011. LEAD SCREENING PROGRAM 2010—A report into the results of a blood lead screening program of 1-4 year old children in Mount Isa, Queensland. https://www.health.qld.gov.au/__data/assets/pdf_file/0016/430180/lead_report_2010.pdf (accessed 31.07.17)

Rabito, FA. 1998. Childhood lead poisoning in high risk residents of Orleans Parish. Tulane University, Unpublished Doctoral Thesis.

Roberts, J. W., Wallace, L. A., Camann, D. E., Dickey, P., Gilbert, S. G., Lewis, R. G., 2009. Monitoring and Reducing Exposure of Infants to Pollutants in House Dust. In Whitacre, D. M. (Ed.), Review of Environmental Contamination and Toxicology. Springer, pp. 1-39.

Rodrigues, E. G., Bellinger, D. C., Valeri, L., Hasan, M. O. S. I., Quamruzzaman, Q., Golam, M., Kile, M. L., Christiani, D. C., Wright, R. O., Mazumdar, M., 2016. Neurodevelopmental outcomes among 2- to 3-year-old children in Bangladesh with elevated blood lead and exposure to arsenic and manganese in drinking water. Environmental Health 15: 44. https://doi.org/10.1186/s12940-016-0127-y.

Rouillon, M., Harvey, P. J., Kristensen, L. J., George, S. G., Taylor, M. P., 2017. VegeSafe: A community science program measuring soil-metal contamination, evaluating risk and providing advice for safe gardening. Environmental Pollution 222, 557-566.

Sadler, R. C., LaChance, J., Hanna-Attisha, M., 2017. Social and Built Environmental Correlates of Predicted Blood Lead Levels in the Flint Water Crisis. American Journal of Public Health 107, 763-769.

Safruk, A. M., McGregor, E., Whitfield Aslund, M. L., Cheung, P. H., Pinsent, C., Jackson, B. J., Hair, A. T., Lee, M., Sigal, E. A., 2017. The influence of lead content in drinking water, household dust, soil and paint on blood lead levels of children in Flin Flon, Manitoba and Creighton, Saskatchewan. Science of the Total Environment 593-594, 202-210.

Schwartz, J., 1994. Low-Level Lead Exposure and Children′s IQ: A Metaanalysis and Search for a Threshold. Environmental Research 65, 42-55.

Searle, A. K., Baghurst, P. A., van Hooff, M., Sawyer, M. G., Sim, M. R., Galletly, C., Clark, L. S., McFarlane, A. C., 2014. Tracing the long-term legacy of childhood lead exposure: A review of three decades of the Port Pirie Cohort study. NeuroToxicology 43, 46-56.

Simon, D. L., Maynard, E. J., Thomas, K. D., 2007. Living in a sea of lead — changes in blood- and hand-lead of infants living near a smelter. Journal of Exposure Science and Environmental Epidemiology 17, 248-259.

Skerfving, S., Löfmark, L., Lundh, t., Mikoczy, Z., Strömberg, U., 2015. Late effects of low blood lead concentrations in children on school performance and cognitive functions. NeuroToxicology 49, 114-120.

Solomon, R. J., 1988. The richest lode: Broken Hill 1883-1988. Hale & Iremonger, Sydney.

Son, J. Y., Lee, J., Paek, D., Lee, J. T., 2009. Blood levels of lead, cadmium, and mercury in the Korean population: Results from the Second Korean National Human Exposure and Bio-monitoring Examination. Environmental Research 109, 738-744.

South Australia (SA) Health, 2017. Port Pirie Blood Lead Levels. http://www.sahealth.sa.gov.au/wps/wcm/connect/7aa9a380426ce340ac97aeadc5e910c3/Port+Pirie+Blood+Lead+Levels+Analysis+for+the+first+half+of+2017+%281+January-30+June+2017%29.pdf?MOD=AJPERES&CACHEID=7aa9a380426ce340ac97aeadc5e910c3 (accessed 30.10.17).

Staes, C., Matte, T., Copley, C. G., Flanders, D., Binder, S., 1994. Retrospective study of the impact of lead-based paint hazard remediation on children's blood lead levels in St. Louis, Missouri. American Journal of Epidemiology 139, 1016-1026.

Thompson, A. J., Hamlet, W. M., Thomas, J., 1893. Report of Board Appointed to Inquire into the Prevalence and Prevention of Lead Poisoning at the Broken Hill Silver-Lead Mines to the Honorable the Minister for Mines and Agriculture. New South Wales: Legislative Assembly. New South Wales.

Tong, S., Baghurst, P., McMichael, A., Sawyer, M., Mudge, J., 1996. Lifetime exposure to environmental lead and children's intelligence at 11-13 years: the Port Pirie cohort study. BMJ 312, 1569. https://doi.org/10.1136/bmj.312.7046.1569.

U.S. Department of Housing and Urban Development (US HUD), 2017. Revised Dust-Lead Action Levels for Risk Assessment and Clearance; Clearance of Porch Floors. https://www.hud.gov/sites/documents/LEADDUSTCLEARANCE.PDF (accessed 13.01.18).

von Lindern, I., Spalinger, S., Stifelman, M. L., Stanek, L. W., Bartrem, C., 2016. Estimating Children’s Soil/Dust Ingestion Rates through Retrospective Analyses of Blood Lead Biomonitoring from the Bunker Hill Superfund Site in Idaho. Environmental Health Perspectives 124, 1462-1470.

Western NSW Public Health Unit, 1994. Risk of factors for blood lead levels in preschool children in Broken Hill 1991-1993.

Western NSW Health, 2017. Lead Report 2016: Broken Hill children less than 5 years old, Revised (2016 Census). http://leadsmart.nsw.gov.au/wp-content/uploads/2017/12/2016-Lead-Report-Revised-Census-2016.pdf (accessed 24.01.18).

White, B. M., Bonilha, H. S., Ellis, C. Jr., 2016. Racial/Ethnic Differences in Childhood Blood Lead Levels Among Children <72 Months of Age in the United States: a Systematic Review of the Literature. Journal of Racial and Ethnic Health Disparities 3, 145-153.

Willmore, A., Sladden, T., Bates, L., Dalton, C. B., 2006. Use of a geographic information system to track smelter-related lead exposures in children: North Lake Macquarie, Australia, 1991–2002. International Journal of Health Geographics 5: 30. https://doi.org/10.1186/1476-072X-5-30.

Wilson, D., Esterman, A., Lewis, M., Roder, D., Calder, I., 1986. Children's Blood Lead Levels in the Lead Smelting Town of Port Pirie, South Australia. Archives of Environmental Health 41, 245-250.

Woodward, O. H., 1965. A review of the Broken Hill Lead-Silver-Zinc Industry. West Publishing Corporation Pty. Ltd, Sydney, NSW.

Xie, X., Ding, G., Cui, C., Chen, L., Gao, Y., Zhou, Y., Shi, R., Tian, Y., 2013. The effects of low-level prenatal lead exposure on birth outcomes

Yang, K., Cattle, S. R., 2015. Bioaccessibility of lead in urban soil of Broken Hill, Australia: A study based on in vitro digestion and the IEUBK model. Science of the Total Environment 538, 922-933.

Yang, K., Cattle, S. R., 2017. Effectiveness of cracker dust as a capping material for Pb-rich soil in the mining town of Broken Hill, Australia. Catena 148, 81-91.

Young, A. R. M., Bryant, E. A., Winchester, H. P. M., 1992. The wollongong lead study: an investigation of the blood lead levels of pre-school children and their relationship to soil lead levels. Australian Geographer 23, 121-133.

Zahran, S., Mielke, H. W., Weiler, S., Gonzales, C. R., 2011. Nonlinear associations between blood lead in children, age of child, and quantity of soil lead in metropolitan New Orleans. Science of the Total Environment 409, 1211-1218.

Zhang, B., Xia, W., Li, Y., Bassig, B. A., Zhou, A., Wang, Y., Li, Z., Yao, Y., Hu, J., Du, X., Liu, J., Xue, W., Ma, Y., Pan, X., Peng, Y., Zheng, T., Xu, S., 2015. Prenatal exposure to lead in relation to risk of preterm low birth weight: A matched case–control study in China. Reproductive Toxicology 57, 190-195.

Zhu, M., Fitzgerald, E. F., Gelberg, K. H., Lin, S., Druschel, C. M., 2010. Maternal Low-Level Lead Exposure and Fetal Growth. Environmental Health Perspectives 118, 1471-1475.

Chapter 5: Influences of contemporary mining activities on childhood blood Pb and dust Pb deposits in Broken Hill

Chapter Five presents the following paper:

- Paper Four: Blood lead effects of child exposure to contemporary emissions in an Australian mining community. **Dong, C.,** Taylor, M. P., Zahran, S.
  Draft for submission to *Environmental Health Perspectives*

The results from the geochemical and SEM analyses in Chapter Three showed that current mining activities in Broken Hill were a significant source of contemporary outdoor dust Pb deposition (μg/m^2/day) across the city's urban environment. However, the impact of current mining activities on dust Pb deposition was not quantitatively evaluated. Chapter Five addresses this knowledge gap via generalised linear regression modelling of contemporary (2012–2016) dust Pb deposits along with corresponding Pb ore production from Broken Hill.

Statistical analyses in Chapter Four revealed that blood Pb was associated with soil Pb and indoor dust Pb. However, the soil and indoor dust contamination in Broken Hill is the consequence of legacy and ongoing emissions from mining operations. This chapter aims to specify the contribution of current emissions to childhood blood Pb in Broken Hill. To investigate this, we leveraged information on the direction of prevailing winds in the region. After considering of the covariates influencing blood Pb in Broken Hill identified in Chapter Four, contemporary blood Pb was found to decrease with distance away from current mining operations. In terms of the impact of current emissions, we expect that contemporary emissions are acted upon more strongly by prevailing winds the negative effect of distance on blood Pb levels should be steeper for downwind versus upward children. Additionally, children proximate to the local mining operations residing in the direction of prevailing winds ought to have higher blood Pb levels and an increased risk of elevated blood Pb (≥5 μg/dL). Furthermore, blood Pb levels ought to correlate with Broken Hill Pb ore production. In 2009 Broken Hill was visited by a massive dust storm, and for the two years following, the observed trend of soil Pb concentrations decreasing with distance appeared to diminish in the region. In other words, if legacy exposure is the only source of blood Pb outcomes in the Broken Hill region, then the blood Pb-distance gradient should diminish in a similar fashion to the soil Pb-distance gradient. The generalised linear regression analysis of the contemporary outdoor dust Pb deposits corroborate the mechanism of current emissions as a significant source of variation in blood Pb concentrations. The relevant outcomes of this

research reveal the importance of controlling ongoing emissions to bring local blood Pb levels down.

Blood lead effects of child exposure to contemporary emissions in an Australian mining community−Broken Hill

Chenyin Dong,[1*] Mark Patrick Taylor,[1,2] Sammy Zahran,[3]

[1]Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, Sydney, New South Wales, Australia

[2]Energy and Environmental Contaminants Research Centre, Macquarie University, Sydney, New South Wales, Australia

[3]Department of Economics, Centre for Disaster and Risk Analysis, Colorado State University, Fort Collins, Colorado, USA

* Corresponding author:

Phone: +61 9850 4221; email: chenyin.dong@hdr.mq.edu.au

Background:

The Broken Hill community in New South Wales is home to Australia's oldest silver–zinc–lead (Ag–Pb–Zn) mine. As with other mining communities, child exposure to Pb is a serious hazard. Among children in Broken Hill under five years of age who were sampled (n=4,852) between 2011−2015, 42.6% presented with elevated blood Pb (PbB) (≥5 μg/dL). The precise source of Pb exposure for children, such as natural soil enrichment, legacy deposition and current mining emissions, is a subject of considerable debate.

Objective:

To test whether contemporary mining emissions independently affect child PbB outcomes in Broken Hill.

Methods:

To quantify the PbB effects of child exposure to current mining emissions, we first analyse: 1) child PbB outcomes from 2011–2015 as a function of residential distance to mining operations, leveraging wind direction as an exogenous source of variation in current emissions exposure; and 2) child PbB outcomes for a subset of children with measured residential soil Pb (PbS) to address confusion regarding legacy exposure risk. Second, to corroborate the mechanism of current emissions as a significant source of variation in child PbB outcomes, we analyse: 3) aggregate child PbB outcomes as a function of ore production at the mine over time; 4) a natural experiment involving the Australian dust storm of 2009, testing whether the PbB-distance gradient is affected by the re-distribution of legacy sources of Pb exposure (i.e., PbS) caused by the storm; and 5) the effects of distance and ore production on dust Pb deposits throughout the city.

Results:

Indicative of a current emissions effect, we find that downwind children proximate to the mine have substantially higher PbB outcomes than similarly distant upwind children. The impact of housing age (indicative of Pb-paint exposure) is negligible among children residing in the direction of prevailing winds, as current emissions appear to overwhelm this legacy exposure risk. Intuitively, the housing age effect is a more significant determinant of child PbB outcomes for upwind children. These relationships hold with the inclusion of PbS in statistical models. We find striking correlations between average annual child PbB and Pb ore production at the mine. Across subsets of children, PbB levels respond near unit elastically with production activities at the mine. Corroborating the current emissions channel, we find

that the PbB-distance gradient is statistically undisturbed following the dust storm of 2009. Finally, we find that dust Pb depositions across the city increase significantly with proximity to and production activities at the mine.

Conclusions:

Across an ensemble of tests, we find consistent evidence that child PbB outcomes in Broken Hill are significantly impacted by exposure to current mining emissions.

Keywords

Blood lead; soil; dust; mining emission; residential distance; housing age

1. Introduction

Broken Hill, in far west New South Wales (NSW), Australia, has the world's largest silver–lead–zinc (Ag–Pb–Zn) ore deposit (Solomon, 1988). The ore deposit was discovered in 1883 and has been mined continuously ever since (Kristensen and Taylor, 2016), with more than 200 million tonnes of ore extracted (Perilya Limited, 2015; Morland and Webster, 1998). Smelting of ore was conducted from 1886 to 1897 until operations were relocated to Port Pirie due to a lack of local fuel sources for smelting (Woodward, 1965; Solomon, 1988). Between 1886 to 1897 an estimated 11,000−18,400 tonnes of Pb was emitted by smelting activities (van Alphen, 1991). Contemporary atmospheric Pb emissions in Broken Hill during the period 1998−2016 are estimated 167 tonnes (Supplementary Table S1).

Mining and smelting activities in Broken Hill have left a legacy of widespread Pb contamination in the surrounding residential community. A series of studies about sources and pathways of environmental Pb and blood lead (PbB) were conducted in the 1990s (e.g., Woodward-Clyde Pty Ltd, 1993; Gulson et al., 1994a, b, c; Boreland et al., 2002). However, the precise source of exposure—natural enrichment in soils, legacy depositions and/or contemporary emissions—and its relationship to elevated PbB remain a subject of much debate (Kristensen and Taylor 2016; Dong and Taylor, 2017). Similar disputes about the sources of Pb have prevailed in other mining and smelting communities as well, stymying effective intervention and remedial actions (Taylor et al. 2010; Taylor, 2012; Mackay et al. 2013; Spear et al., 2015; Sullivan 2014; Kristensen and Taylor, 2016).

In Broken Hill, the prevailing argument has been that current mining operations were not the dominant source of contamination compared to other sources (Woodward-Clyde Pty Ltd, 1993). Stable Pb isotopic composition analysis conducted in the early 1990s showed that childhood PbB in Broken Hill was predominantly derived from the local ore body, but some individuals had a dominant source (up to 50%) of Pb from gasoline or paint at the time (Gulson et al., 1994a). Despite the wealth of research examining the Pb problem in Broken Hill, there remains a significant knowledge gap regarding whether current mining emissions meaningfully affect childhood PbB risk in the city, which could in turn impact the effectiveness of the relevant remediation program aiming to reduce Pb exposure in the region.

Yang and Cattle (2015) reported that Broken Hill total soil Pb (PbS) concentrations, an indicator of legacy emissions, and PbS bioaccessibility were elevated and appeared to be linked to childhood PbB levels according to Integrated Exposure Uptake Biokinetic (IEUBK)

modelling. Moreno et al. (2009) found that particles <10 μm (PM_{10}) collected from the surrounding area of Broken Hill were sourced from local desert soils, indicating that soil resuspension processes are active and an important component of particulate sources. In addition, contemporary atmospheric Pb sources in Broken Hill remain elevated, with Pb-in-air levels averaging 244 ng/m^3 (range from 26 to 707 ng/m^3) between 2012-2016 (Zhou et al., 2017) and 28,000 kg of mine-related Pb emissions being released in 2015/2016 (NPI, 2017a). Finally, dust deposited in and around the urban environment contain elevated levels of a range of mine-related contaminants (e.g. Ag, As, Cd, Pb, Zn) (Taylor et al., 2014; Dong et al., 2015; Dong and Taylor, 2017). Nevertheless, specifying the relative contributions from multiple potential environmental sources (e.g. current emission, legacy contamination) to PbB exposure remains a mystery that has stymied targeted clean-up and prevention programs for decades (Taylor and Schniering, 2010; Spear et al., 2015).

This study aims to quantify the independent effects of current mining emissions on childhood PbB. Toward this aim, we first investigate the effect of child residential proximity to mining operations under prevailing wind conditions. In terms of measuring the impact of current emissions, our expectation is that children proximate to the mine residing in the direction of prevailing winds ought to have higher PbB levels and an increased risk of elevated PbB (i.e. ≥5 μg/dL). Second, for a subset of children, we investigate the effect of current emissions on child PbB outcomes while controlling for residential PbS concentrations, a well-established indicator of legacy emissions. Third, we analyse annual variation in child PbB as a function of mining operations in terms of the tonnages of ore produced per annum. Here we test whether the child PbB levels behave dose-responsively according to the intensity of mining activities over decades. Fourth, exploiting the Australian dust storm of 2009 as a natural experiment for the re-distribution of legacy sources of Pb exposure (i.e., PbS), we test whether child PbB-distance gradient was disturbed by the dust storm. Fifth, we aim to corroborate the role played by contemporary emissions as an exposure pathway via analyses of dust Pb (PbD) around the city, linking PbD sampling sites proximity and mining production activities to PbD outcomes. The ensemble of analyses performed can inform future policy initiatives, with respect to management strategies for mitigating child exposure to current mining emissions, in order to improve child welfare in Broken Hill.

2. Methods

2.1 Study area

Broken Hill (Figure 1) is situated approximately 1,100 km west of Sydney in far-west New South Wales (NSW). The city experiences a hot and arid climate, with an annual precipitation and wind speed (9 am) of 260 mm and 13 km/h, respectively (Bureau of Metrology, 2016a). Prevailing winds blow from the south to north across the city (Bureau of Metrology, 2016b). Broken Hill has approximately 18,900 residents, of which 7.5% are of Aboriginal identity (ABS, 2017). An estimated 218 children are born in Broken Hill every year (ABS, 2017).

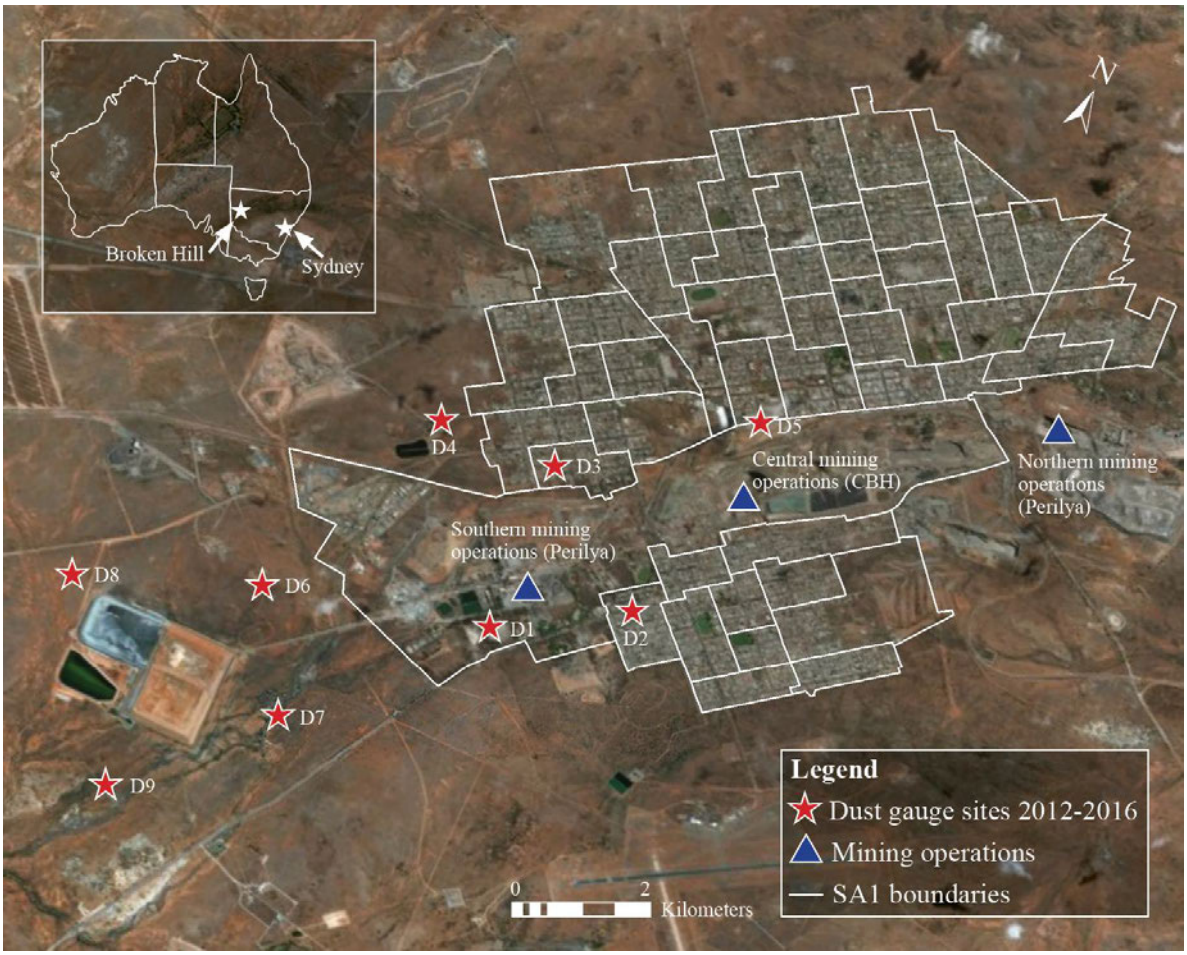


Figure 1. Broken Hill with 52 statistical areas of Level 1 (SA1 areas), mining companies and the dust gauge sites around the active southern and central mining operations. The boundaries of the statistical areas are from the ABS (2016).

The Broken Hill orebody, known locally as the "Line of Lode", was formed about 1.7 billion years ago (Page et al., 2005), and has been mined in recent times by two mining companies: CBH Rasp Mine and Perilya Limited (Figure 1). Perilya Limited has northern and southern mining operations in Broken Hill (hereafter referred to as the northern and southern operations), while CBH Rasp Mine mines the central area of the 'Line of Lode' (hereafter referred to as the central operations). After more than 130 years of mining, all extractive

operations are now carried out underground with the ore brought to the surface for processing and concentrating.

The reported atmospheric Pb emissions for CBH Rasp Mine and Perilya Limited in 2015/2016 were 0.095 and 28 tonnes, respectively (NPI, 2017b, c). Since 2011, atmospheric Pb emissions have averaged to about 30 tonnes per year, ranking Perilya Limited as the 3rd largest emitter of atmospheric Pb in Australia (NPI, 2017a). The uncovered tailings dumps associated with the central operations were considered one of the primary sources of dust Pb emissions in the early 1990s (Gulson et al., 1994c), with these unconsolidated wastes being capped at the end of the 1990s (Broken Hill Environmental Lead Program, 2016). The northern operations have been inactive since 1993 (ABC, 2016). Therefore, the active southern operations of Perilya Limited form the focus of this investigation.

2.2 Data sources

2.2.1 Child Blood lead (PbB) and Soil Pb (PbS) Data

We obtained PbB and PbS data from the Broken Hill Child & Family Health Centre (BHCFHC) for the period 2011–2015. Data use and analysis was subject to ethics approval from NSW Health and Macquarie University. Since October 2008, children have had their PbB screened using the finger-prick method (Lesjak and Jones, 2016). Before 2008 PbB was tested using the venous sample method. Thus, the majority of the PbB data for the period 2011-2015 was collected via the finger-prick method and analysed using a LeadCare® II instrument. The LeadCare® II is used widely for blood Pb screening and has lower and upper detections limits of 3.3 µg/dL and 65 µg/dL (Magellan Diagnostics, 2015). The finger-prick method is considered comparable to venous PbB sampling (Boreland et al., 2015). Where a child's blood Pb test was >25 µg/dL, a second test was conducted using venous sampling. The dataset analysed contains some individual cases where multiple blood Pb tests were taken from the same child in a year. Repeat testing was offered to children who initially presented with a blood Pb >10 µg/dL. The PbB data analysed for this study was collected by the BHCFHC personnel and reported as µg/dL. In addition to PbB information, the BHCFHC data contain information on the residence of each child, date of blood sample collection, child age (0 to 5 years), sex (male=1; female=0) and Aboriginality identity (Aboriginal=1; non-Aboriginal=0). For a subset of children (n=317), information was available on the concentration of total Pb (mg/kg) in residential soils. In Broken Hill, three to five soil samples were collected from the yard surface at a depth of 0–5 cm around a resident's home. Samples were processed by an accredited laboratory using standard acid digestion procedures. While

the individual sample analysis information is not available, Australian laboratories typically process soils using an acid extractable digest (e.g. aqua regia comprising 1:3 nitric acid:hydrochloric acid). Current laboratories are also required for NATA (National Association of Testing Authorities (NATA), Australia) purposes to run certified reference materials or internal laboratory standards, duplicates, replicates, blanks and matrix spikes. The current requirements for NATA laboratories are that analytical accuracy must be within 75-120% of the reference value, and for Pb this is typically better at ±10% of the reference materials. Moreover, the PbS has been deemed adequate by the BHCFHC for determining Pb exposure mitigation advice and intervention procedures at a child's home. Soil Pb at each residence is calculated as the average of the samples taken. The distance from a child's residence to the southern operations is measured in kilometres.[1]

2.2.2 Housing Age Data

With information in hand on the residential location of each child at the time of blood draw in the BHCFHC data, we then obtained parcel information from the Broken Hill Environment Protection Authority (NSW EPA) to determine the housing age of child residence. Previous studies have shown that older houses have elevated environmental Pb exposure and PbB concentrations, which is normally caused by the use of lead-based paints (Staes et al., 1994; Gulson et al., 1995; Markus and McBratney, 1996; Potula et al., 2001; Jacobs et al., 2002; Laidlaw and Taylor et al., 2011; Rouillon et al., 2017). The purpose here is to proxy for possible effects of housing age in Broken Hill. In analyses of child PbB that follow, we include an indicator variable =1 if the child's residence was constructed before 1940, and 0 otherwise. This time division is corroborated in statistical models, showing that children residing in homes built before 1940 are at a substantially higher risk of elevated PbB levels compared to children residing in homes built after 1940.[2]

[1] In all analyses that follow, we estimate the direction and distance of each home and dust gauge site to the southern mining operations of Perilya Limited. Bearing was used to identify houses under prevailing and non-prevailing wind directions in combination with wind rose data for Broken Hill during 2011-2015 (Supplementary Figure S2). The prevailing wind direction is from the SSE to SSW. The other directions are defined as being in the non-prevailing wind direction (hereafter referred as downwind).

[2] We considered various operationalisations of Pb-based paint exposure risk, including before and after 1970, and an ordinal version used by the municipality of pre-1914, 1915-1939, 1940 to 1970, and ≥1971. Of all operations tested, the pre/post-1940 division provided the best possible statistical signal of Pb-based paint exposure risk. All results pertaining to contemporary emissions exposure are robust to all Pb-based paint operations.

2.2.3 Socio-Economic Index for Areas (SEIFA)

Socio-economic status is a known predictor of child PbB outcomes (Mahaffey et al., 1982; Krieger et al., 2003). In the absence of socioeconomic information specific to each child, we match the latitude and longitude coordinates of each home to neighbourhood data (Statistical Areas, Level 1) from the Australian Bureau of Statistics on the Index of Relative Socio-Economic Advantage and Disadvantage (IRSAD). The IRSAD ranks areas on a scale from most disadvantaged (low index) to advantaged (high index). The IRSAD composite includes variables of income, education, employment, occupation, housing and other indicators of relative advantage and disadvantage (ABS, 2013). In Broken Hill, there are 52 SA1 neighbourhoods (Figure 1).

2.2.4 Pb Ore Production Data

We extracted Broken Hill ore production data (measured in tonnages) between 1991–2013 from Mudd et al. (2017). The data reflects the intensity of mining activities and is organised both quarterly and annually. The annual series is used as a predictor of average annual child PbB (see Eq. 5), and the quarterly ore production data are used as a predictor of dust Pb (see Eq. 7).

2.2.5 Dust Gauge Data

Dust Pb deposition monitoring data from Perilya Limited (2012–present) was extracted from the company's environmental reports (Perilya Limited, 2017). Dust sampling and analysis were undertaken in accordance with Australian standard methods (Standard Australia, 2003). The company's environmental monitoring data are relatively close to the southern operations, as dictated by the terms of its Environment Protection Licence (NSW EPA, 2017). By contrast, Dong and Taylor's (2017) PbD data cover the broader community, with the available data covering only one calendar year (Nov 2014 to Nov 2015). Previous studies have shown that PbD loadings decreased in distance from mining operations in Broken Hill (Dong and Taylor, 2017), as well as in other mining and smelting communities (e.g. Benin et al., 1999; Taylor et al., 2010; Soto-Jiménez and Flegal, 2011; Qu et al., 2012).

To corroborate analyses that indicate contemporary emissions are involved in deleterious child PbB outcomes, we analyse PbD loadings at dust gauge sites as a function of both distance (in kilometres) to the active southern mine operations and ore production intensity (tonnes).

2.2.6 Meteorological Data

Given that local weather conditions can influence atmospheric Pb concentrations and the transport of contaminant-rich dust, weather variables from 2011–2015 are included as controls in PbD loading models. Control variables assessed include wind direction, wind speed and rainfall (Bureau of Metrology, 2017).

2.3 Statistics analysis

2.3.1 Child Blood Pb on Distance and Wind

We begin by estimating a generalised linear model of the PbB level of child i in neighbourhood j at time t:

$$\ln(PbB_{ijt}) = \beta_0 + \beta_1(\ln D_{it}) + \beta_2 h_{it} + \beta_3 A_{it} + B_4 A_{it}^2 + \beta_4 r_{it} + \beta_5 s_{it} + \beta_6 SES_{jt} + \varepsilon_{ijt} \quad (1)$$

where, D_{it} is the distance (in kilometres) from the child's home to the centroid of the southern operations, h_{it} is an indicator variable =1 if the home a child resides in was constructed before 1940, A_{it} is the child's age at the time of survey with a quadratic term to account for the known non-linear effect of age on child PbB outcomes (Zahran et al., 2011), r_{it} is = 1 if the child is of Aboriginal identity, s_{it} is the child's sex = 1 if the child is male, SES_{jt} is the Index of Relative Socio-Economic Advantage and Disadvantage (IRSAD) in a child's neighbourhood, and ε_{ijt} is the disturbance term with standard normal distribution. By taking the natural log of both PbB_{ijt} and D_{it}, the coefficient $\beta_1$has the interpretation of elasticity, where a one percent change in D_{it} induces a percent change in PbB_{ijt}. All other coefficients have the interpretation of a semi-elasticity, where a unit change in an independent variable produces a percent change in the in PbB_{ijt}.

While the direction of the estimated parameter β_1 in Eq. (1) is indicative of an emissions exposure effect, it imperfectly distinguishes contemporary versus legacy emissions exposure due to the fact that both sources of exposure decline with distance from the mine. To distinguish current and legacy emissions, we leverage information on the direction of prevailing winds in Broken Hill (see Supplementary Figure S2). Given that contemporary emissions are more likely to be entrained more strongly by prevailing winds the negative effect of distance on child PbB should be steeper for downwind versus upward children. Stovern et al.'s (2016) study examining the association between PbD deposition, distance and atmospheric transport has shown that PbD loadings decrease more rapidly under the prevailing wind direction compared to other wind directions after adjusting for topographic

factors. Stated differently, if current emissions matter, then children proximate to the mine and in the direction of prevailing winds ought to have higher PbB levels than similarly proximate children residing in the non-prevailing wind direction (i.e. all the other directions besides the prevailing wind direction; hereafter referred as upwind). If, however, the PbB outcomes of mine-proximate upwind versus downwind children are statistically indistinguishable, then current emissions are unlikely involved in PbB outcomes. Finally, if contemporary emissions matter, we expect that the positive effect of residing in an older home should attenuate for children living downwind versus upwind, as contemporary emissions overwhelm the effect of Pb-based paint exposure (housing age). In pursuit of these hypotheses, we estimate the following regression:

$$\ln(PbB_{ijt}) = \beta_0 + \beta_1(\ln D_{it}) + \beta_2 h_{it} + \beta_3 w_{it} + \delta_1(\ln D_{it} \times w_{it}) + \delta_2(h_{it} \times w_{it}) + \beta_4 A_{it} + B_5 A_{it}^2 + \beta_6 r_{it} + \beta_7 s_{it} + \beta_8 SES_{jt} + \varepsilon_{ijt} \quad (2)$$

all terms carry from Eq. (1), with the exception of w_{it} which is = 1 if a child resides in the direction of prevailing winds. The estimated coefficients of interest are δ_1 and δ_2, reflecting the effects distance and housing age by whether or not a child is in the direction of prevailing winds. Our expectation is that δ_1 should be negative, indicating a steeper residential proximity effect for downwind versus upwind children, and that δ_2 should be negative, indicating attenuation of the Pb-based paint exposure effect for children living downwind.

2.3.2 Elevated Child Blood Pb on Distance and Wind

The Australian upper maximum guideline for child safety from lead exposure is 5 μg/dL (NHMRC, 2015). Following the same sequence of tests in 2.3.1, we estimate the probability of child i in neighbourhood j at time t having an elevated PbB ≥5 (*EPbB*), with the following binary generalised linear model:

$$\text{Prob}\left(EPbB_{ijt} = 1 | D_{it}, h_{it}, A_{it}, r_{it}, s_{it}, SES_{jt}\right) = \Lambda\left[\beta_0 + \beta_1 D_{it} + \beta_2 h_{it} + \beta_3 A_{it} + B_4 A_{it}^2 + \beta_4 r_{it} + \beta_5 s_{it} + \beta_6 SES_{jt}\right] \quad (3)$$

where, $\Lambda[\cdot]$ is the CDF of the logistic distribution, with all other terms carrying from Eq. (1). In the presentation of logit model results, we exponentiate estimated coefficients to give the meaning of an odds ratio. Again, given that β_1 in Eq. (3) is inconclusive with respect to the research question of the potential effects of contemporary emissions on the risk of elevated child PbB (*EPbB*), we also estimate the following regression:

$$\text{Prob}(EPbB_{ijt} = 1|D_{it}, h_{it}, w_{it}, A_{it}, r_{it}, s_{it}, SES_{jt})$$
$$= \Lambda[\beta_0 + \beta_1 D_{it} + \beta_2 h_{it} + \beta_3 w_{it} + \delta_1(D_{it} \times w_{it}) + \delta_2(h_{it} \times w_{it}) + \beta_4 A_{it} + B_5 A_{it}^2 + \beta_6 r_{it} + \beta_7 s_{it} + \beta_8 SES_{jt}] \quad (4)$$

all terms carry from Eq. (2) and (3). Again, the coefficients δ_1 and δ_2 are of main analytic interest, reflecting the effects distance and housing age by whether or not a child resides in the direction of prevailing winds. Our expectation is that exponentiated coefficients $exp^{\delta_{1\&2}} < 1$, indicating a steeper residential proximity effect for downwind versus upwind children, and an attenuation of the Pb-based paint exposure risk effect for children living downwind.

2.3.3 Child Blood on Soil Pb, Distance, and Wind

For a subset of children (n = 317), we have data on the concentration of Pb in residential soils. Soil Pb is a well-known indicator of legacy emissions, and a significant predictor of child PbB outcomes (e.g. Mielke and Reagan, 1998; Mielke et al., 2007; Zahran et al., 2011; Laidlaw et al., 2016). To address potential PbS confounding of our current emissions exposure tests, we recapitulate Eq. (2) & (4) with and without control for PbS. Insofar as current emissions matter, our estimated parameter δ_1 should be unchanged across models with and without PbS.

2.3.4 Child Blood Pb and Ore Production in Time

Next, we estimate the effect of contemporaneous emissions on child PbB by regressing the annual average child PbB levels, $\frac{1}{N}\sum PbB_t$, in Broken Hill from 1991 to 2013 on average quarterly ore production in year t, capturing the intensity of mining activities. Toward this end, we execute the following least squares model:

$$\ln\left(\frac{1}{N}\sum PbB_t\right) = \beta_0 + \beta_1 \ln\left(\frac{1}{N}\sum M_t\right) + \varepsilon_t \quad (5)$$

where, $\frac{1}{N}\sum M_t$ is the annual average of quarterly tonnages of Pb extracted from the mine. Given that this test extends the observation period back in time, it is not, technically, an analysis of the effect of current emissions on child PbB outcomes. However, this test has the analytic merit of demonstrating the extent to which child PbB outcomes are responsive to the intensity of production activities in time. To test the robustness of the production activity as a correlate, we render a series of regressions for subgroups of children by housing age and Aboriginal identity. Insofar as child PbB is meaningfully impacted by exposure to

contemporaneous emissions from the mine, we expect β_1 to be positive and statistically significant.

2.3.5 Child Blood Pb, Distance, and Dust Storm Natural Experiment

On September 22nd to 24th of 2009, the Australian states of New South Wales and Queensland were impacted by a colossal dust storm (Jayaratne et al., 2011). The dust storm originated just north of Broken Hill (Jayaratne et al., 2011). The storm appeared to have the effect of redistributing surface PbS concentrations throughout the city, decreasing the standard deviation in PbS and substantially reducing the PbS-distance gradient. In addition, this dust storm brought massive quantities of low metal deposits, dominated by crustal oxides of Al, Si and Fe, originating from the adjacent desert area (i.e. Lake Eyre Basin) (Aryal et al., 2012; Gunawardena et al., 2013), which likely moderated local residual PbS contamination in Broken Hill. In the two years before the event, the elasticity of PbS with respect to distance was -0.67 ($p = 0.06$), and indistinguishable from zero two years after the dust storm (95% CI -1.67, 2.989). If legacy exposure is the only source of child PbB outcomes, then the child PbB-distance gradient should similarly dissolve in the post-dust storm period. To test this idea, and limiting observations to 2 years before and after the dust storm event, we estimate the following equation:

$$\ln(PbB_{ijt}) = \beta_0 + \beta_1(\ln D_{it}) + \beta_2 p_{it} + \beta_3 h_{it} + \delta_1(\ln D_{it} \times p_t) + \beta_4 A_{it} + B_5 A_{it}^2 + \beta_6 r_{it} + \beta_7 s_{it} + \varepsilon_{ijt} \quad (6)$$

all terms carry from Eq. (3), with the exception of p_t that assumes a value of 1 if a child was sampled 1 to 730 days after the end of the dust storm on September 24th, 2009 and 0 if the child was sampled no less than 730 days before the dust storm. Insofar as contemporary emissions matter, the estimated parameter $\delta_1 \cong 0$, indicates no disturbance to the PbB-distance gradient following a disturbance to the PbB-distance gradient.

2.3.6 Dust Pb loading on Distance and Mining Activities

Finally, to corroborate the mechanism of current emissions as a significant source of variation in child PbB outcomes, we estimate the effect of distance and current mining activities on the PbD deposits. Adjusting for local weather conditions $\boldsymbol{\chi}_{it}$, we regress PbD at dust gauge site i in month t on monthly mining intensity M_{it} and distance D_{it} of the Pb loading gauge site to the southern operations with the following model:

$$\ln(PbD_{it}) = \beta_0 + \beta_1(\ln D_{it}) + \beta_2(\ln M_{it}) + \beta_3(\ln \chi_{it}) + \varepsilon_{it} \quad (7)$$

Insofar as current emissions are a significant independent source of child blood outcomes, we expect β_1 to be negative (corresponding to distance) and β_2 to be positive (corresponding to mining intensity).

3. Results

Table 1 reports descriptive statistics on child PbB outcomes by variables of interest. The geometric mean PbB of sampled children is 4.31 μg/dL, with 42.56% of tested children having PbB in excess of 5 μg/dL. With respect to demographic characteristics, the data show that males have higher PbB than females (4.41 vs 4.20 μg/dL), that Aboriginal children have remarkably higher PbB than non-Aboriginal children (7.03 vs 3.70 μg/dL), that children residing in homes built before 1940 have higher PbB than counterparts in homes built after 1940 (4.61 vs 4.07 μg/dL), and that children residing in neighbourhoods with higher socioeconomic status (SES) have lower PbB than children residing in neighbourhoods of lower SES (3.94 vs 4.73 μg/dL). The data also show that the geometric mean PbB concentrations for all age groups beyond 1 year of age exceed the Australian safety standard of 5 μg/dL.

As expected, child PbB levels decrease with residential distance from the mine. Geometric mean PbB levels decrease from 5.25 to 4.49 to 3.89 μg/dL for children residing at <2 km, 2-4 km, and >4 km from the mine, respectively. The risk of a child exceeding 5 μg/dL decreases similarly with residential distance from the mine. The only seemingly counter-intuitive result in Table 1 involves the comparison of children by whether or not they reside in the direction of prevailing winds. The observed difference in PbB outcomes results from the fact that downwind children are disproportionately non-Aboriginal (80.4 vs 19.6%), are more distant from the mine (3.9 vs 3.5 km), reside in higher SES neighbourhoods (919.4 vs 876.0), and have a higher percentage of children sampled <1 year of age (25.2 vs 23.1%) (Supplementary Table S3). As we show later, adjusting for these factors, the prevailing wind effect behaves as expected, with children living downwind suffering higher PbB levels.

Table 1. Descriptive statistics on child PbB outcomes by variables of interest.

Variable	N (%)	PbB (μg/dL) GM (95% CI)	$PbB \geq 5$ μg/dL (%)
Total	4,852 (100)	4.31 (4.21, 4.41)	42.56
Male	2,494 (51)	4.41 (4.28, 4.57)	39.95
Female	2,358 (49)	4.20 (4.07, 4.34)	45.03
Age (months)			
0-12	1,189 (24)	1.86 (1.79, 1.94)	9.48
12-24	1,498 (31)	5.39 (5.22, 5.56)	50.07
24-36	784 (16)	6.06 (5.77, 6.37)	56.67
36-48	611 (13)	6.04 (5.72, 6.37)	55.81
48-60	770 (16)	5.53 (5.29, 5.79)	51.95
Aboriginality	1,158 (24)	7.03 (6.69, 7.40)	70.21
Non-Aboriginality	3,694 (76)	3.70 (3.61, 3.79)	33.89
Low SES	2,389(51)	4.73 (4.57, 4.90)	48.93
High SES	2,461 (49)	3.94 (3.82, 4.06)	36.33
Not Prevailing Wind	2,411 (50)	4.92 (4.75, 5.09)	51.10
Prevailing Wind	2,441 (50)	3.79 (3.68, 3.91)	34.13
Pre-1940 Housing	2,510 (52)	4.61 (4.46, 4.76)	46.97
Post-1940 Housing	1,897 (48)	4.07 (3.93, 4.22)	38.80
Distance < 2 km	782 (16)	5.25 (4.93, 5.59)	53.71
Distance 2-4 km	1,872 (39)	4.49 (4.31, 4.66)	45.35
Distance > 4 km	2,198 (45)	3.89 (3.77, 4.01)	36.22

Table 2 reports results from models Eq. (1) and (2), estimating child PbB effects from residential proximity to the southern operations, with and without the prevailing wind condition variable. In Model 1 we find that a 1% increase in residential distance is associated with a -0.173% (95% CI: -0.211, -0.135%) reduction in child PbB. Other things held equal, we also find that children living in houses constructed before 1940, male children, and Aboriginal children have PbB levels that are 7.5% (95% CI: 3.9, 11.2%), 7.2% (95% CI: 3.7, 10.8%) and 42.7% (95% CI: 38.5, 46.9%) higher than counterparts, respectively. Model 2 more explicitly captures the effect of current emissions. As expected, we find that the distance gradient significantly steepens for children residing in the direction of prevailing winds (Distance × Prevailing Wind elasticity = -0.295, 95% CI: -0.386, -0.204). Also consistent with a current emissions effect, we find that the effect of a child residing in a home built before 1940 attenuates for children residing in the direction of the prevailing winds (Housing Age × Prevailing Wind elasticity = -0.097, 95% CI: -0.170, -0.025).

Table 2. Coefficients estimating child PbB effects in Broken Hill, 2011-2015.

	Model 1 ln PbB (μg/dL)	Model 2 ln PbB (μg/dL)
ln Distance (km)	-0.173***	-0.078***
	(0.019)	(0.024)
Housing Age	0.075***	0.132***
	(0.018)	(0.026)
Prevailing Wind		0.254***
		(0.061)
Distance × Prevailing Wind		-0.295***
		(0.046)
Housing Age × Prevailing Wind		-0.097***
		(0.037)
Child Age	1.050***	1.048***
	(0.022)	(0.022)
Child Age^2	-0.181***	-0.181***
	(0.005)	(0.005)
Aboriginality	0.427***	0.423***
	(0.021)	(0.021)
Male	0.072***	0.072***
	(0.018)	(0.018)
SES	-0.001***	-0.000*
	(0.000)	(0.000)
Constant	1.784***	0.818***
	(0.156)	(0.193)
Log Likelihood	-3,955.54	3905.66
AIC	1.799	1.777
BIC	-35,358.4	-35,368.0
N	4,407	4,407

Figure 2 shows predicted child PbB levels (derived from Table 2, Model 2) as a function of distance under combinations of residential housing age and wind direction. Fixing other model covariates at their means, Figure 2 shows that the distance gradient is significantly steeper for children residing in the direction of prevailing winds, with children at 0.25 km from the southern operations having PbB levels approaching double that of upwind children at the similar distance. Note also the negligible difference (i.e. overlapping intervals of confidence) among downwind children residing in different classes of housing age (before or after 1940). This indicates that the effect of exposure to current emissions overwhelms the effect of residing in a home with a house age that has higher potential exposure risk from the Pb-based paint. Also note the inverse logic in the comparison of predicted child PbB by housing age for upwind children. Intuitively, the PbB effect of residing in a home built prior to 1940 (as compared to residing in a home built after 1940) amplifies for upwind children. That is, in the relative absence of exposure to current emissions, exposure to legacy sources of Pb like Pb-based paint become important.

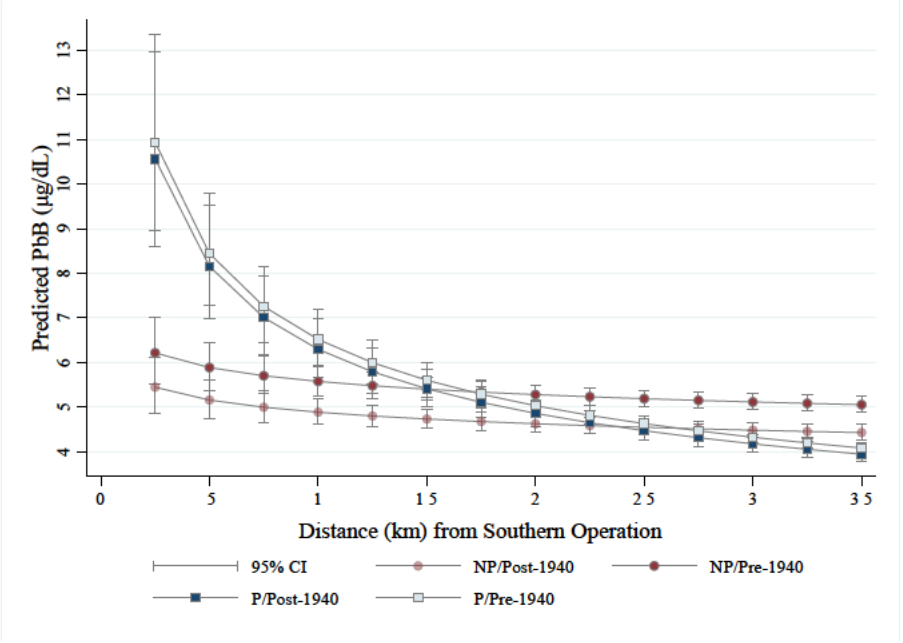


Figure 2. Predicted child PbB (µg/dL) by distance, housing age, and prevailing wind condition. Predicted child PbB (and 95% confidence intervals) are derived from Eq. (2), Model 2 in Table 3 and exponentiated to return to non-transformed values. All other model covariates are fixed at sample means in post-estimation. NP stands for not residing in the direction of prevailing winds, and P denotes children residing in the direction of prevailing winds.

Repeating the logic of Table 2 (and showing results from Eq. 3 & 4), Table 3 reports odds ratios estimating the risk of a child presenting with PbB ≥5 µg/dL. In Model 1 we find that a 1 km increase in child residential distance from the mine decreases the odds of eclipsing the 5 µg/dL threshold by 13.5% (95% CI: 9.02, 17.6%). With respect to demographic characteristics, the results show that of children residing in homes built prior to 1940, male children, and Aboriginal children have significantly higher risk of elevated PbB, exceeding counterparts by multiplicative factors of 1.285 (95% CI: 1.114, 1.482), 1.394 (95% CI: 1.213, 1.602), and 3.898 (95% CI: 3.298, 4.607), respectively. Consistent with a current emissions effect, Model 2 indicates a steepening of the distance coefficient for downwind children (Distance × Prevailing Wind OR=0.776, 95% CI: 0.690, 0.874). Similar to results in Table 2, we also observe an attenuation of the housing effect among downwind children (Housing Age × Prevailing Wind OR=0.727, 95% CI: 0.542, 0.975). According to our model, among children within 1 km of the mine, the predicted probability of eclipsing 5 µg/dL approaches or exceeds 50% regardless of condition. Table 3 provides considerable evidence of a current emissions effect, showing a steepening of the distance effect for downwind children, an attenuation of the distance effect for upwind children, and an amplification of the housing age effect for upwind children.

Table 3. Odds ratios estimating the risk of child PbB ≥5 μg/dL in Broken Hill, 2011-2015.

	Model 1 $EPbB$ (μg/dL ≥5)	Model 2 $EPbB$ (μg/dL ≥5)
Distance (km)	0.865***	0.928**
	[0.824, 0.908]	[0.874, 0.984]
Housing Age	1.285***	1.588***
	[1.114, 1.482]	[1.302, 1.937]
Prevailing Wind		1.621**
		[1.018, 2.583]
Distance × Prevailing Wind		0.776***
		[0.690, 0.874]
Housing Age × Prevailing Wind		0.727**
		[0.542, 0.975]
Child Age	8.314***	8.529***
	[6.769, 10.212]	[6.930, 10.496]
Child Age^2	0.697***	0.694***
	[0.669, 0.726]	[0.665, 0.723]
Aboriginality	3.898***	3.911***
	[3.298, 4.607]	[3.302, 4.633]
Male	1.394***	1.404***
	[1.213, 1.602]	[1.219, 1.616]
SES	0.994***	0.997***
	[0.992, 0.995]	[0.995, 0.999]
BIC	-32,160.07	-32, 213.52
N	4,407	4,407

Note: EIM Standard errors, *** p<0.01, ** p<0.05, * p<0.1, with 95% confidence intervals reported in braces. Distance is to the southern mine operation.

To address confounding from potential child exposure to legacy emissions (i.e. PbS), Figure 3 displays results from the analysis detailed in Section 2.3.3 pertaining to the inclusion of PbS in models Eq. (2) & (4). For a subset of children (n = 317), we have data on the concentration of Pb in residential soils. Insofar as the current emissions effect detailed above is not confounded by PbS, predicted child PbB outcomes should behave similarly across models with and without PbS. Confirming this expectation, in Figure 3 we find that there is a negligible statistical difference for the effect of current emissions on PbB (as indicated by the distance effect for downwind children) with and without adjustment for PbS. It should be noted that the PbS significantly predicts child PbB outcomes, indicating that legacy sources also matter in Broken Hill. Other things held equal, we find that a 1% increase in PbS is associated with a 0.130% (95% CI: 0.045, 0.216%) increase in child PbB.

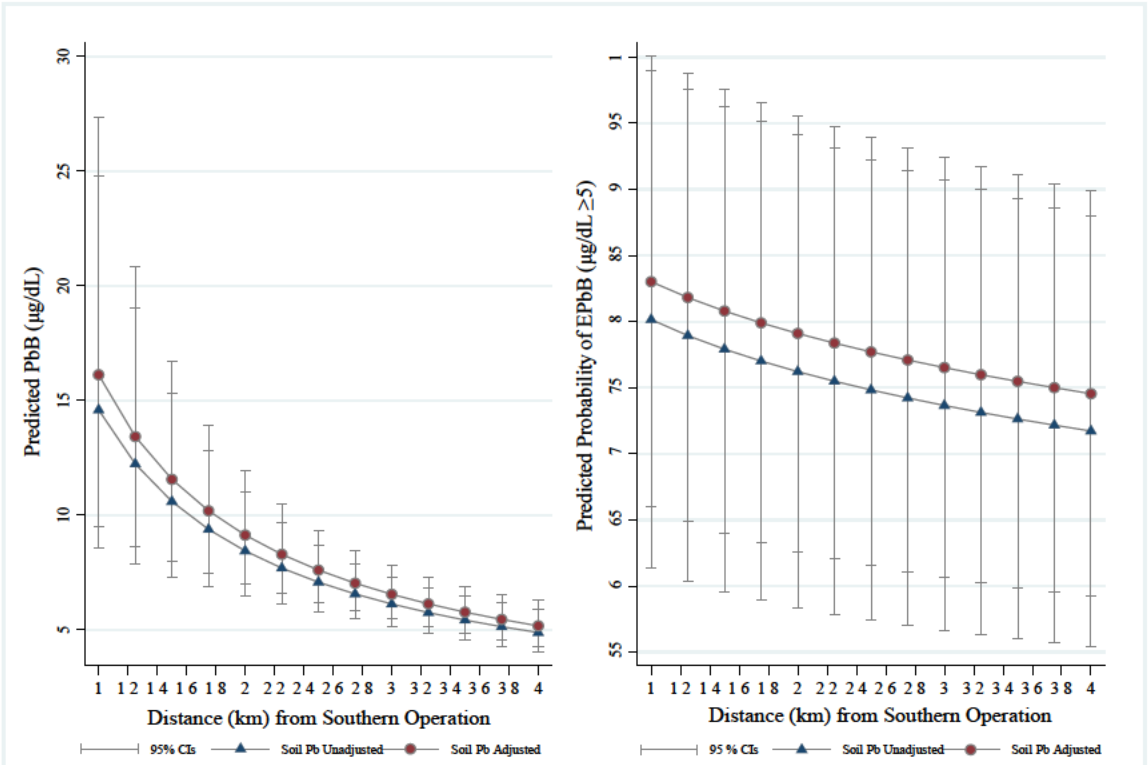


Figure 3. Predicted child PbB (µg/dL) and child EPbB (≥5 µg/dL) by distance for downwind children by PbS adjustment. Predicted child PbB (and 95% confidence intervals) are derived from Eq. (2) and exponentiated to return to non-transformed values, with and without soil Pb. All other model covariates are fixed at sample means in post-estimation. Predicted child EPbB (and 95% confidence intervals) are derived from Eq. (4) with and without soil Pb, again with all other model covariates are fixed at sample means in post-estimation.

Table 4 and Figure 4 show results from analyses of the coincidental behaviour of average child PbB (for various subsets of children) and production activities at the mine in time (1991 to 2013). Technically, Table 4 and Figure 4 are not tests of the effect of current emissions, but instead of contemporaneous associations between production activities at the mine and population-level PbB outcomes in children. Results are logically compatible with a role for current emissions in explaining child PbB risk. Figure 4 shows the child PbB outcomes unmistakably move with production activities at the mine, drifting downward together over time. In fact, as shown in Table 4 Model 1 (involving all children), the relationship between production activities and child PbB is near unit elastic, with a 1% increase in Pb ore production associated with a 0.837% (95% CI: 0.665, 1.010%) increase in average child PbB.

Table 4. Coefficients estimating annual average PbB effects of Pb ore production in Broken Hill, 1991-2013.

	Model 1 All Children ln *PbB* (µg/dL)	Model 2 Aboriginal Children ln *PbB* (µg/dL)	Model 3 Non-Aboriginal Children ln *PbB* (µg/dL)	Model 4 Pre-1940 Home Children ln *PbB* (µg/dL)	Model 5 Post-1940 Home Children ln *PbB* (µg/dL)
ln Pb Production	0.837***	0.519***	0.995***	0.815***	0.828***
	(0.083)	(0.118)	(0.077)	(0.085)	(0.091)
Constant	-6.093***	-2.650**	-7.751***	-5.782***	-6.115***
	(0.819)	(1.164)	(0.767)	(0.841)	(0.902)
N	22	22	22	22	22
R^2	0.837	0.494	0.892	0.822	0.805
F	102.38	19.49	164.83	92.05	82.45

Note: Standard errors in parentheses, *** p<0.01, ** p<0.05, * p<0.1. Pb ore production and average *PbB* are natural log transformed, giving coefficients the interpretation of an elasticity.

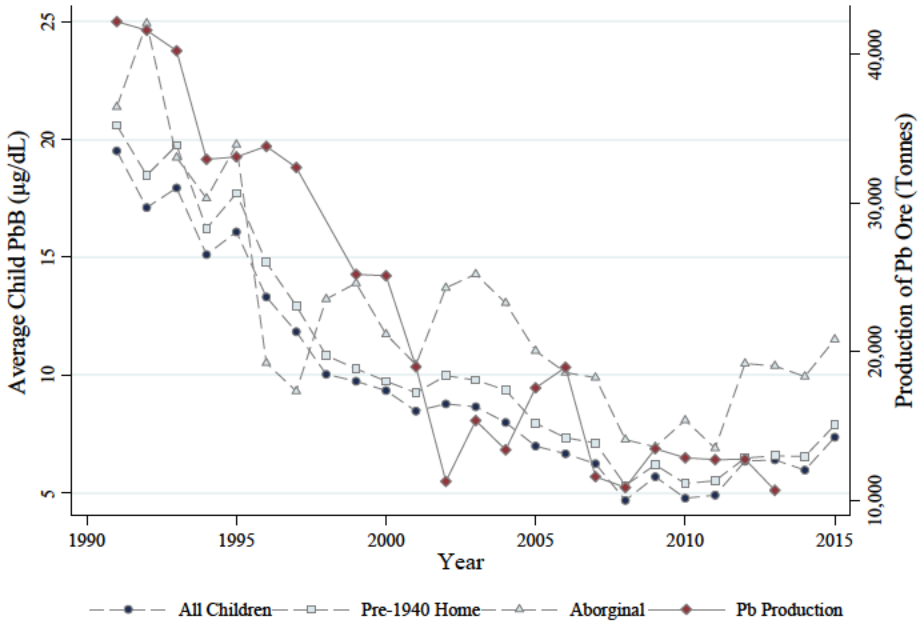


Figure 4. Connected graph of annual average child PbB (µg/dL) and production of Pb ore at Mine.

Figure 5 shows results from our second test of contemporaneous effects of mine emissions. As described previously, in late September of 2009, Broken Hill was visited by a breathtaking multi-day dust storm that had the effect of redistributing surface PbS concentrations throughout the city, attenuating the PbS-distance gradient. If child exposure to legacy emissions is the only source of child PbB outcomes, then the child PbB-distance gradient should similarly dissolve in the post-dust storm period. Conversely, if current emissions matter in this period then the child PbB-distance gradient should discernibly remain. As a likely response to the spatial re-distribution of

PbS caused by the 2009 dust storm, the post-dust storm PbB values (maroon circles) fall below pre-dust storm values (navy triangles). Nevertheless, it is evident that a PbB distance-decay pattern remains. This corroborates results in Figure 3 indicating the importance of PbS as an independent source of child PbB. Importantly, for the aim of our paper, the convexity of the PbB-distance gradient for children remains with the disturbance of the PbB-distance gradient, indicating that contemporary emissions independently influence child PbB outcomes.

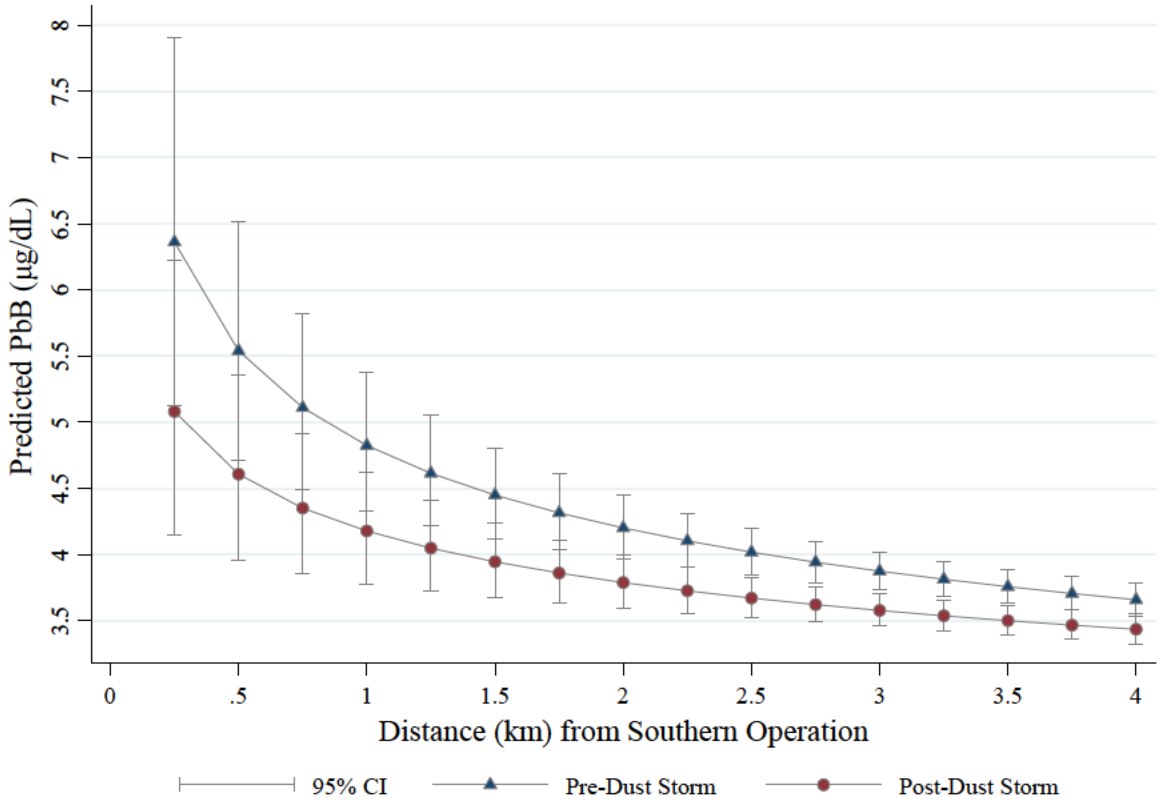


Figure 5. Predicted child PbB (µg/dL) by distance and Pre- or Post-dust storm period. Predicted child PbB (and 95% confidence intervals) are derived from Eq. (6) and exponentiated to return to non-transformed values. All other model covariates are fixed at sample means in post-estimation.

Finally, to corroborate the mechanism of current emissions as a significant source of variation in child PbB outcomes, we estimate the effects of distance and current mining activities on the dust Pb (PbD) deposits throughout the city. Table 5 shows the results. Focusing on fully saturated Model 4, we find that a 1% increase in dust gauge distance from the mine is associated with -0.501% (95% CI: -0.728, -0.275) reduction in PbD (µg/m^2/day). Consistent with a current emissions pathway, we find that a 1% increase in production intensity at the mine increases the expected amount of PbD by 1.487% (95% CI: 0.537, 2.437%). Figure 6 displays result from Model 4, showing the independent effects of distance (in km) and monthly Pb ore production (tonnes) on PbD.

Table 5. Coefficients estimating monthly PbD effects of distance and Pb ore production in Broken Hill, 2012-2016.

	Model 1	Model 2	Model 3	Model 4
	ln *PbD* (µg/m²/day)	ln *PbD* (µg/m²/day)	ln *PbD* (µg/m²/day)	ln *PbD* (µg/m²/day)
ln Distance	-0.327***		-0.462***	-0.501***
	(0.062)		(0.111)	(0.116)
ln Pb production		1.671***	1.741***	1.487***
		(0.482)	(0.457)	(0.485)
ln Rainfall				0.018
				(0.080)
ln Gust Wind				0.138
				(0.560)
ln Wind Speed (km/h)				-0.123
				(0.157)
Constant	5.271***	-8.807**	-9.074**	-7.241*
	(0.060)	(3.977)	(3.767)	(4.215)
Log Likelihood	-475.49	-196.41	-188.06	-172.59
AIC	2.430	2.756	2.654	2.626
BIC	-2,077.05	-576.71	-585.86	-537.88
N	393	144	144	136

Note: Standard errors in parentheses *** p<0.01, ** p<0.05, * p<0.1. Distance from southern operations; Pb ore production is estimated monthly. *PbD* and all model covariates are natural log transformed, giving coefficients the meaning of an elasticity.

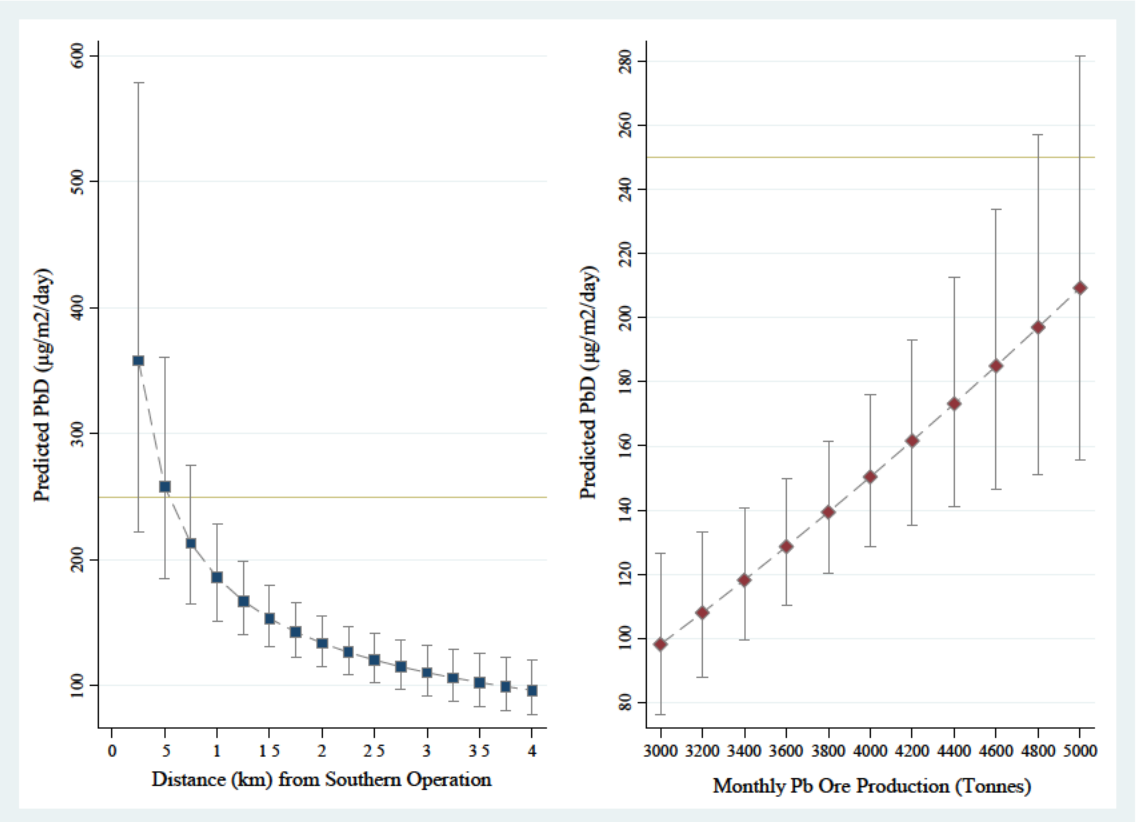


Figure 6. Predicted *PbD* (µg/m²/day) by distance and monthly Pb ore production.

4. Discussion

In this paper, we sought to quantify the PbB effects of child exposure to contemporary emissions in Broken Hill, Australia. To achieve this, we developed a series of statistical tests leveraging breathtakingly detailed environmental and PbB data. Utilising wind direction and residential distance data to capture the PbB effects of contemporary emissions exposure, we found that downwind children proximate to the mine were at greatest risk of elevated PbB. The greater PbB exposure risk under the downwind direction of contamination origin is also observed in other communities (e.g. Rahbar et al., 2002; Maynard et al., 2003; Caravanos et al., 2006; Garcia-Vargas et al., 2014; Zhang et al., 2016; Zahran et al., 2017). For example, an aviation gasoline study conducted in Michigan showed that child PbB concentrations around airports increased in response to the percentage of downwind days from the source (Zahran et al., 2017). In Torreón, Mexico, a smelting community, elevated PbB outcomes (range 3.6-14.7 μg/dL) clustered in the downwind direction of the world's fourth largest Pb-Zn metal smelter (Garci-Vargas et al., 2014).

Furthermore, all other factors held equal, we found that downwind children at ≤0.25 km from the mine had estimated PbB levels that were about 75% higher than similarly proximate upwind children (Figure 2). Previous studies have shown that age of house, usually used as a proxy of Pb-based paint exposure, was one of the potential factors of PbB outcomes (Mielke et al., 1997; Jacobs et al., 2002; Etchevers et al., 2014; Raymond et al., 2014; McClure et al., 2016). This study also considered potential effects of housing age. The results showed that children at ≤0.25 km downwind from the mine had statistically indistinguishable high PbB levels whether or not they were residing in a home with high Pb-based paint exposure risk (Pre-1940: 10.94 versus Post-1940: 10.56 μg/dL) (Figure 2). Estimated PbB differences between down and upwind persist until a distance of around 1.5 to 2 km from the mine (Figure 2). Also consistent with a current emissions hypothesis, we found an attenuation of the distance effect and an amplification of the housing age effect for upwind children. That is, children residing upwind from the mine have PbB levels that are less distance-dependent and more legacy exposure-dependent (i.e., housing age) than children living downwind of mine (Pre-1940 versus Post-1940; Figure 2).

The effect of residual soil Pb contamination on PbB concentration was determined via the generalised linear modelling with respect to combinations of residential distance and wind direction based upon a subsample of children with measured PbS concentration. As shown in Figure 3, predicted child PbB outcomes behave similarly across models with and without PbS. In

fact, we found statistically negligible differences in the PbB effects of current emissions, as indicated by the distance effect for downwind children, with and without adjustment for PbS. Consistent with prior research, PbS is also a statistically significant predictor of child PbB in Broken Hill, with a 1% increase in PbS associated with a 0.13% increase in child PbB. While PbS exposure appears to meaningfully influence PbB levels in children, with respect to the analytic aim of our study, controlling statistically for the PbS exposure pathway cannot upend the significance of the contemporary emissions exposure effect.

To examine the contemporary emissions hypothesis, we conducted a series of tests involving historical PbB and mining data. In our first test, we showed that as production activities at the mine decreased in time, so too did the average PbB of children in Broken Hill. Statistically, the relationship was near unit elastic, with a 1% reduction in production associated with a 0.837% decrease in average child PbB (95% CI: 0.665, 1.010%) (Table 4). In fact, across all subsets of children (regardless of ethnicity or age of housing) PbB levels unmistakably co-vary with production activities at the mine, drifting together downward over time (Figure 4).[3]

We followed with a second test that uniquely exploited the Australian dust storm of 2009. This colossal storm had the effect of disturbing the observed PbS-distance gradient. That is, before the storm, PbS increased measurably in proximity to the mine. After the storm, the spatial distribution of PbS at sampled residences in Broken Hill had no statistically discernible pattern with respect to distance from mine (95% CI: -1.670, 2.989). The redistribution of surface PbS contamination by natural processes is not limited to atmospheric deposition. In New Orleans, Louisiana, massive quantities of low metal sediment originating from the coastal environment washed into the city when Hurricane Katrina occurred (Mielke et al., 2016). Consequently, after Hurricane Katrina, PbS contamination was also reduced in New Orleans, Louisiana (Mielke et al., 2016). In terms of this study, if exposure to legacy sources of Pb (like PbS) predominately drive PbB outcomes in Broken Hill, then the disturbance of the soil-Pb distance gradient should similarly disturb the PbB-distance gradient. As shown in Figure 5, we found that the convexity of

[3] The results from this test pose a substantial logical challenge to claims that exposure to legacy sources of Pb drive PbB outcomes in Broken Hill. Consider a basic stock versus flow distinction of emissions from the mine. Current emissions represent the flow of Pb, with the stock of Pb constituting the accumulation flows over time. Insofar as the flow of Pb exceeds the leakage of Pb from the lived environment (through weathering and/or interventions), then the stock of Pb must increase with the flow of Pb over time. The presumed increase in the stock of Pb over time is logically incompatible with observed decline in child PbB levels.

the estimated PbB-distance gradient for children remained after the storm, supporting the supposition that contemporary emissions independently influence child PbB outcomes.

Lastly, and to corroborate the mechanism of contemporary emissions as a significant independent source of variation in child PbB outcomes, we estimated the effects distance and current mining activities on PbD deposits at gauges located throughout the city. Importantly adjusting for local weather conditions that drive the potential resuspension of contaminated soils, we found the quantity of Pb recorded at dust gauges increased significantly with both production activities and spatial proximity to the mine. Similar spatial PbD distribution has been observed in other mining and smelting communities (Albalak et al., 2003; Telmer et al., 2004; Soto-Jiménez and Flegal, 2011; Qiu et al., 2016; Stovern et al., 2016). Some of these studies attributed atmospheric transport and deposition of contaminants away from the mining and smelting operations to be the primary mechanism for their spatial distribution in dust (Soto-Jiménez and Flegal, 2011; Felix et al., 2015; Stovern et al., 2016). In Broken Hill, the diminishing size of current PbD particles with distance away from the active southern operations supports atmospheric transport of current emissions (Dong and Taylor, 2017). Regarding responses of PbB to wind directions and the 2009 dust storm in Broken Hill, it is evident that the current emissions are influencing PbB outcomes in Broken Hill via transport of atmospheric particulates. More broadly, the approaches utilised here to distinguish source contribution could be applied to other mining and smelting communities to apportion the significance of emissions in the context of widespread residual soil contamination. Resolution of this fundamental conundrum is likely to promote more targeted and effective remediation programs.

5. Conclusion

Across our ensemble of statistical tests, we found consistent evidence that contemporary Pb emissions from the mine affect child PbB outcomes in Broken Hill. While it is acknowledged that other sources of environmental Pb matter given that we found consistent evidence that both Pb-based paint (as captured through age of housing) and PbS exposure risks correlate with child PbB outcomes, the evidence for the significant role of current emissions in PbB concentrations is incontrovertible. The data demonstrates that current emissions from the mine are a significant and independent source of Pb exposure risk to children in Broken Hill. Moving forward, all intervention or remediation efforts to limit child harm from environmental Pb ought to be multi-pronged, addressing the panoply of pathways that include current emissions.

With respect to the question of harm, and regardless of the precise source or combination of sources involved in the delivery of Pb exposure risk, an exceptionally high fraction of sampled children in Broken Hill have PbB levels in exceedance of the Australian upper maximum guideline for child safety. In Broken Hill today, 42.56% of sampled children have PbB levels in excess of 5 μg/dL.[4] Among Aboriginal children, an astonishing 70.21% have PbB levels that eclipse the Australian threshold of safety. In fact, by leveraging coefficients reported in Table 2, we estimate that downwind children residing less than 2 km from the mine, on average, have PbB levels in excess of 5 μg/dL. Our analyses indicate that 2 km from the mine is a minimum buffer of safety for the typical child. Given that the consequences of childhood Pb exposure are lasting, the Pb exposed children are suffering, probabilistically, "an unfolding series of adverse behavioural outcomes" (Reyes, 2015), as well as depressed life chances in terms of expected earnings over the career course (Reuben et al., 2017; Zahran et al., 2017).

[4] It should be noted that while 5 μg/dL is guidance threshold, on the basis of substantial epidemiological evidence, both the United States Center for Disease Control and Environmental Protection Agency have concluded that there is no known safe level of Pb exposure (Zahran et al., 2017).

Notes

The authors declare no competing financial interest. M.P. Taylor completed an independent Review of the New South Wales Environment Protection Authority's Management of Contaminated Sites for the NSW Minister for the Environment (available at http://www.epa.nsw.gov.au/resources/epa/Contaminated-Sites-Review-2016.pdf) in December 2016 and is also an advisor to the Broken Hill Environmental Lead Program. The other authors have no potential conflicts of interest to declare.

Acknowledgements

The authors are grateful to Peter Oldsen, Frances Boreland (NSW EPA, Broken Hill Environmental Lead Program), Margaret Lesjak (NSW Health Far West Local Health District) and Elizabeth Guest (Broken Hill City Council) for their help in accessing the relevant environmental and human health data. We acknowledge the Child and Family Health Centre at Broken Hill for their support in collecting the PbB and residential soil Pb data. Dr Marek Rouillon and Prof. Bruce Lanphear are thanked for comments on draft versions of the manuscript. C. Dong is funded via an International Macquarie University Research Excellence Scholarship (iMQRES No. 2014098). He received technical and practical support from the Broken Hill Environmental Lead Program (BHELP) as part of a Macquarie University–BHELP collaboration agreement.

References

Albalak, R., McElroy, R. H., Noonan, G., Buchanan, S., Jones, R. L., Flanders, D. W., 2003. Blood lead levels and risk factors for lead poisoning among children in a Mexican smelting community. Arch. Environ. Health 58, 172-183.

Aryal, R., Kandel, D., Acharya, D., Chong, M. N., Beecham, S., 2012. Unusual Sydney dust storm and its mineralogical and organic characteristics. Environmental Chemistry 9, 537-546.

Australian Broadcasting Corporation (ABC), 2016. Perilya expecting layoffs at Broken Hill mine as restructure plan prepared. http://www.abc.net.au/news/2016-03-09/perilya-expecting-layoffs-at-broken-hill-mine/7231858 (accessed 09.06.17)

Australian Bureau of Statistics (ABS), 2013a. 2033.0.55.001 – Census of Population and Housing: Socio-Economic Indexes for Areas (SEIFA), Australia, 2011. http://www.abs.gov.au/AUSSTATS/abs@.nsf/DetailsPage/2033.0.55.0012011?OpenDocument (accessed 09.06.17)

Australian Bureau of Statistics (ABS), 2013b. Technical Paper – Socio-Economic Indexes for Areas (SEIFA) 2011. http://www.ausstats.abs.gov.au/Ausstats/subscriber.nsf/0/22CEDA8038AF7A0DCA257B3B00116E34/$File/2033.0.55.001%20seifa%202011%20technical%20paper.pdf (accessed 03.06.2017)

Australian Bureau of Statistics (ABS), 2016. 1270.0.55.001 – Australian Statistical Geography Standards (ASGS): Volume 1 – Main Structure and Greater Capital City Statistical Areas, July 2016. http://www.abs.gov.au/AUSSTATS/abs@.nsf/DetailsPage/1270.0.55.001July%202016?OpenDocument#Data (accessed 03.06.2017).

Australian Bureau of Statistics (ABS), 2017. Broken Hill (C) (LGA), New South Wales. http://stat.abs.gov.au/itt/r.jsp?RegionSummary&region=11250&dataset=ABS_REGIONAL_LGA&geoconcept=REGION&datasetASGS=ABS_REGIONAL_ASGS&datasetLGA=ABS_REGIONAL_LGA&regionLGA=REGION&regionASGS=REGION (accessed 09.06.17)

Benin, A. L., Sargent, J. D., Dalton, M., Roda, S., 1999. High Concentration of Heavy Metals in Neighborhoods Near Ore Smelters in Northern Mexico. Environ. Health Perspect. 107, 279-284.

Boreland, F., Lyle, D. M., Brown, A., Perkins, D., 2015. Effectiveness of introducing point of care capillary testing and linking screening with routine appointments for increasing blood lead screening rates of young children: a before-after study. Archives of Public Health 73:60. DOI: 10.1186/s13690-015-0111-y.

Boreland, F., Lyle, D. M., Wlodarczyk, J., Balding, W. A., Reddan, S., 2002. Lead dust in Broken Hill homes—a potential hazard for young children? Australian and New Zealand Journal of Public Health 26, 203-207.

Broken Hill Environmental Lead Program, 2016. STEERING COMMITTEE ANNUAL REPORT 2015-2016. http://leadsmart.nsw.gov.au/wp-content/uploads/2017/03/DOC17-

125421-02-Attachment-B-Broken-Hill-Environmental-Lead-Program-BHELP-Steering-Committee-Annual-Report-2015-2016.pdf (accessed 03.07.17).

Bureau of Metrology, 2016a. Climate statistics for Broken Hill. http://www.bom.gov.au/climate/averages/tables/cw_047007.shtml (accessed 24.07.16).

Bureau of Metrology, 2016b. Wind speed and direction rose at Broken Hill. http://www.bom.gov.au/cgi-bin/climate/cgi_bin_scripts/windrose_selector.cgi?period=Annual&type=9&location=47007 (accessed 24.07.16).

Bureau of Metrology, 2017. Climate data for Broken Hill. http://www.bom.gov.au/climate/data-services/charges.shtml (accessed 10.14.16).

Caravanos, J., Weiss, A. L., Blaise, M. J., Jaeger, R. J., 2006. A survey of spatially distributed exterior dust lead loadings in New York City. Environmental Research 100, 165-172.

Dong, C., Taylor, M. P., Kristensen, L. J., Zahran, S., 2015. Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes. Environmental Pollution 207, 345-356.

Dong, C., Taylor, M. P., 2017. Applying geochemical signatures of atmospheric dust to distinguish current mine emissions from legacy sources. Atmospheric Environment 161, 82-89.

Etchevers, A., Bretin, P., Lecoffre, C., Bidondo, M. L., Strat, Y. L., Glorennec, P., Tertre, A. L., 2014. Blood lead levels and risk factors in young children in France, 2008-2009. International Journal of Hygiene and Environmental Health 217, 528-537.

Felix, O. I., Csavina, J., Field, J., Rine, K. P., Sáez, A. E., Betterton, E. A., 2015. Use of lead isotopes to identify sources of metal and metalloid contaminants in atmospheric aerosol from mining operations. Chemosphere 122, 219-226.

Garcia-Vargas, G. G., Rothenberg, S. J., Silbergeld, E. K., Weaver, V., Zamoiski, R., Resnick, C., Rubio-Andrade, M., Parsons, P. J., Steuerwald, A. J., Navas-Acién, A., Guallar, E., 2014. Spatial clustering of toxic trace elements in adolescents around the Torreón, Mexico lead-zinc smelter. Journal of Exposure Science & Environmental Epidemiology 24, 634-642.

Gulson, B. L., Mizon, K. J., Law, A. J., Korsch, M, J., Davis, J. J., 1994a. Source and Pathways of Lead in Humans from the Broken Hill Mining Community – An Alternative Use of Exploration Methods. Economic Geology 89, 889-908.

Gulson, B. L., Davis, J. J., Mizon, K. J., Korsch, M. J., Law, A. J., Howarth, D., 1994b. Lead Bioavailability in the Environment of Children: Blood Lead Levels in Children Can Be Elevated in a Mining Community. Archives of Environmental Health 49, 326-331.

Gulson, B. L., Howarth, D., Mizon, K. J., Law, A. J., Korsch, M. J., Davis, J. J., 1994c. Source of lead in humans from Broken Hill mining community. Environmental Geochemistry and Health 16, 19-25.

Gulson, B. L., Davis, J. J., Bawden-Smith, J., 1995. Paint as a source of recontamination of houses in urban environments and its role in maintaining elevated blood leads in children. Science of the Total Environment 164, 221-235.

Gunawardena, J., Ziyath, A. M., Bostrom, T. E., Bekessy, L. K., Ayoko, G. A., Egodawatta, P., Goonetilleke, A., 2013. Characterisation of atmospheric deposited particles during a dust storm in urban areas of Eastern Australia. Science of the Total Environment 461-462, 72-80.

Jacobs, D. E., Clickner, R. P., Zhou, J. Y., Viet, S. M., Marker, D. A., Rogers, J. W., Zeldin, D. C., Broene, P., Friedman, W., 2002. The prevalence of lead-based paint hazards in U.S. housing. Environmental Health Perspectives 110, A599-A606.

Jayaratne, E. R., Johnson, G. R., McGarry, P., Cheung, H. C., Morawska, L., 2011. Characteristics of airborne ultrafine and coarse particles during the Australian dust storm of 23 September 2009. Atmospheric Environment 45, 3996-4001.

Krieger, N., Chen, J. T., Waterman, P. D., Soobader, M. J., Subramanian, S. V., Carson, R., 2003. Choosing area based socioeconomic measures to monitor social inequalities in low birth weight and childhood lead poisoning: The Public Health Disparities Geocoding Project (US). Journal of Epidemiology and Community Health 57, 186-199.

Kristensen, L. J., Taylor, M. P., 2016. Unravelling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. Environmental Geochemistry and Health 38, 1015-1027.

Laidlaw, M. A. S., Filippelli, G. M., Sadler, R. C., Gonzales, C. R., Ball, A. S., Mielke, H. W., 2016. Children's Blood Lead Seasonality in Flint, Michigan (USA), and Soil-Sourced Lead Hazard Risks. International Journal of Environmental Research and Public Health 13, 358.

Laidlaw, M. A. S., Taylor, M. P., 2011. Review: Potential for childhood lead poisoning in the inner cities of Australia due to exposure to lead in soil dust. Environ. Pollut. 159, 1-9.

Lesjak, M., Jones, T., 2016. Lead Health Report 2015 – Children less than 5 years old in Broken Hill. Population Health Unit, NSW Government, Western NSW & Far West Local Health District. http://leadsmart.nsw.gov.au/wp-content/uploads/2016/12/Broken-Hill-Lead-Health-Report-2015-children-aged-0%E2%80%934.pdf (accessed 26.07.17).

Mackay, A. K., Taylor, M. P., Munksgaard, N. C., Hudson-Edwards, K. A., Burns-Nunes, L., 2013. Identification of environmental lead sources and pathways in mining and smelting town: Mount Isa, Australia. Environmental Pollution 180, 304-311.

Magellan Diagnostics, 2015. LeadCare® II Blood Lead Analyzer User's Guide. N. Billerica, Massachusetts, USA. http://www.leadcare2.com/getmedia/73ac501b-35e3-4d74-b6a9-9e7fc51adef0/70-6551_Rev_07_User-s_Guide,_LeadCare_II_(PRINT)-1.pdf.aspx (accessed 22.01.18).

Mahaffey, K. R., Annest, J., Roberts, J., Murphy, R. S., 1982. National estimates of blood lead levels: United States, 1976-1980: association with selected demographic and socioeconomic factors. The New England Journal of Medicine 307, 573-579.

Markus, J. A., McBratney, A. B., 1996. An urban soil study: heavy metals in Glebe, Australia. Aust. J. Soil Res. 34, 453-465.

Maynard, E., Thomas, R., Simon, D., Phipps, C., Ward, C., Calder, I., 2003. An evaluation of recent blood lead levels in Port Pirie, South Australia. Science of the Total Environment 303, 25-33.

McClure, L. F., Niles, J. K., Kaufman, H. W., 2016. Blood Lead Levels in Young Children: US, 2009-2015. Journal of Pediatrics 175, 173-181.

Mielke, H. W., Dugas, D., Mielke, P. W., Smith, K. S., Smith, S. L., Gonzales, C. R., 1997. Associations between Soil Lead and Childhood Blood Lead in Urban New Orleans and Rural Lafourche Parish of Louisiana. Environmental Health Perspectives 105, 950-954.

Mielke, H. W., Gonzales, C. R., Powell, E. T, Jartun, M., Mielke, P. W., 2007. Nonlinear association between soil lead and blood lead of children in metropolitan New Orleans, Louisiana: 2000-2005. Science of the Total Environment 388, 43-53.

Mielke, H. W., Gonzales, C. R., Powell, E., Mielke, P. W., 2016. Spatiotemporal dynamic transformations of soil lead and children's blood lead ten years after Hurricane Katrina: New grounds for primary prevention. Environment International 94, 567-575.

Mielke, H. W., Reagan, P. L., 1998. Soil is an important pathway of human lead exposure. Environmental Health Perspectives 106, 217-229.

Moreno, T., Amato, F., Querol, X., Alastuey, A., Elvira, J., Gibbons, W., 2009. Bedrock controls on the mineralogy and chemistry of PM_{10} extracted from Australian desert sediments. Environmental Geology 57, 411-420.

Morland, R., Webster, A. E., 1998. Broken Hill lead–zinc–silver deposit. In D. A. Berkman & D. H. Mackenzie (Eds.), Geology of Australian and Papua New Guinean Mineral Deposits (pp. 619–626). Melbourne: Australian Institute of Mining and Metallurgy.

Mudd, G. M., Jowitt, S. M., Werner, T. T., 2017. The world's lead-zinc mineral resources: Scarcity, data, issues and opportunities. Ore Geology Reviews 80, 1160-1190.

NHMRC, 2015. NHMRC STATEMENT: EVIDENCE ON THE EFFECTS OF LEAD ON HUMAN HEALTH. https://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh58_nhmrc_statement_lead_effects_human_health_a.pdf (accessed 01.07.2017)

National Pollutant Inventory (NPI), 2017a. Search by form. http://www.npi.gov.au/npidata/action/load/advance-search (accessed 08.08.17).

National Pollutant Inventory (NPI), 2017b. 2015/2016 report for BROKEN HILL OPERATION PTY LTD, CBH Resources – Rasp Mine – Broken Hill, NSW. http://www.npi.gov.au/npidata/action/load/individual-facility-detail/criteria/state/NSW/year/2016/jurisdiction-facility/1333 (accessed 09.06.17).

National Pollutant Inventory (NPI), 2017c. 2015/2016 report for PERILYA BROKEN HILL LIMITED, Perilya Broken Hill Operations – Broken Hill, NSW. http://www.npi.gov.au/npidata/action/load/individual-facility-detail/criteria/state/NSW/year/2016/jurisdiction-facility/125 (accessed 09.06.17)

New South Wales Environment Protection Agency (NSW EPA), 2017. Notice of Variation of Licence No. 2688, Notice Number 1551204, File Number EF13/3441. http://www.epa.nsw.gov.au/prpoeoapp/ViewPOEONotice.aspx?DOCID=-1&SYSUID=1&LICID=2688 (accessed 19.08.17)

Page R.W., Stevens B. P. J., Gibson G. M., 2005. Geochronology of the Sequence Hosting the Broken Hill Pb-Zn-Ag Orebody, Australia. Economic Geology 100, 633-661.

Perilya Limited. 2015. Broken Hill. http://www.perilya.com.au/our-business/operations/broken-hill (accessed 08.06.17).

Perilya Limited. 2017. Monthly Reports: Environmental Reporting. http://www.perilya.com.au/articles/april-2017-report2/April_2017_Report2.pdf (accessed 09.06.17).

Potula, V., Hegarty-Steck, M., Hu, H., 2001. Blood Lead Levels in Relation to Paint and Dust Lead Levels: The Lead-Safe Cambridge Program. American Journal of Public Health 91, 1972-1974.

Qiu, K., Xing, W., Scheckel, K. G., Cheng, Y., Zhao, Z., Ruan, X., Li, L., 2016. Temporal and seasonal variations of As, Cd and Pb atmospheric deposition flux in the vicinity of lead smelters in Jiyuan, China. Atmospheric Pollution Research 7, 170-179.

Qu, C., Ma, Z., Yang, J., Liu, Y., Huang, L., 2012. Human Exposure Pathways of Heavy Metals in a Lead-Zinc Mining Area, Jiangsu Province, China. PLoS ONE 7, e46793.

Rahbar, M. H., White, F., Agboatwalla, M., Hozhabri, S., Luby, S., 2002. Factors associated with elevated blood lead concentrations in children in Karachi, Pakistan. Bulletin of the World Health Organization 80, 769-775.

Raymond, J., Wheeler, W., Brown, M. J., 2014. Lead screening and prevalence of blood lead levels in children aged 1-2 years--Child Blood Lead Surveillance System, United States, 2002-2010 and National Health and Nutrition Examination Survey, United States, 1999-2010. Morbidity and Mortality Weekly Report 63 (2), 36-42.

Reuben, A., Caspi, A., Belsky, D. W., Broadbent, J., Harrington, H., Sugden, K., Houts, R. M., Ramrakha, S., Poulton, R., Moffitt, T. E., Association of Childhood Blood Lead Levels With Cognitive Function and Socioeconomic Status at Age 38 Years and With IQ Change and Socioeconomic Mobility Between Childhood and Adulthood. JAMA 317, 1244-1251.

Reyes, J. W., 2015. LEAD EXPOSURE AND BEHAVIOR: EFFECTS ON ANTISOCIAL AND RISKY BEHAVIOR AMONG CHILDREN AND ADOLESCENTS. Economic Inquiry 53, 1580-1605.

Rouillon, M., Harvey, P. J., Kristensen, L. J., George, S. G., Taylor, M. P., 2017. VegeSafe: A community science program measuring soil-metal contamination, evaluating risk and providing advice for safe gardening. Environmental Pollution 222, 557-566.

Solomon, R. J., 1988. The richest lode: Broken Hill 1883-1988. Hale & Iremonger, Sydney, NSW.

Soto-Jiménez, M. F., Flegal, A. R., 2011. Childhood lead poisoning from the smelter in Torreón, México. Environmental Research 111, 590-596.

Spear, M., Thomas, R., Shrader-Frechette, K., 2015. Commentary: Flawed Science Delays Smelter Cleanup and Worsens Health. Accountability in Research 22, 41-60.

Standard Australia, 2003. Australian/New Zealand 3580.10.1:2003. Determination of particulate Matter – Deposited Matter – Gravimetric Method. http://infostore.saiglobal.com/store/details.aspx?ProductID.373364 (accessed 25.01.18).

Staes, C., Matte, T., Copley, C. G., Flanders, D., Binder, S., 1994. Retrospective Study of the Impact of Lead-based Paint Hazard Remediation on Children's Blood Lead Levels in St. Louis, Missouri. American Journal of Epidemiology 139, 1016-1026.

Stovern, M., Guzmán, H., Rine, K. P., Felix, O., King, M., Ela, W. P., Betterton, E. A., Sáez, A. E., 2016. Windblown Dust Deposition Forecasting and Spread of Contamination around Mine Tailings. Atmosphere 7, 16: doi:10.3390/atmos7020016.

Sullivan, M., 2014. Tainted Earth: Smelters, Public Health and the Environment. Rutgers University Press, New Brunswick (US).

Taylor, M. P., 2012. Lead poisoning of Port Pirie Children: a long history of looking the other way. https://theconversation.com/lead-poisoning-of-port-pirie-children-a-long-history-of-looking-the-other-way-8296 (accessed 03.07.2017).

Taylor, M. P., Mackay, A. K., Hudson-Edwards, K. A., Holz, E., 2010. Soil Cd, Cu, Pb and Zn contaminants around Mount Isa city, Queensland, Australia: Potential sources and risks to human health. Applied Geochemistry 25, 841-855.

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

Taylor, M. P., Schniering, C., 2010. The public minimization of the risks associated with environmental lead exposure and elevated blood lead levels in children, Mount Isa, Queensland, Australia. Archives of Environmental & Occupational Health 65, 45-48.

Telmer, K., Bonham-Carter, G. F., Kliza, D. A., Hall, G. E. M., 2004. The atmospheric transport and deposition of smelter emissions: evidence from the multielement geochemistry of snow, Quebec, Canada. Geochimica et Cosmochimica Acta 68, 2961-2980.

van Alphen, M., 1991. The History of Smelting and Ore Dressing in Broken Hill and the

Potential for Mine Derived Lead Contamination in Broken Hill. Unpublished report.

Woodward, O. H., 1965. A review of the Broken Hill Lead-Silver-Zinc Industry. West Publishing Corporation Pty. Ltd, Sydney, NSW.

Woodward-Clyde Pty Limited, 1993. Evaluation of environmental lead at Broken Hill. Prepared for Environment Protection Authority. Project No. 3328. Sydney, NSW.

Yang, K., Cattle, S. R., 2015. Bioaccessibility of lead in urban soil of Broken Hill, Australia: A study based on in vitro digestion and the IEUBK model. Science of the Total Environment 538, 922-933.

Zahran, S., Iverson, T., McElmurry, S. P., Weiler, S., 2017. The effect of leaded aviation gasoline on blood lead in children. Journal of the Association of Environmental and Resource Economists 4, 575-610.

Zahran, S., Mielke, H. W., Weiler, S., Gonzales, C. R., 2011. Nonlinear associations between blood lead in children, age of child, and quantity of soil lead in metropolitan New Orleans. Science of the Total Environment 409, 1211-1218.

Zhang, F., Liu, Y., Zhang, H., Ban, Y., Wang, J., Liu, J., Zhong, L., Chen, X., Zhu, B., 2016. Investigation and Evaluation of Children's Blood Lead Levels around a Lead Battery Factory and Influencing Factors. International Journal of Environmental Research and Public Health 13, 541.

Zhou, X., Taylor, M. P., Davies, P. J., Prasad, S., 2017. Identifying Sources of Environmental Contamination in European Honey Bees (Apis mellifera) Using Trace Elements and Lead Isotopic Compositions. Environmental Science & Technology, DOI: 10.1021/acs.est.7b04084.

Chapter 6: Influences of environmental contamination on the children educational and behavioural performance

Chapter Five presents the following paper:

- Paper Five: 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.

Previous chapters have addressed disputes over the contemporary outdoor dust Pb contamination in Broken Hill (Chapter Three) and discussed relationships between mining activities, environmental Pb and blood Pb in Broken Hill (Chapter Four and Five). As consequences of environmental contamination, the deleterious effects of blood Pb and environmental Pb on children behavioural and cognitive abilities have been widely reported outside Australia. We first applied the Australian National Assessment Program–Literacy and Numeracy (NAPLAN) and Australian Early Development Census (AEDC) data to demonstrate the severity of environmental contamination to children health consequences in Broken Hill and another two Australian mining and smelting communities: Mount Isa and Port Pirie. Since universal blood Pb screening is not performed in Australia (NHMRC, 2009), the approach of this study can be applied to other Australian contaminated sites to estimate adverse impacts of environmental Pb contamination on children's educational and behavioural performance.

Environmental Pollution 207 (2015) 345 356

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

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

Chenyin Dong [a], Mark Patrick Taylor [a, *], Louise Jane Kristensen [a], Sammy Zahran [b]

[a] Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, Sydney, New South Wales 2109, Australia
[b] Department of Economics, Center for Disaster and Risk Analysis, Colorado State University, C-312A Clark Building, Fort Collins, CO 80523-1771, USA

ARTICLE INFO

Article history:
Received 30 June 2015
Received in revised form
11 September 2015
Accepted 12 September 2015
Available online xxx

Keywords:
Arsenic
Broken Hill
Cadmium
Educational performance
Lead

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 μg/m^2; dust deposition: 2950 μg/m^2/day; aerosols: 0.707 μg/m^3. The proportion of children from Broken Hill central, the area with the highest environmental contamination, presented with vulnerabilities in two or more devel opmental 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 environ mental 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.

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 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 oppor tunity 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 lead zinc 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

* Corresponding author.
E-mail address: mark.taylor@mq.edu.au (M.P. Taylor).

http://dx.doi.org/10.1016/j.envpol.2015.09.037
0269-7491/

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 pro portion of children over the recently withdrawn national guideline of 10 μg/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 μg/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 μg/dL (NHMRC, 2015). The study applies an ecological approach to assess the spatial relationship between the potential risk of harm from environ mental 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 cor responding 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 refer ence 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 μg/wipe for As and <0.05 μg/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 (SiO_2) 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 cur rent operating mining company, CBH Rasp Mine, also has their own air quality monitoring stations. However, the stations with avail able 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 gov ernment 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 vulnera bility, 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:

$$AEDC_{std} \quad \frac{AEDC_{local}}{AEDC_{national}} \times \frac{SEIFA_{local}}{SEIFA_{national}} \tag{1}$$

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

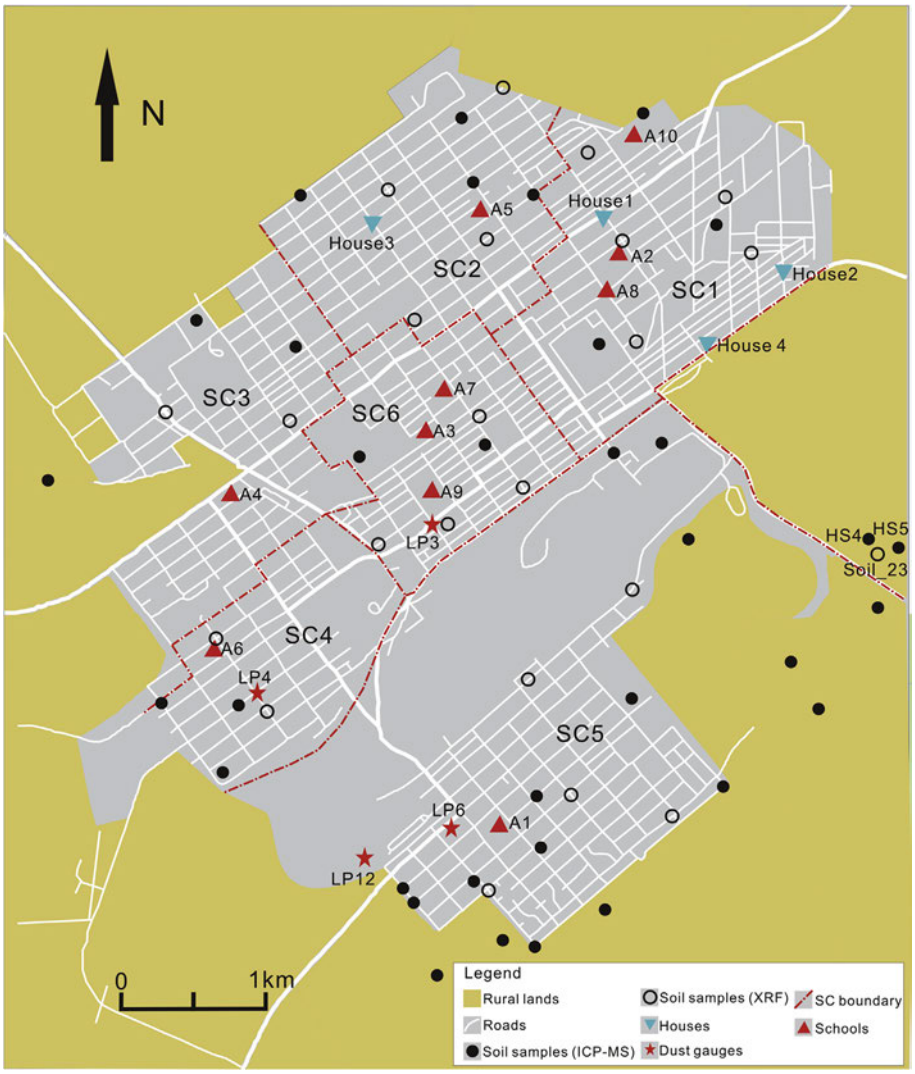


Fig. 1. Locations of surface soil samples collected from the six school catchments in Broken Hill. Dust gauges (LP3, 4 and 6) and a high volume air sampler (HVAS) (LP12) from Perilya's licence monitoring are also shown. Soil samples HS4, HS5 and Soil_23 are included in school catchment SC5 to evaluate 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 do mains 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 socio economic factors on school outcomes, the NAPLAN Index of Com munity Socio Educational Advantage (ICSEA) was integrated into the analyses (ACARA, 2013). The ICSEA measure allows for com parisons 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 back grounds (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:

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

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 (NPI, 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 μg/m^3 and an average of 0.487 μg/m^3 compared to a maximum of 0.357 μg/m^3 and an average of 0.189 μg/m^3 in the other months (Supplementary Table S7). Seasonality of dust re suspension 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 μg/m^3, with maximum 0.707 μg/m^3. The Australia national air quality standard for TSP Pb is set at a maximum value of 0.5 μg/m^3 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 μg/m^3 on a mean moving monthly (or as an annual) standard, but not to exceed 0.5 μg/m^3 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 μg/m^2/day of dust Pb, and Pb loading peaked at 597 μg/m^2/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 μg/m^2. 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 μg/m^2 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 μg/m^2/day) (Supplementary Fig. S8).

Surface dust wipe Pb data from school A9 located in central Broken Hill, ranged from 3298 to 86,061 μg/m^2 (median 13,837 μg/m^2) (Table 1). The maximum value recorded is more than 215 times the Pb clean up goal of 400 μg/m^2 (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 clean up goal (WA Government, 2011) (Table 1), suggesting that contemporary dust deposition continues to pose a significant po tential pathway for Pb exposure. Compared with the four proper ties, As (maximum 687 μg/m^2) and Cd (maximum 404 μg/m^2) values in school A9 dust wipes were elevated by comparison to the daily equivalent values provided in the TA Luft (2002) (As − 4 μg/m^2/day; Cd − 2 μg/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 en compasses school catchments SC5 and SC6 (Fig. 1). School catch ment SC3 in the west of Broken Hill returned the lowest surface soil Pb level (median Pb 116 mg/kg). The Australian National Environ ment 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 (μg/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 (μg/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 (μg/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]

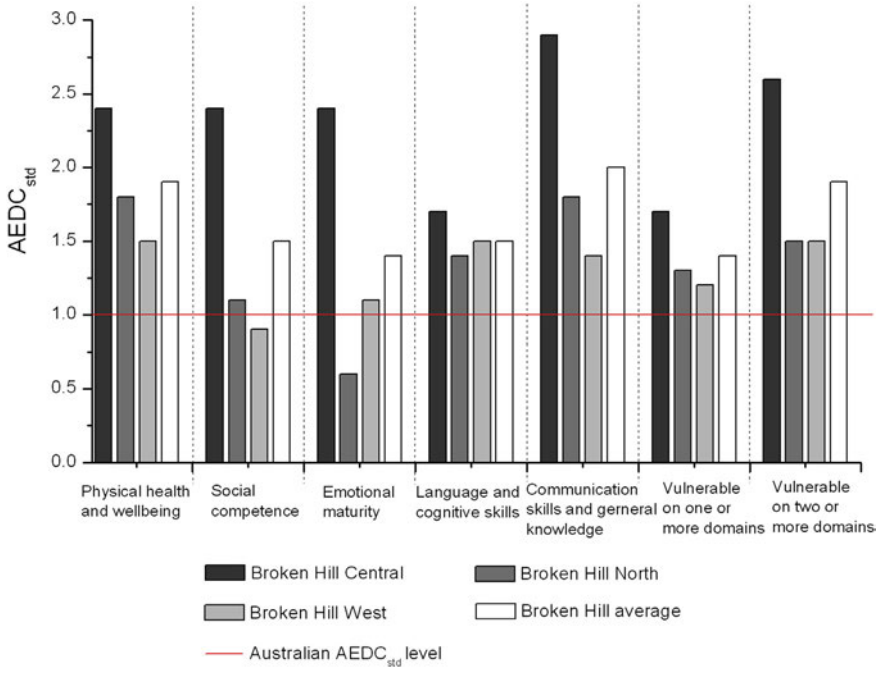


Fig. 2. Australian Early Development Census (AEDC) results across the different geographic areas for Broken Hill standardized according to the Australian Bureau of Statistics SIEFA (Socio-Economic Indexes for Areas, ABS, 2013) index for Broken Hill.

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.

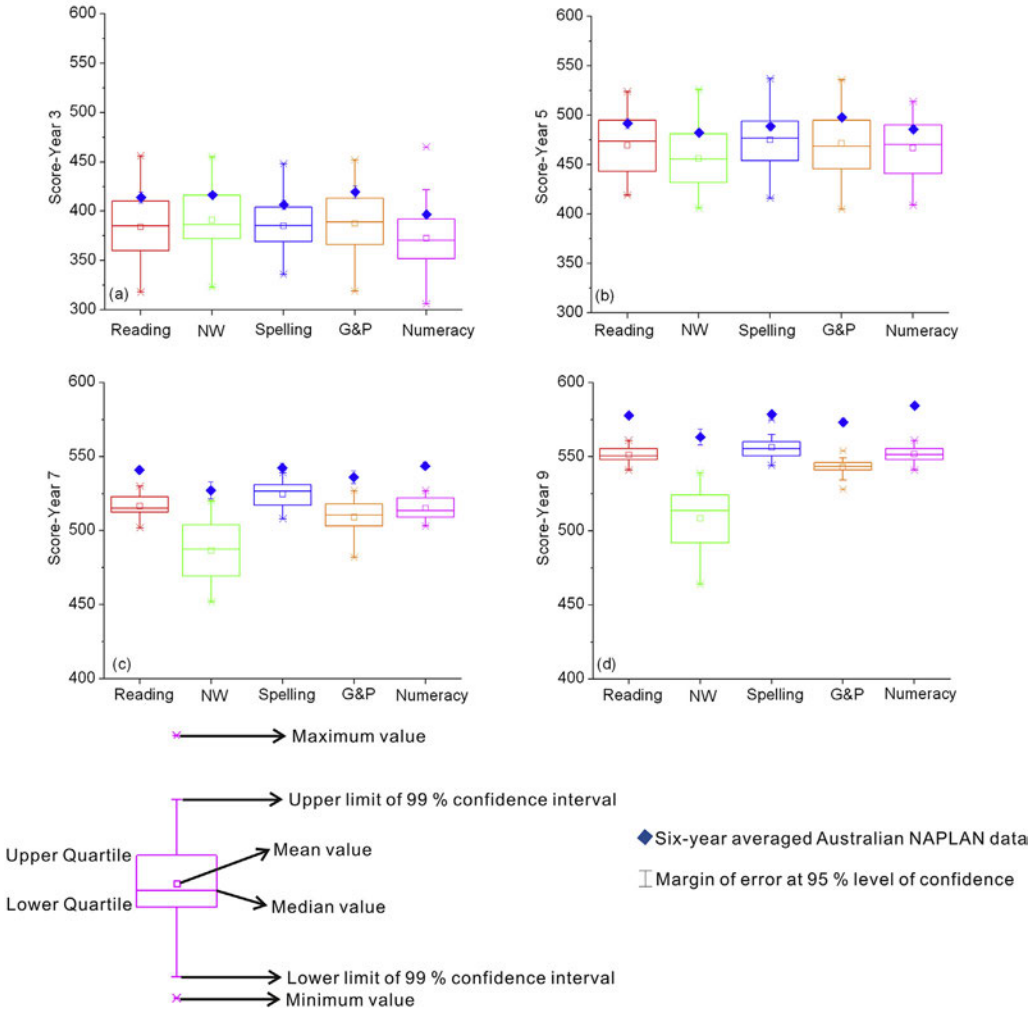


Fig. 3. Box-whisker plots comparing the five educational domains measured in Broken Hill school children. Diamond boxes represent the six-year averaged Australian NAPLAN data for the respective educational domains. NW: narrative writing, G&P: grammar and punctuation.

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 narra tive writing is the lowest performing measure of all the five do mains 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 dis played 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 catch ment 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

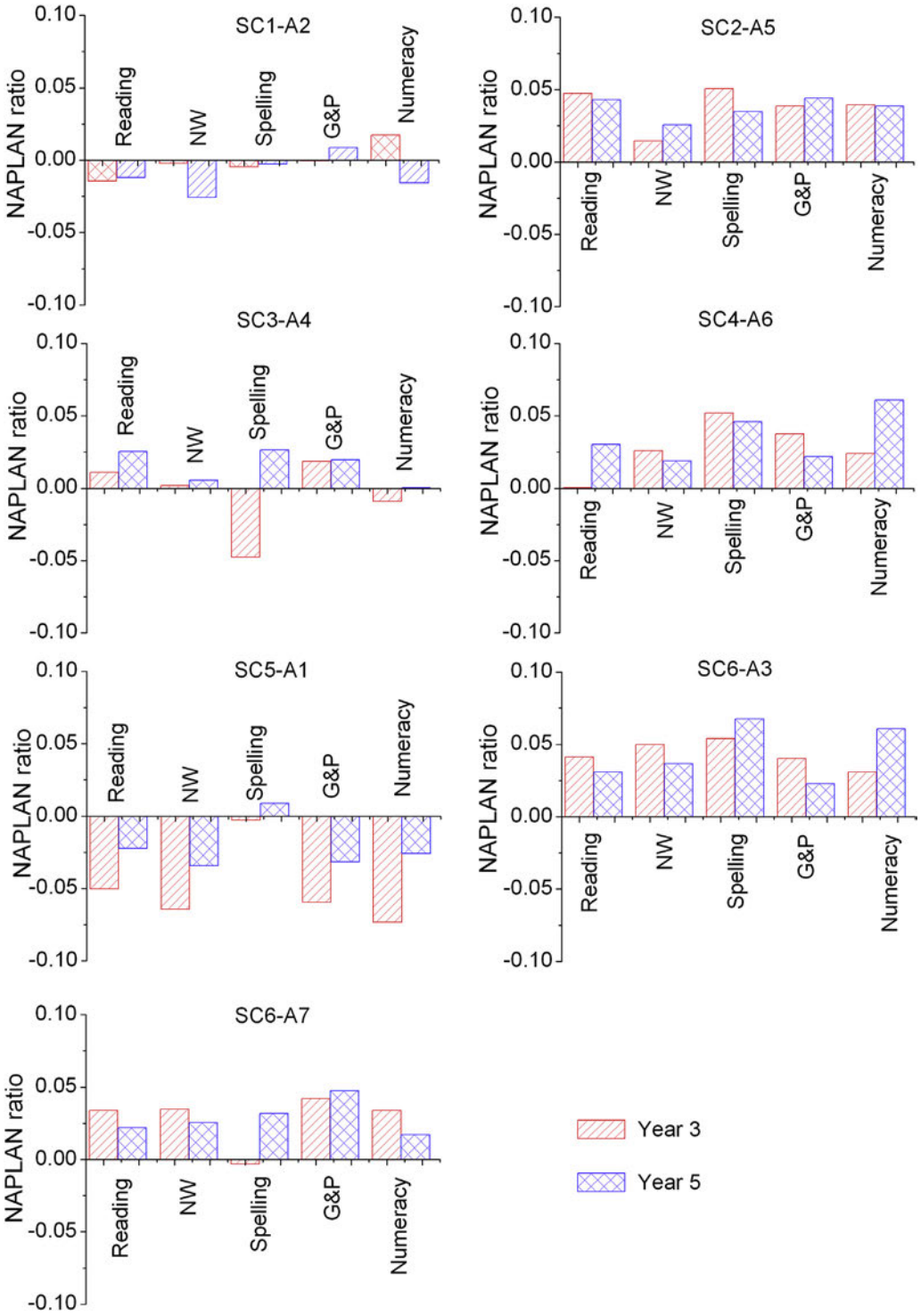


Fig. 4. Ratio of NAPLAN data for years 3 and 5 from Broken Hill schools (A1 A7) compared against NAPLAN data from comparable schools (based upon equivalent ICSEA (Index of Community Socio-Educational Advantage) values (ACARA, 2013). Positive values indicate where Broken Hill schools perform better in 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:

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

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 re sidual 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*** (0.057)	0.308*** (0.0539)	0.265*** (0.060)	0.307*** (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* (54.34)	115.9** (52.47)	156.2*** (58.74)	105.1** (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 (β 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, respec tively. 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, respec tively. 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 chil dren 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 develop mentally 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 atmo spheric 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 $\mu g/m^3$ and 2973 ng/m^3, 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 $\mu g/m^3$ (2011) and 250 ng/m^3 (2009) (Taylor et al., 2014a). Elevated Pb in surface dust and soil and associated elevated blood lead values in children have been iden tified 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 Austra lian 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 neu ropsychological 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,

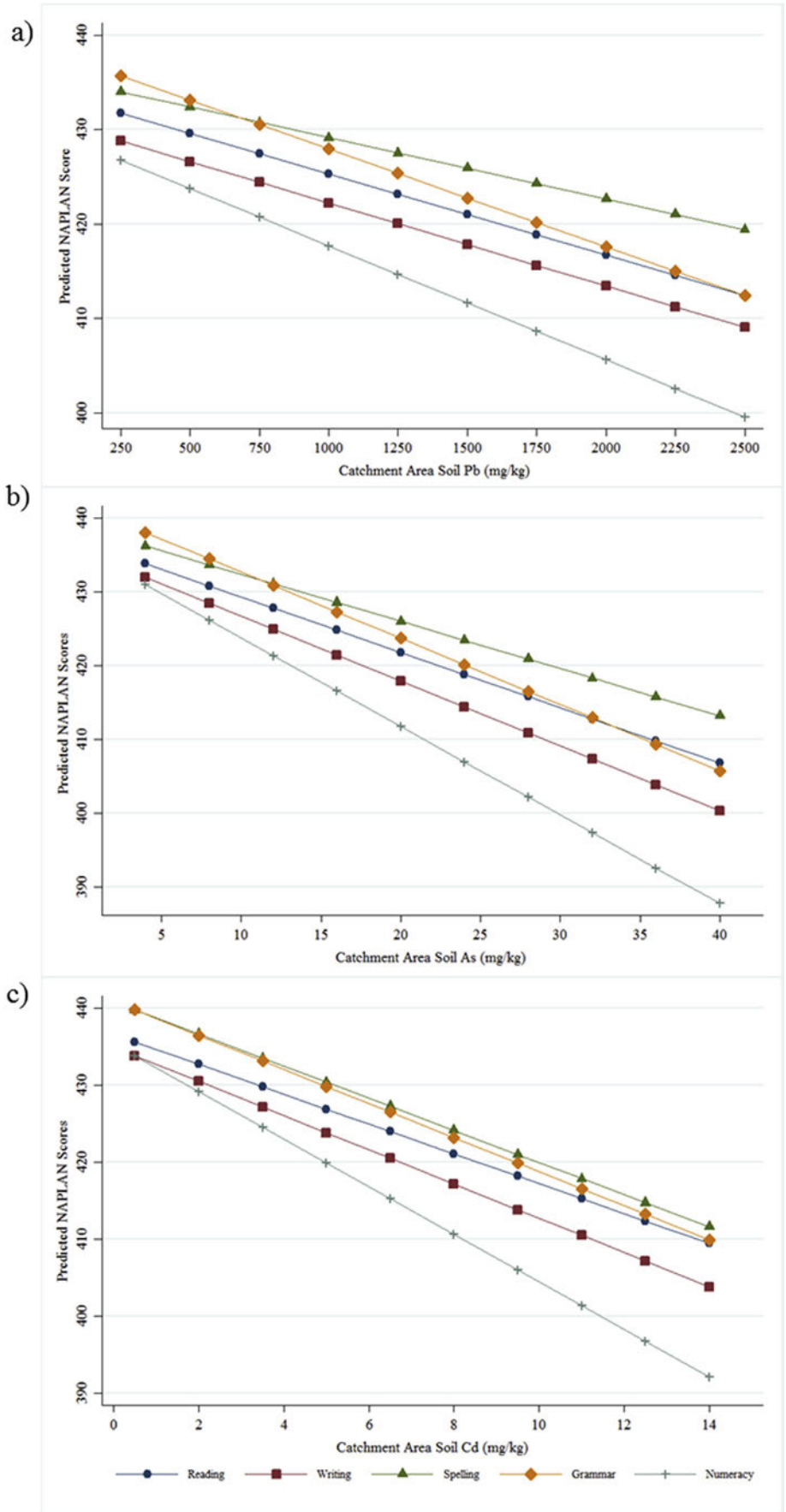


Fig. 5. Predicted test scores by subject by soil metal exposure risk. (a) Predicted NAPLAN school scores (adjusted for socio-economic advantage) versus soil Pb. (b) Panel B: predicted NAPLAN school scores (adjusted for socio-economic advantage) versus soil As. (c) Panel C: predicted NAPLAN school scores (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 μg/dL (NHMRC, 2015). Implementation of 5 μg/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 na ture. The NAPLAN data is limited to school level. While students from each school are drawn predominantly from their corre sponding 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 clas sified as being more vulnerable in all of the five AEDC areas tested, even after adjusting for socio economic measures. Similar out comes 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 limita tions, the combination of the AEDC, NAPLAN and environmental data imply strongly that metal contamination of the urban envi ronment 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 environ mental exposures are a modifiable risk factor, it is not an unrea sonable 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.

Acknowledgements

The soil and dust analysis for this study was funded by Mac quarie University's LEAP Program, which is part of the Australian Federal Government's Higher Education Participation and Part nerships Program. The two anonymous reviewers are thanked for their valuable feedback. Dr Margaret Lesjak and Frances Boreland are thanked for their comments on an earlier draft of this work. C. Dong is funded by an International Macquarie University Research Excellence Scholarship (No. 2014098). L.J. Kristensen is funded by an Australian Postgraduate Award. M.P. Taylor is a member of the Broken Hill Lead Reference Group. The authors declare no competing financial interests.

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.

References

Australian Bureau of Statistics (ABS), 2013. 2033.0.55.001 - Census of Population and Housing: Socio-Economic Indexes for Areas (SEIFA), Australia, 2011. http://www.abs.gov.au/AUSSTATS/abs@.nsf/DetailsPage/2033.0.55.0012011?OpenDocument (accessed 02.05.15).

Amato, M.S., Moore, C.F., Magzamen, S., Imm, P., Havlena, J.A., Anderson, H.A., Kanarek, M.S., 2012. Lead exposure and educational proficiency: moderate lead exposure and educational proficiency on end-of-grade examinations. Ann. Epidemiol. 22, 738 743.

American Society for Testing and Materials, 2003. Standard Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequenct Lead Determination. http://www.astm.org/Standards/E1728.htm (accessed 10.06.15).

Australian Curriculum Assessment and Reporting Authority (ACARA), 2008. 2008 NAPLAN National Report. http://www.nap.edu.au/verve/_resources/2ndStageNatlionaReport_18Dec_v2.pdf (accessed 10.03.15).

Australian Curriculum Assessment and Reporting Authority (ACARA), 2013. Guide to Understanding 2012 Index of Community Socio-educational Advantage (ICSEA) Values. http://www.acara.edu.au/verve/_resources/Guide_to_understanding_2012_ICSEA_values.pdf (accessed 10.03.15).

Australian Curriculum Assessment and Reporting Authority (ACARA), 2015. My School. http://www.myschool.edu.au/ (accessed 15.05.15).

Australian Early Development Census (AEDC), 2013. AEDC 2012 Summary Report. https://www.aedc.gov.au/resources/detail/aedc-2012-summary-report (accessed 10.03.15).

Baghurst, P.A., Tong, S.L., McMichael, A.J., Robertson, E.F., Wigg, N.R., Vimpani, G.V., 1992. Determinants of blood lead concentrations to age 5 years in a birth cohort study of children living in the lead smelting city of Port Pirie and surrounding areas. Arch. Environ. Health 47, 203 210.

Bellinger, D.C., Stiles, K.M., Needleman, H.L., 1992. Low-level lead exposure, intelligence and academic achievement: a long-term follow-up study. Pediatrics 90, 855 861.

Bureau of Meteorology, 2015. Climate Statistics for Australian Locations. Australian Government. http://www.bom.gov.au/climate/averages/tables/cw_047007_All.shtml (accessed 21.08.15).

Burns, J.M., Baghurst, P.A., Sawyer, M.G., McMichael, A.J., Tong, S.L., 1999. Lifetime low-level exposure to environmental lead and children's emotional and behavioral development at ages 11 13 years: the Port Pirie cohort study. Am. J. Epidemiol. 149, 740 749.

Calderon, J., Navarro, M.E., Jimenez-Capdeville, M.E., Santos-Diaz, M.A., Golden, A., Rodriguez-Leyva, I., Borja-Aburto, V., Diaz-Barriga, F., 2001. Exposure to arsenic and lead and neuropsychological development in Mexican children. Environ. Res. 85, 69 76.

Cartwright, B., Merry, R.H., Tiller, K.G., 1976. Heavy metal contamination of soils around a lead smelter at Port Pirie, South Australia. Aust. J. Soil Res. 15, 69 81.

CBH Resources Limited, 2012. Air Quality Monitoring Program. http://www.cbhresources.com.au/files/1013/5302/6105/BHOP_Air_Quality_Monitoring_Program_V2.pdf (accessed 17.05.15).

Ciesielski, T., Bellinger, D.C., Schwartz, J., Hauser, R., Wright, R.O., 2013. Associations between cadmium exposure and neurocognitive test scores in a cross-sectional study of US adults. Environ. Health 12, 13.

Drew, G.J., 2011. Australia's first mining era. MESA J. 61, 42 46.

Earl, R., Burns, N., Nettelbeck, T., Baghurst, P., 2015. Low-level environmental lead exposure still negatively associated with children's cognitive abilities. Aust. J. Psychol. http://dx.doi.org/10.1111/ajpy.12096.

Environmental Protection Authority (EPA), 2012. Environmental Protection Licence No.2688. Perilya Broken Hill Ltd. http://www.epa.nsw.gov.au/prpoeoapp/ViewPOEOLicence.aspx?DOCID 31560&SYSUID 1&LICID 2688 (accessed 10.03.15).

Ghose, M.K., Majee, S.R., 2000. Sources of air pollution due to coal mining and their impacts in Jharia coalfield. Environ. Int. 26, 81 85.

Government of Western Australia (WA Government), 2011. Lead Cleanup and Recovery Plan. An Overview of the Sampling and Cleaning Process. http://www.oncue.org.au/docs/ECRP_cleanup_overview.pdf (accessed 03.05.15).

Gulson, B.L., Mizon, K.J., Law, A.J., Korsch, M.J., Davis, J.J., Howarth, D., 1994. Source and pathways of lead in humans from the broken hill mining community an alternative use of exploration methods. Econ. Geol. 89, 889 908.

Hang, N.T., Kim Oanh, N.T., 2014. Chemical characterization and sources apportionment of fine particulate pollution in a mining town of Vietnam. Atmos. Res. 145 146, 214 225.

Humphries, K., 2015. NSW Government Commits More than $13 Million to Reduce Lead Levels at Broken Hill. Media release: Kevin Humphries MP Minister for Natural Resources, Lands and Water Minister for Western NSW, 13th February 2015. http://www.epa.nsw.gov.au/resources/MinMedia/EPAMin150213.pdf

(accessed 02.06.2015).
Jusko, T.A., Henderson, C.R., Lanphear, B.P., Cory-Slechta, D.A., Parsons, P.J., Canfield, R.L., 2008. Blood lead concentrations <10 microg/dL and child intelligence at 6 years of age. Environ. Health Perspect. 116, 243 248.
Kristensen, L.J., Taylor, M.P., Morrison, A.L., 2015. Lead and zinc dust depositions from ore trains characterised using lead isotopic compositions. Environ. Sci. Process Impacts 17, 631 637.
Kristensen, L. J., Taylor, M. P., Unravelling the 'miner's myth' that Environmental Contamination in Mining Towns Is Naturally Occurring. *Environ. Geochem. Health*, in review.
Laidlaw, M.A.S., Mielke, H.W., Filippelli, G.M., Johnson, D.L., Gonzales, C.R., 2005. Seasonality and children's blood lead levels: developing a predictive model using climatic variables and blood lead data from Indianapolis, Indiana, Syracuse, New York, and New Orleans, Louisiana (USA). Environ. Health Perspect. 113, 793 800.
Laidlaw, M.A.S., Zahran, S., Mielke, H.W., Taylor, M.P., Filippelli, G.M., 2012. Resuspension of lead contamianted urban soil as a dominant source of atmospheric lead in Birmingham, Chicago, Detroit and Pittburgh, USA. Atmos. Environ. 49, 302 310.
Lanphear, B.P., Matte, T.D., Rogers, J., Clickner, R.P., Dietz, B., Bornschein, R.L., Succop, P., Mahaffey, K.R., Dixon, S., Galke, W., Rabinowitz, M., Farfel, M., Rohde, C., Schwartz, J., Ashley, P., Jacobs, D.E., 1998. The contribution of lead-contaminated house dust and residential soil to children's blood lead levels. A pooled analysis of 12 epidemiologic studies. Environ. Res. 79, 51 68.
Lesjak, M., Gough, N., Belshaw, D., Tall, J., Jones, T., 2013. Lead Health Report 2012-Children Less than 5 Years Old in Broken Hill. Population Health Unit, NSW Government, Western NSW & Far West Local Health District. http://www.wnswlhd.health.nsw.gov.au/UserFiles/files/FarWest/ANNUAL%20LEAD%20REPORT%202012%20Final.pdf (accessed 10.03.15).
Lucchini, R.G., Zoni, S., Guazzetti, S., Bontempi, E., Micheletti, S., Broberg, K., Parrinello, G., Smith, D.R., 2012. Inverse association of intellectual function with very low blood lead but not with manganese exposure in Italian adolescents. Environ. Res. 118, 65 71.
Mackay, A.K., Taylor, M.P., Munksgaard, N.C., Hudson-Edwards, K.A., Burn-Nunes, L., 2013. Identification of environmental lead sources and pathways in a mining and smelting town: Mount Isa, Australia. Environ. Pollut. 180, 304 311.
Malm, O., 1998. Gold mining as a source of mercury exposure in the Brazilian Amazon. Environ. Res. 77, 73 78.
Mazumdar, M., Bellinger, D.C., Gregas, M., Abanilla, K., Bacic, J., Needleman, H.L., 2011. Low-level environmental lead exposure in childhood and adult intellectual function: a follow-up study. Environ. Health 10, 24. http://dx.doi.org/10.1186/1476-069X-10-24.
McLaine, P., Navas-Acien, A., Lee, R., Simon, P., Diener-West, M., Agnew, J., 2013. Elevated blood lead levels and reading readiness at the start of kindergarten. Pediatrics 131, 1081 1089.
McMichael, A.J., Baghurst, P.A., Wigg, N.R., Vimpani, G.V., Robertson, E.F., Roberts, R.J., 1988. Port Pirie Cohort study: environmental exposure to lead and children's abilities at the age of four years. N. Engl. J. Med. 319, 468 475.
Mighall, T.M., Abrahams, P.W., Grattan, J.P., Hayes, D., Timberlake, S., Forsyth, S., 2002. Geochemical evidence for atmospheric pollution derived from prehistoric copper mining at Copa Hill, Cwmystwyth, mid-Wales, UK. Sci. Total Environ. 292, 69 80.
Miranda, M.L., Kim, D., Galeano, M.A., Paul, C.J., Hull, A.P., Morgan, S.P., 2007. The relationship between early childhood blood lead levels and performance on end-of-grade tests. Environ. Health Perspect. 115, 1242 1247.
Morrison, A.L., Gulson, B.L., 2007. Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. Sci. Total Environ. 382, 30 42.
Munksgaard, N.C., Taylor, M.P., Mackay, A., 2010. Recognising and responding to the obvious: the source of lead pollution at Mount Isa and the likely health impacts. Med. J. Aust. 193, 131 132.
National Environment Protection Measure (NEPM), 2013. Schedule B1: Guideline on Investigation Levels for Soil and Groundwater. http://www.nepc.gov.au/system/files/resources/93ae0e77-e697-e494-656f-afaaf9fb4277/files/schedule-b1-guideline-investigation-levels-soil-and-groundwater-sep10.pdf (accessed 10.03.15).
National Health and Medical Research Council (NHMRC), 2015. NHMRC Statement: Evidence on the Effects of Lead on Human Health. http://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh58_nhmrc_statement_lead_effects_human_health_a.pdf (accessed 29.08.15).
National Pollutant Inventory (NPI), 2014a. 2012/2013 Data within Broken Hill. http://www.npi.gov.au/npidata/action/load/emission-by-facility-result/criteria/lga/25/destination/ALL/source-type/ALL/substance-name/All/subthreshold-data/Yes/year/2013 (accessed 10.03.15).
National Pollutant Inventory (NPI), 2014b. 2012/2013 Data within Mount Isa. http://www.npi.gov.au/npidata/action/load/emission-by-substance-result/criteria/lga/20/destination/ALL/source-type/ALL/substance-name/All/subthreshold-data/Yes/year/2013 (accessed 10.03.15).
National Pollutant Inventory (NPI), 2014c. 2012/2013 Data within Port Pirie. http://www.npi.gov.au/npidata/action/load/emission-by-substance-result/criteria/lga/354/destination/ALL/source-type/ALL/substance-name/All/subthreshold-data/Yes/year/2013 (accessed 10.03.15).
New South Wales (NSW) Government, 2014. Lead It's in Our Hands. http://www.leadnsw.com.au/ (accessed 18.08.15).
Nriagu, J.O., 1994. Mercury pollution from the past mining of gold and silver in the Americas. Sci. Total Environ. 149, 167 181.
O'Bryant, S.E., Edwards, M., Menon, C.V., Gong, G., Barber, R., 2011. Long-term low-level arsenic exposure is associated with poorer neuropsychological functioning: a Project FRONTIER study. Int. J. Environ. Res. Public Health 8, 861 874.
Perilya Limited, 2015. Monthly Reports: Environmental Reporting. http://www.perilya.com.au/health safety environment/environment/reports (accessed 10.03.15).
Roarty, M., 2010. The Australian Resources Sector: its Contribution to the Nation and a Brief Review of Issues and Impacts. Parliamentary Library, Parliament of Australia. http://www.aph.gov.au/About_Parliament/Parliamentary_Departments/Parliamentary_Library/pubs/BN/1011/AustResources#_Toc273016103 (accessed 29.04.15).
Schwartz, J., Angle, C., Pitcher, H., 1986. Relationship between childhood blood lead levels and stature. Pediatrics 77, 281 288.
Selevan, S.G., Rice, D.C., Hogan, K.A., Euling, S.Y., Pfahles-Hutchens, A., Bethel, J., 2003. Blood lead concentration and delayed puberty in girls. N. Engl. J. Med. 348, 1527 1536.
Simon, D., Lewis, C., Pumpa, L., 2015. Technical Paper 2014/4, Analysis of blood lead levels for 2014 (1 January 2014 31 December 2014). South Australia Health, Government of South Australia. http://www.sahealth.sa.gov.au/wps/wcm/connect/055d3800475f352d8629d622c3ec38c5/TECHNICAL+PAPER+No+2014_4+analysis+of+blood+lead+levels+for+2014+%281+January+2014-31+December+2014%29.pdf?MOD AJPERES&CACHEID 055d3800475f352d8629d622c3ec38c5 (accessed 23.05.15).
Solomon, R.J., 1988. The richest lode: broken Hill 1883 1988. Hale & Iremonger, Sydney, p. 424.
South Australia Health, 2013. 2013 Port Pirie Soil Lead Concentrations Report. https://www.sahealth.sa.gov.au/wps/wcm/connect/fe9ace8040cc6bd396eeb66c5432000f/2013+Port+Pirie+Soil+Lead+Concentrations+Report+%28web%29.pdf?MOD AJPERES&CACHCAC fe9ace8040cc6bd396eeb66c5432000f (accessed 23.05.15).
Standards Australia, 1998. AS 4361.2-1998 Guide to lead paint management Part 2: Residential and commercial buildings. https://infostore.saiglobal.com/STORE/PreviewDoc.aspx?saleItemID 380951 (accessed 10.03.15).
Streeton, J.A., 2000. A Review of Existing Health Data on Six Pollutants. http://www.nepc.gov.au/system/files/resources/9947318f-af8c-0b24-d928-04e4d3a4b25c/files/aaq-rpt-review-existing-health-data-6-pollutants-report-streeton-199705-reprint-200006.pdf (accessed 10.03.15).
TA Luft, 2002. Technical Instructions on Air Quality Control. In: First General Administration Regulation Pertaining the Federal Immission Control Act. http://www.bmub.bund.de/fileadmin/bmu-import/files/pdfs/allgemein/application/pdf/taluft_engl.pdf (accessed 10.03.15).
Taylor, M.P., Camenzuli, D., Kristensen, L.J., Forbes, M., Zahran, S., 2013. lead exposure risks associated with children's outdoor playgrounds. Environ. Pollut. 178, 447 454.
Taylor, M.P., Mackay, A.K., Hudson-Edwards, K.A., Holz, E., 2010. Soil Cd, Cu, Pb and Zn contaminants around Mount Isa city, Queensland, Australia: potential sources and risks to human health. Appl. Geochem. 25, 841 855.
Taylor, M.P., Davies, P.J., Kristensen, L.J., Csavina, J.L., 2014a. 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 Res. 14, 35 52.
Taylor, M.P., Mould, S.A., Kristensen, L.J., Rouillon, M., 2014b. Environmental arsenic, cadmium and lead dust emissions from metal mine operations: implications for environmental management, monitoring and human health. Environ. Res. 135, 296 303.
Taylor, M.P., Winder, C., Lanphear, B.P., 2014c. Australia's leading public health body delays action on the revision of the public health goal for blood lead exposures. Environ. Int. 70, 113 117.
Taylor, M.P., Zahran, S., Kristensen, L., Rouillon, M., 2015. Evaluating the efficacy of playground washing to reduce environmental metal exposures. Environ. Pollut. 202, 112 119.
Thompson, A.J., Hamlet, W.M., Thomas, J., 1893. Report of Board Appointed to Inquire into the Prevalence and Prevention of Lead Poisoning at the Broken Hill Silver-Lead Mines to the Honorable the Minister for Mines and Agriculture. Legislative Assembly, New South Wales.
Tong, S.L., Baghurst, P.A., McMichael, A.J., Sawyer, M.G., Mudge, J., 1996. Lifetime exposure to environmental lead and children's intelligence at 11 13 years: the Port Pirie cohort study. BMJ 312, 1569 1575.
Tong, S.L., Baghurst, P.A., Sawyer, M.G., Burns, J., McMichael, A.J., 1998. Declining blood lead levels and changes in cognitive function during childhood: the port pirie cohort study. JAMA 280, 1915 1919.
van Alphen, M., 1999. Atmospheric heavy metal deposition plumes adjacent to a primary lead-zinc smelter. Sci. Total Environ. 236, 119 134.
Wright, R.O., Amarasiriwardena, C., Woolf, A.D., Jim, R., Bellinger, D.C., 2006. Neuropsychological correlates of hair arsenic, manganese, and cadmium levels in school-age children residing near a hazardous waste site. NeuroToxicology 27, 210 216.
Zahran, S., Mielke, H.W., McElmurry, S.P., Filippelli, G.M., Laidlaw, M.A.S., Taylor, M.P., 2013. Determining the relative importance of soil sample locations to predict risk of child lead exposure. Environ. Int. 60, 7 14.
Zahran, S., Mielke, H.W., Weiler, S., Berry, K.J., Gonzales, C., 2009. Children's blood lead and standardized test performance response as indicators of neurotoxicity in metropolitan New Orleans elementary schools. NeuroToxicology 30, 888 897.

Zahran, S., Mielke, H.W., Weiler, S., Hempel, L., Berry, K.J., Gonzales, C.R., 2012. Associations between standardized school performance tests and mixtures of Pb, Zn, Cd, Ni, Mn, Cu, Cr, Co, and V in community soils of New Orleans. Environ. Pollut. 169, 128 135.
Zhang, N.H., Baker, H.W., Tufts, M., Raymond, R.E., Salihu, H., Elliott, M.R., 2013. Early childhood Lead exposure and academic achievement: evidence from Detroit public schools, 2008 2010. Am. J. Public Health 103, e72 e77.
Zhang, X.W., Yang, L.S., Li, Y.H., Li, H.R., Wang, W.Y., Ye, B.X., 2012. Impacts of lead/zinc mining and smelting on the environment and human health in China. Environ. Monit. Assess. 184, 2261 2273.

Chapter 7: Discussion

7.1 Summary of thesis

This thesis primarily investigated environmental Pb contamination in Broken Hill, its potential sources and risks with respect to elevated blood Pb, and its potential impacts on children's health (i.e. educational performance and developmental vulnerabilities). Prior to the initiation of this thesis (2014), soil Pb contamination and its sources have been examined in recent times by Yang and Cattle (2015); Kristensen et al. (2015); Kristensen and Taylor (2016). Yang and Cattle (2015) found that mean Pb concentrations of urban soil were ~20 times greater compared with corresponding regional values, and Pb bioaccessibility of Broken Hill surface soil ranged from 24% to 89%. Kristensen and Taylor (2016) showed that soil Pb contamination was caused by mining activities rather than natural processes (e.g. weathering and erosion of the Pb bearing gossan). Although soil Pb contamination has been thoroughly investigated over the last two decades (e.g. Gulson et al., 1994, 1995), there has been a relative paucity of research examining contemporary dust Pb contamination and its sources in Broken Hill, even though childhood blood Pb levels in the region have continued to remain elevated (cf. Taylor et al., 2014a). Research in the 1990s showed that the Broken Hill Pb ore body was a significant source of the Pb in household dust (Gulson et al., 1995) but since this time significant remediation work has been completed to reduce emissions from waste deposits and mining areas (Broken Hill Environmental Lead Program, 2016). Accordingly, this thesis shifts the focus to investigating potential risks associated with dust Pb deposition balanced against those from soil Pb on children's health. The research findings from this study regarding Broken Hill contamination and human health exposure are presented in detail in Chapters Three, Four, Five and Six. The primary findings are summarised below.

Chapter Three examined contemporary dust Pb deposits, their bioaccessibility and potential sources in Broken Hill. This study revealed that the two dust deposition monitoring sites closest to the current mining operations (i.e. southern mining operations of Perilya Limited referred to in Papers One and Four) had the highest dust Pb loading (μg/m^2/day) of all six sites situated across Broken Hill, with mean values of 255 μg/m^2/day and 248 μg/m^2/day, respectively. These deposition rates exceeded the benchmark value of 100 μg/m^2/day recently suggested by Gulson and Taylor (2017) and Taylor (2015). Moreover, the benchmark value of 100 μg/m^2/day is the same as that promulgated by the German regulation TA Luft (TA Luft, 2002) and used by the Queensland government as a trigger value for Pb dust deposition at Mount Isa (Taylor et al., 2014b). In addition, dust Pb deposits in Broken Hill possess elevated bioaccessibility with a mean of 75% of total Pb. That suggests children living close to the current mining operations

are facing an elevated dust Pb exposure risk. In terms of the sources of Pb dust in the region, analysis of dust Pb isotopic compositions demonstrated it predominantly (94-99%) originated from the Broken Hill ore body. The source of the dust Pb, which is likely dominated by Perilya's southern mining operations, was further confirmed by evaluation of its morphological and geochemical characteristics. These analyses showed that particles collected from sites close to mining operations were associated with the atmospheric Pb emissions of current mining operations.

Chapter Four estimated the relationship between environmental Pb and blood Pb in Broken Hill. This study showed that both soil and dust Pb were significantly associated with children's blood Pb over the period of environmental and human health assessment from 1991–2015. In addition, demographic parameters (e.g. age, gender, ethnicity, age of house and socio-economic status) were significantly associated with childhood blood Pb concentrations in Broken Hill. The evidence from the data indicates that children aged between 12-36 months, and in particular Aboriginal children, should be prioritised for intervention practices.

Chapter Five shifts the emphasis from examining long-term drivers of Pb exposure to investigating the role of current mining (i.e. 2011–2015) activities on Broken Hill childhood blood Pb levels. This study took advantage of two 'natural experiments': (a) prevailing wind conditions in Broken Hill; (b) a major dust storm that occurred in 2009 (Jayaratne et al., 2011) to examine the impact of current mining activities on blood Pb concentrations. This study showed that blood Pb concentrations decreased at a greater rate with distance away from current mining operations for children living in the prevailing wind direction versus those living in the non-prevailing wind direction. Interestingly, the 2009 dust storm redistributed surface soil Pb concentrations in Broken Hill reducing the soil Pb-distance gradient but doing so without attenuating the blood Pb distance decay curve. The disparity between the decline in childhood blood Pb levels versus that seen in soil Pb concentrations at increasing distances away from the mine operations raised the possibility that soil Pb was a less important exposure source than has previously been suggested (Yang and Cattle 2015). In order to examine the role of current emissions in determining child blood Pb outcomes, the effect of distance and current mining activities on the dust Pb deposits was modelled. The analysis showed that atmospheric transport and deposition of contaminants away from the mining operations is a primary mechanism in determining the spatial distribution of childhood blood Pb levels. Consistent with a current emissions pathway (as opposed to legacy contaminants held in soil), blood Pb concentrations also increased with ore production annually. Therefore, the logical conclusion is that soil Pb on

its own cannot explain blood Pb distributions and that dust Pb depositions are a significant factor in driving contemporary exposures.

Chapter Six estimates the potential influences of environmental Pb on children's educational and behavioural performance. This study found that the proportion of children from Broken Hill central, the area with highest soil Pb and dust Pb depositions, presented with vulnerabilities at 2.6 times that of the national average level in two or more of the developmental domains measured as part of the Australian Early Development Census (AEDC), even after adjusting for socio-economic status. Children in school years 3 and 5 from the most contaminated school catchment (SC5; Supplementary Figure S3 of Appendix I) consistently returned the lowest educational scores confirming an association between environmental exposure and lower academic attainment, as identified elsewhere (e.g. Liu et al., 2013; McLaine et al., 2013; Evens et al., 2015). This study was the first Australian study to apply AEDC data and NAPLAN data to estimate potential influences of environmental Pb on children's educational and behavioural performance in Australia. This study further enriches the limited number of other Australian studies that have examined the impacts from mining and smelting emissions on educational and behavioural outcomes in children (e.g. Baghurst et al., 1992; Earl et al., 2016).

Although this thesis focused predominantly on Broken Hill, Australia's two other major lead mining and smelting communities of Mount Isa and Port Pirie (**Paper Five**) along with the industrial city of Newcastle (**Paper Two**), were examined as part of the same PhD research. Overall, the research findings demonstrate the following in relation to understanding the role of current operations and determining sources of contamination:

- A range of geochemical and SEM techniques and approaches for identifying sources of environmental Pb
- Current operations and emissions are intimately related to Pb dust deposition
- Dust Pb depositions are a significant cause of elevated blood Pb
- Pb and other trace metal(loid) depositions are significantly associated with adverse impacts on children's health.

7.2 Potential techniques and approaches for identifying the sources of environmental Pb

In order to prevent contemporary exposure pathways of environmental contamination effectively, the identification of major sources of contemporary environmental contamination is a critical first step. However, in mining and smelting communities, there is often a long history of disputing the major sources of contamination, particularly in communities with a

long history of mining, see section 1.3 of Chapter One. This debate arises because there are various vested interests (Spear et al. 2015) as well as a range of potential sources of contamination in affected communities, including naturally weathered ore debris, legacy emissions from historic mining and smelting activities, paint, petrol and other industrial sources as well as those from current operations. For example, in Broken Hill, an estimated 4.7 million tonnes of the Broken Hill ore body has been removed due to natural weathering and erosion since its formation some 1.6 billion years ago (Webster, 2006). These losses can be set against the 11,000–18,400 tonnes of Pb emitted by smelting activities from 1886 to 1897 (van Alphen, 1991).

Contamination caused by historical mining and smelting activities have been reported globally (e.g. Pestana and Formoso, 2003; Jamieson, 2014; Ordóñez et al., 2014; Li et al., 2016; Lillo et al., 2015; Stovern et al., 2016), including in some Australian communities, such as Bendigo (Martin et al., 2016), Boolaroo (Harvey et al., 2016), Maldon (Abraham et al., 2017), Newcastle (Harvey et al., 2017) and North Queensland (Lottermoser, 2002).

Lead-based paint has been widely considered as another main contributor to childhood blood Pb (Lanphear and Roghmann, 1997; Jacobs et al., 2002; Leighton et al., 2003; Mathee et al., 2007; Levallois et al., 2014). Pb-based paint (1–50 wt% Pb) was used widely on the exterior and interior surfaces in Australian houses built before 1970 (NSW EPA, 2016), including those in Broken Hill (Gulson et al., 1994; Boreland et al., 2009). Consequently, soils at older painted houses are more likely to exceed the 300 mg/kg soil guideline (Rouillon et al., 2017). At Broken Hill, older houses built before the 1940s also displayed elevated soil Pb (Paper Four), but it is unclear as to the specific cause and source of the elevated levels and whether they are due more so to paint or mining emissions and depositions. In other mining and smelting communities (e.g. Port Pirie and Mount Isa), Pb-based paint is taken into account when investigating potential sources of environmental Pb contamination (SA Health, 2013; Noller et al., 2017). In addition, leaded petrol depositions are also a potential contaminant given that this type of petrol was used in Australia for 7–decades between 1932 and 2002. During its 70–years of consumption, more than 240,000 tonnes of Pb from petrol was emitted to the atmosphere in Australia. Consequently, leaded petrol emissions are another potential contributor of Pb contamination in Australian mining and smelting communities (e.g. Gulson et al., 1994, 1996, 1997), requiring its contribution to be assessed. Despite its removal from sale and use in automobiles, leaded petrol depositions remain a persistent environmental contaminant (Gulson et al., 2004; Kristensen et al., 2014; Wu et al., 2016; Zhou et al. 2017).

In order to understand the sources of environmental contamination, this thesis applied a 'multiple lines of evidence' to distinguish different contamination sources in Broken Hill (Paper One). This approach included examinations of trace metal concentrations, Pb isotopic compositions, chemical compositions and morphological characteristics of Pb-rich dust deposition particles. In order to confirm the wider application of this approach, Newcastle (Paper Two) was also investigated using a similar approach. In the Broken Hill study (Paper One), Pb isotopic composition analysis along with geochemical assessment of different orebody sources was used to distinguish naturally weathered ore debris, tailings dumps and atmospheric emissions of current mining activities from non-orebody sources (e.g. leaded petrol, Pb-based paint). While Pb isotopic composition analysis is an established and effective technique for source apportionment (e.g. Gulson et al., 1994, 2004; Soto-Jiménez and Flegal, 2011; Cao et al., 2014; Varrica et al., 2018) it cannot demonstrate unequivocally whether environmental Pb contamination is derived from weathered ore debris, tailings dumps or atmospheric emissions of current mining activities (Paper One).

As a result of this limitation, source apportionment analyses were supplemented by analysis of morphological and chemical characteristics of contaminated particles. Contaminated particles from different sources have their own morphological and chemical characteristics (e.g. Wang et al., 2013; Zhang et al., 2017). For example, recently mined galena (PbS) from the Broken Hill ore body, has good crystallinity and angularity (Kristensen et al., 2015). Recent ore particles also lack surface alteration and elements Fe and Mn (Davis et al., 2016). However, Pb particles from tailings dumps and weathered ore debris are characterised by significant surface alteration, high concentrations of Fe and Mn and a lack of crystallinity and angularity (Paper One). In the Broken Hill study (Paper One), the morphological and chemical characteristics of dust Pb particles emitted from current mining emissions were established to be markedly different from particles sourced from weathered ore debris, tailings dumps and historic smelting emissions. Similarly, the same approach applied in the Newcastle study (Paper Two), showed that slag particles were distinctly different compared to quenched melt droplets formed during smelter emissions. Above all, the application of a multiple lines of evidence approach is a necessary and robust way to identify contamination sources given that similar contamination issues are present in many global industrial cities (National Academies of Sciences, Engineering, and Medicine, 2017).

7.3 Current emissions causing elevated airborne Pb

In some urban areas, resuspension of legacy soil contamination is considered a primary source of airborne contaminants (Young et al., 2002; Laidlaw and Filippelli, 2008; Laidlaw et al., 2012; Zahran et al., 2013). Elevated soil Pb, a consequence of historical mining and smelting activities, has been reported in Broken Hill (Gulson et al., 1994; Yang and Cattle, 2015; Kristensen and Taylor, 2016). However, according to the 2015–2016 NPI data, Broken Hill ranks 2nd (28,000 kg) for point source atmospheric Pb emissions in Australia. The multiple lines of geochemical evidence detailed in Chapter Three revealed that contemporary dust Pb deposits are mainly sourced from current mining emissions. Consistent with a current emission pathway, contemporary dust Pb loading decreased with distance away from the current mining operations. In Chapter Five, the effects of current mining emissions on the contemporary dust Pb loading were quantitatively estimated. The results showed that a 1% increase in distance away from the current mining operations is associated with -0.501% (95% CI: -0.728, -0.275%) reduction in dust Pb loading. In addition, a 1% increase in production intensity at the mine increases the expected amount of dust Pb loading by 1.487% (95% CI: 0.537, 2.437%). Not surprisingly, air Pb levels in Broken Hill are elevated with a mean concentration of 243.86 ng/m^3 during May 2012 to April 2016 compared to those in Sydney that was observed to be around 10.43 ng/m^3 over the same period (Figure 7-1). As the Broken Hill emissions are dispersed across the city, this resulted in a distance-decay contamination pattern away from the primary source and orientated according to the prevailing wind direction (Chapter 3). Similar spatial distributions of dust and airborne contamination have been observed in other mining and smelting communities (Albalak et al., 2003; Telmer et al., 2004; Soto-Jimenez and Flegal, 2011; Qiu et al., 2016; Stovern et al., 2016).

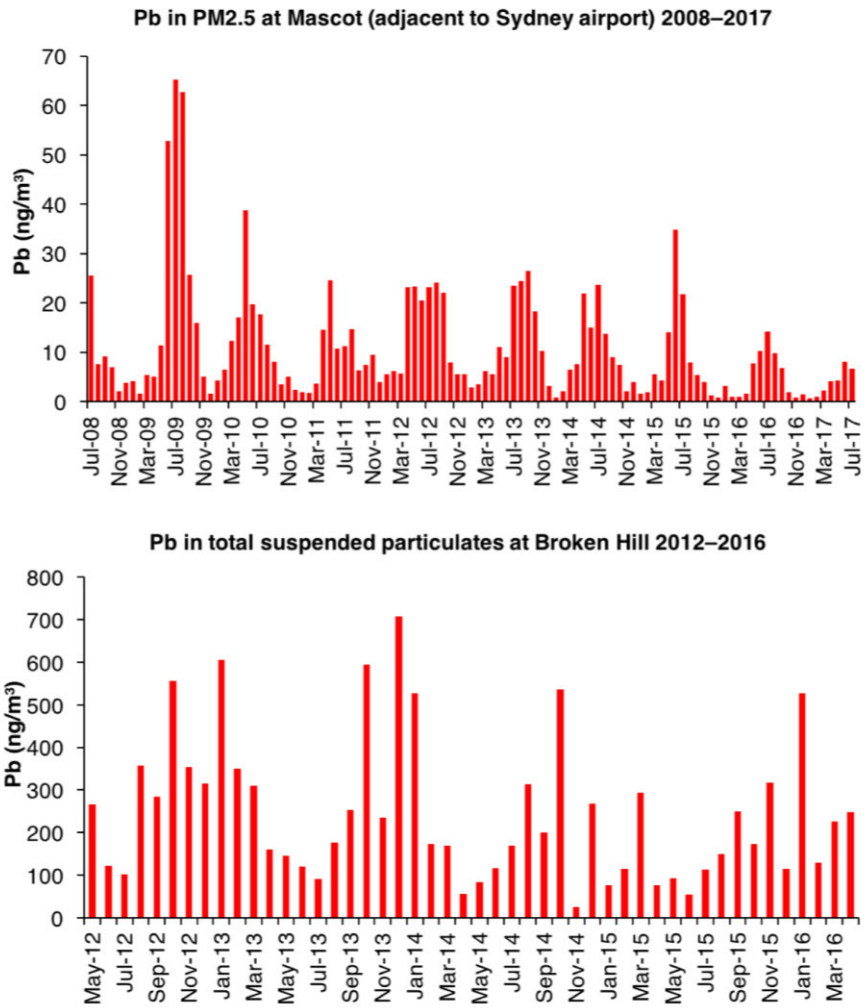


Figure 7-1. Recent monthly average Pb in air Pb concentrations at Sydney (Mascot) and Broken Hill (Data for $PM_{2.5}$ graph provided by Dr Armand J Atanacio, Australian Nuclear Science and Technology Organisation—more limited data is available online). From May 2012 to April 2016, average Pb in air concentrations were 243.86 ng/m^3 and 10.43 ng/m^3 for Broken Hill and Sydney (Mascot), respectively. Figure from Zhou et al. (2017).

7.4 Current emissions causing elevated blood Pb

Chapter Four's data analysis of the full Broken Hill dataset covering the 25-year period from 1991–2015 showed that soil Pb contamination had contributed to elevated blood Pb levels. This finding is a predictable outcome given that international studies have shown that soil Pb contamination can be a dominant pathway of childhood blood Pb exposure (e.g. Lanphear et al., 1998; Mielke et al., 1998; Carrizales et al., 2006; Zahran et al., 2011; Laidlaw et al., 2017). However, in Broken Hill, blood Pb concentrations have declined with annual ore production in the last two decades (Figure 7-2) suggesting mining emissions have driven blood Pb concentrations in Broken Hill.

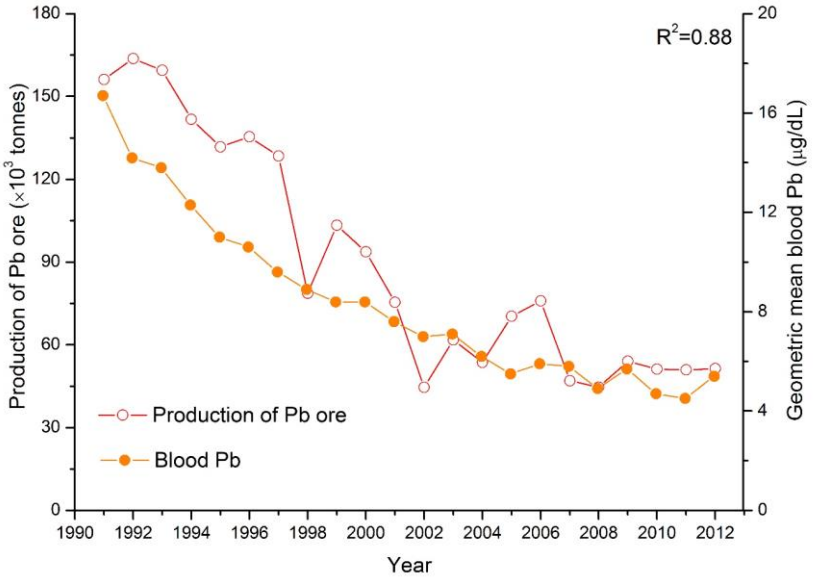


Figure 7-2. Geometric mean blood Pb in all children aged 1-4 years and production of Pb ore, 1991-2013. Lead ore production data is from the Mudd et al. (2017) study, while blood Pb data is from the 2015 Broken Hill annual report (Lesjak and Jones, 2016).

Consistent with a current emission pathway, blood Pb concentrations in Broken Hill decreased with distance away from the current mining operations, which is consistent with the spatial distribution of contemporary dust Pb loading in Broken Hill. Similar spatial distributions of blood Pb have also been observed in other mining and smelting communities (Landrigan et al., 1975; Albalak et al., 2003; Soto-Jiménez and Flegal, 2011; Skalny et al., 2016). These studies all demonstrated that childhood blood Pb concentrations declined with distance away from mining and smelting operations due to a reduction in airborne Pb. In Chapter Five, the analyses indicate that 2 km from the mine is a minimum buffer of safety for a child living under the prevailing wind direction (i.e. South-southeast to South-southwest) in Broken Hill. Further, children located within the prevailing wind direction were at greatest risk of elevated blood Pb compared to those living under the non-prevailing wind directions, even after adjusting for the effects of soil Pb contamination. This further reinforces the argument that atmospheric transport and deposition of contaminants away from the mining operations are the primary mechanism determining the spatial distribution of blood Pb.

7.5 Adverse impacts of environmental Pb exposure on children's health

Lead has been recognised as a neurotoxin for a long time, and its adverse impacts on the developing brain have been reported (e.g. Lidsky and Schneider, 2003). Moreover, there is no safe level of childhood blood Pb concentration (WHO, 2010; CDC, 2012). Intellectual impairment has been observed even at low blood Pb levels (Canfield et al., 2003; Lanphear et al., 2005; Jusko et al., 2008) with no evidence for a lower threshold of no impact (Budtz-

Jørgensen et al., 2012; Earl et al. 2016). The pooled analysis of international cohorts conducted by Lanphear et al. (2005) demonstrated that the estimated IQ point decrements associated with an increase in blood Pb from 2.4 to 10 μg/dL, 10 to 20 μg/dL, and 20 to 30 μg/dL were 3.9 (95% CI, 2.4–5.3), 1.9 (95% CI, 1.2–2.6), and 1.1 (95% CI, 0.7–1.5), respectively, demonstrating that the greatest effects per unit of blood Pb occur at lower exposures. In addition to intellectual impairment, attention deficit hyperactivity disorder (ADHD) emerged as another adverse impact of Pb exposure by the end of the twentieth century (Lanphear, 2015). A study on US children (8–15 years old), Lanphear (2015) showed that the population distribution of ADHD symptoms was 5% when blood Pb concentrations were less than 0.7 μg/dL. However, ADHD symptoms increased in the population to 13% when blood Pb concentrations exceeded 1.3 μg/dL. In Australia, studies on the adverse impacts of Pb exposure, including intellectual impairment and behavioural problems, have largely focused on the smelting community of Port Pirie, South Australia (Wigg et al., 1988; McMichael et al., 1988; Baghurst et al., 1992; Tong et al., 1996; Burns et al., 1999). Recently, a small cohort study involving 127 children (7-8 years old) from Port Pirie (South Australia) and Broken Hill (NSW) inferred that an increase in blood Pb concentrations from 1 to 10 μg/dL was associated with a loss of 13.5 full-scale IQ points after adjusting for other covariates (Earl et al., 2016).

Intellectual impairments and behavioural problems caused by environmental Pb exposure are subtle and can be difficult to identify in individual children (Lanphear, 2015). However, effects of these subtle shifts in intellectual abilities and behaviours are significant at a population level (Lanphear, 2015). For example, among children in the US (0–5 years old), the combined total number of IQ points lost due to Pb exposure is believed to be in the order of 23 million points (Bellinger, 2012). By applying the same strategy regarding the loss of IQ points due to Pb exposure based on children in the US (Bellinger, 2012), approximately 2100 IQ points could be denuded from the 883 Broken Hill children involved in the 2014 blood Pb screening program (Table 7-1).

Table 7-1. IQ points lost to Pb exposure occur in children who have low-to-moderate exposure to Pb in the 2014 Broken Hill cohort. Table adapted from Bellinger (2012).

Range of the blood Pb distribution (μg/dL)	IQ loss	No. of Children	No. of IQ points lost
0-1.43	0.37	135	50
1.43-2.10	0.90	32	29
2.10-7.50	1.6	521	834
>7.5	6.10	195	1189

Consistent with the estimated loss of IQ points (Table 7-1), the analyses completed in Chapter Six showed that the educational performance of Broken Hill children in school years 3 and 5 from the most contaminated school catchment was 7.5% lower than in schools with similar socio-economic status. In addition to cognitive deficits, early childhood developmental vulnerabilities, as measured via the AEDC assessments (Australian Government, 2017), were also observed in Broken Hill children (Chapter Six). The same approach was applied to the mining and smelting communities of Mount Isa and Port Pirie (smelting only) (Paper Five). The analyses further demonstrated that children living and attending schools associated with higher environmental Pb contamination levels recorded higher developmental vulnerabilities after adjusting for their socio-economic status (Paper Five). The approach applied here to assess these Pb mining and smelting communities have clear potential to be applied to assess possible impacts from Pb (or other toxic metal) exposure in other Australian communities that do not have blood Pb screening data.

7.6 Other trace metal(loid) contaminants and their potential impacts on children's health

In addition to elevated Pb found in Broken Hill soils and dusts, elevated levels of As and Cd have also been reported (Paper Five). Median values As and Cd in soils were 16 mg/kg and 4.9 mg/kg, respectively, compared to local background values of 4.9 mg/kg and 0.25 mg/kg (Paper Five). Surface dusts returned maximum values of As – 901 $\mu g/m^2$, Cd – 206 $\mu g/m^2$ and maximum values on hands after 10 minutes of play on the Broken Hill playgrounds closest to current mining operations were 628 $\mu g/m^2$ and 235 $\mu g/m^2$ for As and Cd, respectively (Taylor et al., 2014a). By contrast, in playgrounds distal from mining operations, maximum values for As and Cd dust were 7 $\mu g/m^2$ and 4 $\mu g/m^2$ (Taylor et al. 2014a).

Similar to Pb, other environmental metal(loid)s such as As and Cd are neurotoxic (e.g. Vahidnia et al., 2007; Wang and Du, 2013). The deleterious effects of As and Cd on children's neurological systems, behavioral and cognitive abilities have been identified even at low levels of exposure (Calderón et al., 2001; Wright et al., 2006; O'Bryant et al., 2011; Ciesielski et al., 2013; Wasserman et al., 2011, 2016). After adjusting for socio-economic status, children's school test scores decreased with increasing soil As and Cd concentrations, with each mg/kg increase in soil As and Cd reducing school test scores by 0.896 and 2.346 points, respectively (Chapter Six). Further, the cumulative effect of As, Cd and Pb in soil per mg/kg unit increased the standardized sum of potential toxic metal exposure and was associated with a 3.25 point reduction in NAPLAN test scores (Chapter Six). This finding bolsters previous research (Mielke et al., 2005; Zahran et al. 2012; do Nascimento et al., 2015; Sanders et al., 2015; Valeri

et al., 2017) indicating that exposure to multiple environmental metal(loid)s causes a cumulative impact on children's cognitive development. Furthermore, the toxic environmental metal(loid)s referred to in these previous studies are not limited to Pb, As and Cd, but include other elements such as Mn (Dobson et al., 2004), Zn (Konoha et al., 2006) and Hg (Davidson et al., 2004). Further, organic contaminants have also been strongly associated with decreases in children's cognitive and behavioural functioning, such as PBDEs used as flame retardants (e.g. Roze et al., 2009; Gascon et al., 2012; Zhang et al., 2017), bisphenol A and phthalates used in plastics (e.g. Kim et al., 2009; Cho et al., 2010; Meeker and Ferguson, 2011; Perera et al., 2012a; Ejaredar et al., 2015); Chlorpyrifos, a common agricultural pesticide (e.g. Rauh et al., 2011). In addition, elevated environmental concentrations of PAHs, which are associated with ferrous metal smelting, coal processing or burning of fossil fuels in communities (Paper Two) have previously been shown to have an adverse impact on behavioral and cognitive abilities (e.g. Edwards et al., 2010; Perera et al., 2012b; Peterson et al., 2015).

In addition to the presence of elevated neurotoxic pollutants in the Pb smelting communities examined in this study, acute, short-term concentrations of sulfur dioxide (SO_2) are causative factors for increased respiratory illness (Smargiassi et al., 2009). For example, in 2014 there were 29 and 68 hourly exceedences of emissions over the National Environment Protection Measure (NEPM) guideline level (1-hour standard: 0.2 ppm) at Mount Isa and Port Pirie, respectively (Figure 7-3), with a similarly large number of exceedences of the NEPM SO_2 standard over the last decade at Mount Isa and Port Pirie (Figure 7-3). Interestingly, there are significant disparities in the prevalence of respiratory illnesses in these two communities when compared to other areas (Taylor et al., 2014b). In Mount Isa, hospitalisation rates (n=109) were significantly higher (80%) compared to the rest of Queensland, and asthma mortality rates (n=5) were similarly higher, being 322% higher than the rest of the Queensland (Taylor et al., 2014b). At Port Pirie, the data from 2007/2008 showed that the Port Pirie City district area had hospital admissions for respiratory illness at a rate of 3774 per 100,000 people, compared with 2036 per 100,000 people for the remainder of South Australia (Taylor et al., 2014b). In addition to the adverse respiratory outcomes associated with SO_2 exposures, arsenic exposure is also considered another causative factor for poor lung function and development (Ramsey et al., 2013). Interestingly, it is worth noting that Aboriginal children in Mount Isa recorded very poor lung functions compared to non-Indigenous children in the area (Janu et al., 2014), which is consistent with racial disparities in blood Pb (Chapter Four).

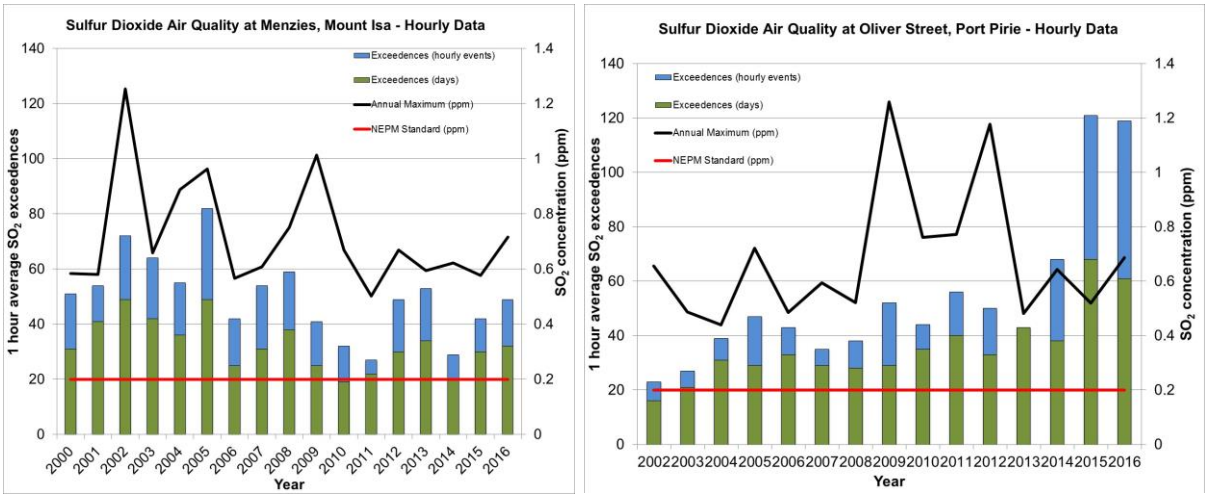


Figure 7-3. Sulfur dioxide air quality data (ppm) as reported for the National Environment Protection (Air Quality) Measures for Mount Isa (Menzies site, 2000–2016) and Port Pirie (Oliver Street, 2002–2016) (data updated from Taylor et al., 2014b). In 2013 the exceedences for days and hourly events overlap on the graph, i.e. have the same number (43 exceedences).

Above all, the data implies that cognitive impairments, behavioural problems and health outcomes are linked to exposure to multiple neurotoxic contaminants (e.g. Pb, As, Cd, PAHs) in mining and smelting communities. With the combination of adverse respiratory contaminants (e.g. SO_2, As, particulate matter) in mining and smelting towns, it is unsurprising that children have poor cognitive development and respiratory health.

7.7 Potential exposure risk management arising from this research

In order to better manage health costs (e.g. cognitive impairments, behavioural problems and respiratory illness) especially for children raised in contaminated environments, exposure risk management is needed. Previous studies have demonstrated that exposure risk management can result in significant benefits for the corresponding communities. For example, in Tongliang, China, following the closure of a local coal-burning plant, neurocognitive development measures in children were improved (Tang et al., 2014). Gould (2009) calculated that for every (US) dollar spent on controlling Pb exposure, some $17–221 is returned to society, which further supports the use of primary prevention as a key component of an exposure risk management strategy. However, instead of controlling emissions at their source, it is commonplace in Australian mining and smelting communities to push the burden of prevention onto the local community (Sullivan, 2014; Sullivan and Green, 2016; Taylor et al. 2017). The advice given to those communities is dominated by educational information and recommendations to keep homes clean and free of Pb contaminated dust even though the evidence shows that such advice has limited benefit in mitigating exposures (Nussbaumer-Streit et al., 2016).

7.7.1 Importance of mitigating ongoing emissions

To reduce environmental exposure risk, application of 'end-of-pipe' technologies, contamination prevention and cleaner production are required (Gavin, 2000). 'End-of-pipe' technologies aim to remediate pollution problems after they have occurred, rather than tacking them before they develop (Gavin, 2000). Approaches that address contamination prevention and cleaner production reduce levels of pollutants in waste streams prior to their release on the mining lease or into the ambient environment. Without a proper pollution prevention strategy to control off site emissions, the efficacy of 'end-of-pipe' technologies is often diminished. For example, at Port Pirie, Taylor et al. (2013) found that atmospheric emissions from the smelter were related directly to the accumulation of surface dust metal(loid)s. In light of this research, the Port Pirie Council and the smelter company, Nyrstar Port Pirie Limited Pty Ltd, agreed to a joint program of playground washing (Taylor et al., 2015). While playground washing reduced dust metal(loid)s deposits, Taylor et al., (2015) showed that parks needed to be washed at least daily to keep dust metal(loid)s deposits under acceptable values due to ongoing emissions. However, while washing playgrounds can provide temporary cleaning of surfaces, the failure to limit off site emissions means that its value to the wider community is limited to those who remain exposed to elevated depositions of toxic dust.

Globally, the benefit resulting from reduction of ongoing emissions in mining and smelting communities has been confirmed in multiple locations. For example, in a mining and smelting community located in Fujian province, China, a follow-up study, conducted after the local Pb mining and smelting operations closed for one year, showed a significant reduction of 5 μg/dL for childhood blood Pb concentrations (Lin et al., 2011). Similarly, at Bunker Hill, USA, mean childhood blood Pb concentrations were significantly reduced following the closure of the local smelter in 1981 (von Lindern et al., 2003). In northern Sweden, following the closure of Pb mine operations, Pb and Zn concentrations in local moss samples, reflecting atmospheric metal deposition, decreased by around 35% and 50%, respectively (Berglund et al., 2010). In the community of Boolaroo, NSW which was home to the former Pasmico Pb-Zn smelter, approximately 30% of children had blood Pb ≥10 μg/dL from 1997 to 2003 before the smelter closed in September 2003 (Dalton and Bates, 2005). After closure, the percentage of children with a blood Pb ≥10 μg/dL declined markedly to 18% and 9% at 9 months and 22 months post-closure, respectively (Dalton and Bates, 2005). A recent blood Pb screening program conducted in Boolaroo revealed that all the children tested had blood Pb concentrations ≤5 μg/dL (NSW Health, 2015). After phasing out leaded petrol, blood Pb in Australian cities declined markedly (Figure 7-4; Kristensen et al., 2017), which is consistent with other international studies (e.g.

Pirkle et al., 1994; Bono et al., 1995; Wietlisbach et al., 1995; Schuhmacher et al., 1996; Hwang et al., 2004; Nichani et al., 2006). Thus, better emission control, closure of operations (e.g. mines and smelters) or improvements in fuel quality (e.g. leaded petrol phase out) provide strong evidence that controlling contaminant release at its source is a critical prevention strategy and the only one likely to yield long term benefits to a community.

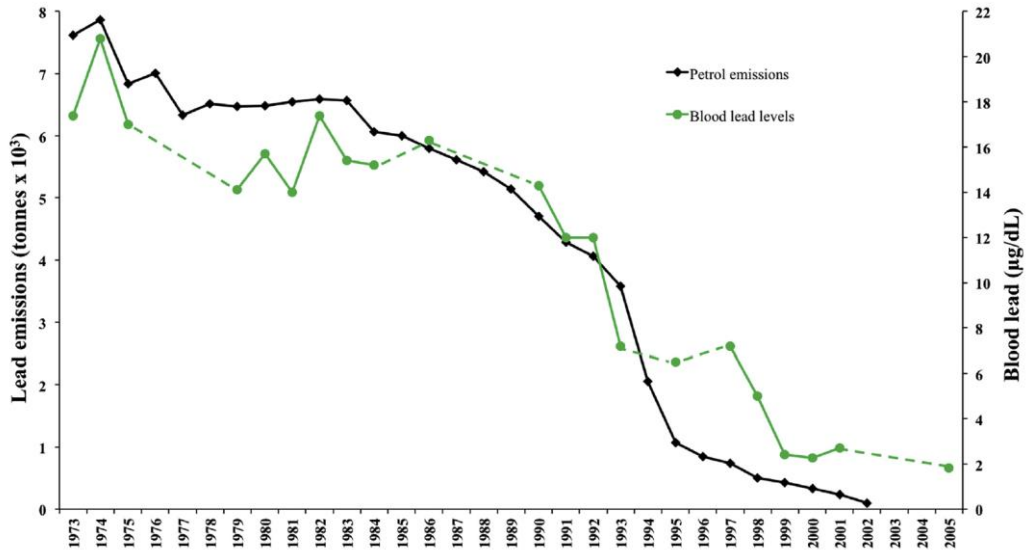


Figure 7-4. Declining blood Pb concentrations in Australian children and Pb emissions (sourced from Kristensen et al., 2017).

The results presented in this thesis have shown that both contemporary dust Pb deposits and blood Pb concentrations are driven mainly by current mining emissions in Broken Hill, and that these emissions are influencing blood Pb concentrations via the dust Pb deposits in the region. This highlights the need to reduce emissions in mining and smelting communities, particularly in Broken Hill.

7.7.2 Potential strategies of mitigating ongoing emissions

Ongoing emissions from current mining and smelting operations typically comprise atmospheric emissions (e.g. particulate matter, CO_2, SO_2, NO_x), sewage water and solid wastes (e.g. tailings dumps and slags) (Dudka and Adriano, 1997). However, atmospheric emissions are a high-priority issue in the Australian non-ferrous mining and smelting towns of Broken Hill, Mount Isa and Port Pirie (NPI, 2017). To control atmospheric emissions from the smelters, advanced smelting technology can play an important role in capturing airborne stack-related emissions of metal(loid)s, dust, SO_2, CO_2, NO_x and other contaminants more efficiently. In addition, general dust control measures are critical to reduce fugitive atmospheric emissions from mining operations (Csavina et al., 2012). There are a range of dust control methods

employed at Australian mineral and coal mining operations, with the key approaches summarised in Table 7-2.

Table 7-2. Summarised key dust controls employed in Australian mining operations (Driussi and Jansz, 2006; NSW Government, 2010; SA Government, 2017; Mount Isa Mines, 2017).

Targets	Key Controls
Dust from mining processes	Negative pressure exhaust ventilation, dust capture systems, enclosure of operations such as conveyors or sheds, wetting of materials, and mist or fog sprays to suppress dust emission.
Dust from storage of ore materials and solid wastes	Wetting stockpiles, use of agents to bind stockpile surface, capping tailings dumps, Onsite materials contained in sheds, windbreaks, stockpiles cover, surface roughening of stockpiles.
Dust from transportation of ores	Vehicle wash down and tyre cleaning facilities, road cleaning equipment, established containment zones to reduce silt trackage, covering vehicle loads, sealing of previously unsealed roads, vehicle speed restrictions, covering rail wagons.
Air quality monitoring	Identify major sources of dust emission and establish site specific practice dust controls.

In terms of practices in Broken Hill, some of the dust controls detailed in Table 7-2 have been implemented to date including covering rail wagons, wetting materials and capping tailings dumps (Kristensen et al., 2015; Perilya Limited, 2017). In 2017 the NSW EPA imposed new conditions on Perilya that required them to implement additional measures to reduce dust emissions from their facility (NSW EPA, 2017). CBH Resources Limited was also required to reduce emissions from their mining activities (CBH Resources Limited, 2012). However, despite these interventions, Chapter Three revealed large amounts of contemporary dust Pb were still being sourced from current mining activities at Broken Hill. Obvious sources of emissions include the piles of crushed Pb and Zn ore stored outside in an uncontained manner (Figure 7-5).

Figure 7-5. Lead and zinc ore pile at the head of Perilya Limited's Mine in Broken Hill, NSW, Australia.

The video in Paper One (Chapter Three) showed dust blowing off the Pb and Zn ore pile at Perilya's southern operations. Simple mitigation strategies for these emissions would include enclosure of operations or the relocation of crushing facilities out of the Broken Hill city area, similar to the strategies undertaken in Mount Isa (Mount Isa Mines, 2017). Previous studies have shown that a lack of enforcement of regulations results in further failure to protect communities (Taylor et al., 2014b). At Broken Hill is it evident that there is a need to implement and actively enforce more stringent emission management strategies, coupled with a lowering of environmental contaminant benchmark standards, to reduce exposure risk in the community. For example, while there is a Pb in air standard (0.5 $\mu g/m^2$) there is no upper maximum standard set for Pb dust deposition, even though its measurement is a requirement of both CBH and Perilya's licence conditions and it is clearly a dominant source of childhood Pb exposure (Chapters Three and Five).

7.7.3 Mitigating the household soil Pb (residual contamination) exposure

Even though section 7.5.1 highlighted the critical importance of controlling ongoing emissions, it is evident that outdoor soil, as a reservoir of legacy Pb from multiple anthropogenic activities, can adversely influence childhood blood Pb concentrations (e.g. von Lindern et al., 2003; Zahran et al., 2013; Mielke et al., 2016; Schwarz et al., 2016; Laidlaw et al., 2017). For example, in Bunker Hill, USA, although the local smelter closed in 1981, children born since the smelter closure still had elevated blood Pb concentrations even in the context of falling levels across the community as a whole (von Lindern et al., 2003). In Bunker Hill, it was concluded that accidental ingestion of residual contamination in community soils and dusts, via ordinary hand-to-mouth behaviour and play activities, was a primary route of exposure (von

Lindern et al., 2003, 2016). Similarly, in Detroit, USA, Zahran et al. (2013) demonstrated that resuspended legacy soil Pb was driving variations in childhood blood Pb outcomes.

Although the analysis of Broken Hill data showed that recent (2011–2015) childhood blood Pb outcomes were being impacted by exposure to current mining emissions, lead in household soils was also found to be contributing to blood Pb (Chapters Four and Five). In the 1990s, the indoor dust Pb deposition rate was correlated strongly with household soil Pb concentrations in Broken Hill (Chapter Four). Other studies have demonstrated that soil Pb concentrations and indoor household dust Pb levels are related (e.g. Lanphear et al., 2003; Gulson et al., 2014; Laidlaw et al., 2014). Previous studies have detailed the transport pathway for household soil Pb, which can be transported inside homes via shoes and family pets, thereby becoming indoor dust deposits (Hunt et al., 2006; Layton and Beamer, 2009). Therefore, the available data from Broken Hill indicates that residual household soil Pb contamination also needs to be addressed in addition to ongoing emissions to help reduce Pb exposures in Broken Hill.

The intervention approach of soil Pb normally includes removing and capping the surface contaminated soil (e.g. Weitzman et al., 1993; Aschengrau et al., 1997; Lanphear et al., 2003; Schoof et al., 2016; Tirima et al., 2016; Ericson et al., 2018). For example, in Midvale, Utah, the top 46 cm soil was excavated and disposed (Lanphear et al., 2003) and the effect of soil abatement evaluated. Lanphear et al. (2003) stated that:

"*After adjustment for child's age, mouthing behavior, socio-economic status, and year of study, there was an estimated 2.3 μg/dL decline in blood Pb concentration associated with soil abatement for children who were 6 to 72 months of age (p=0.14).*"

In Dong Mai, Vietnam, in order to mitigate the risk from residential soil, contaminated yard soil was first capped with 5 cm of sand and geotextile, and with further layers of either 20 cm of sand, 20 cm of compacted soil, pavers (bricks) or concrete (Ericson, 2014). One year after the soil abatement, average blood Pb concentrations decreased by 35% (39 to 25 μg/dL). Ericson et al. (2018) suggested that capping contaminated soil (USD$1000 per house) was more economic compared with removing it (USD$9475 per house). In terms of the houses from Broken Hill included in this thesis research, >1900 of the houses have been subject to environmental assessment over the last two decades, of which 67% have soil Pb concentrations exceeding the Australian residential Health Investigation level-A guideline of 300 mg/kg (NEPM, 2013). The cost for capping contaminated soil in Broken Hill with clean fill to a depth

of 10 cm to reduce soil Pb levels below 300 mg/kg is approximately AUD$10,000, which is derived from assessments from the Broken Hill Environmental Lead Program. Therefore, approximately AUD$12 million is required to remediate contaminated Broken Hill residential gardens involved in this research, such that they would have a soil Pb concentration less than 300 mg/kg.

Community education to control environmental Pb exposure has been long criticised in the scientific community for its lack of efficacy, particularly given that its use is difficult to support in the absence of other management and primary prevention measures (e.g. Rosner and Markowitz, 2005; Yeoh et al., 2014; Nussbaumer-Streit et al., 2016). However, community education programs detailing risks and domestic preventative measures can be used as a supplementary intervention approach to keep community exposure as low as possible.

7.8 Broader contribution of thesis findings

The NSW Government announced in early 2015 that AUD$13 million was allocated to '*rejuvenate the Broken Hill Environment Lead Program to address the issue of blood lead levels in local children'* (Humphries, 2015). Towards this aim of lowering blood Pb levels, this thesis research has addressed the long-standing dispute over contemporary airborne contamination sources in Broken Hill (i.e. contemporary mining emission or resuspended legacy pollutants), to help provide direction for the program's future remediation strategies. Previous studies of Broken Hill exposures involved analysis of the relationship between environmental Pb (i.e. soil and dust) and blood Pb using the Integrated Exposure Biokinetic (IEUBK) model (Yang and Cattle, 2015) and small cohorts of participants (n=74) (Boreland et al., 2006). While these studies provided useful insights to the problem, they had data limitations. To address this, the research presented herein is the first comprehensive analysis of the long-term and city-wide human and environmental dataset available from Broken Hill (including more than 24,000 blood Pb samples and 10,000 soil Pb samples) to evaluate the dose-response relationship between environmental Pb and blood Pb (Chapter Four).

The data analysis has elucidated the causal factors driving childhood blood Pb exposures including a child's age, gender, ethnicity, socio-economic status, age of house and distance away from mining operations (Chapters Four and Five). These outcomes show that children aged around 2 years old, especially those of indigenous origin and living within 2 km of mining operations are most at risk. After adjusting for other covariates, the recent data (2011–2015) shows that contemporary mining emissions are driving contemporary blood Pb concentrations

in Broken Hill, with residual household soil Pb making a minor contribution to blood Pb. These findings support the future remediation activities of the Broken Hill Environment Lead Program by providing evidence-based targets for intervention and maximum outcomes.

Prior to this research, only one study (i.e. Earl et al., 2016) has used a combination of cognitive and covariate data from 49 Broken Hill children to estimate impact of environmental Pb exposure on children's cognitive abilities. The research in this thesis, however, is the first to take advantage of national early childhood (AEDC) and school educational assessments (NAPLAN) to estimate potential impacts from exposure to contaminants at a community scale. The findings show that all Broken Hill children performed worse in cognitive abilities and behavioural development compared to national averages after the results were adjusted for socioeconomic status. This further highlights the need for exposure risk management. The data herein shows that ongoing emission control is a priority when it comes to reducing exposure in Broken Hill, coupled with house specific remediation, including the abatement or removal of contaminated household soil. Interestingly, the data shows that the home remediation conducted between 1994 and 1996 in Broken Hill did not reduce children's blood Pb concentrations (Boreland et al., 2009), which took place in the absence of complete 'ongoing' emission controls at the time.

Although Broken Hill has been a focus of this research, disputes over contamination sources and their potential impacts on children's health in mining and smelting communities are commonplace in Australian and overseas communities, e.g. Port Pirie (Taylor, 2012), Mount Isa (Taylor and Schniering, 2010), Kalgoorlie Consolidated Gold Mines (ABC News, 2003) in Australia, and Tacoma and Salt Lake Valley in the United States (Sullivan, 2014). The disputes arise because there may be various potential sources of contamination in a community, including naturally weathered ore debris, emissions from historic/ongoing mining and smelting activities and other non-orebody sourced pollutants (e.g. legacy petrol emission and Pb-based paints) (Kristensen and Taylor 2016). This research provides a multiple lines of evidence approach to better identify potential sources of contemporary contamination and its impacts in mining and smelting communities.

Outside Australia, the association between environmental Pb (including soil, dust and water) and blood Pb concentrations at the city scale have been well reported (e.g. Lanphear et al., 1995, 1998; Hanna-Attisha et al., 2016; Safruk et al., 2017). However, city-wide studies in Australia have focused mainly on Port Pirie (SA) and Boolaroo (NSW) (e.g. Wilson et al., 1986;

McMichael et al., 1988; Baghurst et al., 1992; Tong et al., 1996; Burns et al., 1999; Earl et al., 2016; Willmore et al., 2016), whereas smaller cohort analyses have been completed in other Australian locations, such as Boolaroo (Willmore et al., 2006) and Sydney (Gulson and Taylor, 2017). As such, this study's research enriches knowledge of the association between environmental Pb and its sources and blood Pb in Australia.

To reduce exposure in the mining and smelting communities effectively, this research demonstrates the need to determine current sources and emission patterns alongside residual contamination. The association between residual soil Pb contamination and blood Pb exposure has been observed in other mining and smelting communities which were still subject to significant 'ongoing' emissions at the time: Port Pirie in Australia – McMichael et al. (1985); El Paso in United States – Landrigan et al. (1976); Torreón in Mexico – Albalak et al. (2003); Soto-Jimenez and Flegal (2011). However, because these studies were completed while there were significant ongoing Pb emissions that formed Pb depositions in the adjoining communities, it was not possible to separate current dust Pb sources from residual soil Pb contamination. Indeed, the study by Yang and Cattle (2015) is a good example of this conundrum. Yang and Cattle (2015) found that the spatial distribution of recent blood Pb exposures in Broken Hill could be explained by the corresponding soil Pb distribution, modelled using the US EPA's IEUBK model. In this study, the authors used soil Pb concentrations to derive a dust Pb value in residential homes. However, the soil in Broken Hill has also been contaminated by airborne Pb dispersal and deposition, making the situation more complicated (Kristensen and Taylor, 2016). As a result, the spatial distribution of soil Pb values is strongly associated with dust Pb deposition values (Chapter 4). This results in a marked decline in both soil and dust Pb values with increasing distance from mining operations, making it difficult to separate residential contamination (soils) from ongoing emissions. However, the process of dust Pb contamination of the environment continues unabated (Dong and Taylor, 2017). These depositions have been shown (Chapter 5) to be the dominant cause of the blood Pb levels recently measured in children (2011–2015). Even when surface soil Pb concentrations were ameliorated following the 2009 dust storm, this produced limited influence on the spatial distribution of children's blood Pb exposures (Chapter 5).

Without specific examination of the possible sources and their apportionment to an individual's exposure, it is likely that mis-directed intervention strategies may be developed (Sullivan and Green, 2016) which fail to alleviate the burden on residents. Therefore, as identified in other communities subject to 'ongoing' emissions (e.g. Boolaroo, Australia (Dalton and Bates, 2005);

Bunker Hill, USA (von Lindern et al., 2003); and Sanming, China (Lin et al., 2011)), in the absence of emission controls it is unlikely that soil abatement treatments on their own will reduce exposure risks to an acceptable level, i.e. where all children's blood Pb is <5 μg/dL.

7.9 Future research direction

This PhD study has demonstrated that current mining emissions remain a significant source of children's blood Pb exposure at Broken Hill. However, it is clear that exposure risks are also influenced by the physiochemical properties of contaminated particles, including the speciation of metal(loid)s (e.g. Rasmussen et al., 2011; Han et al., 2012; Fujimori et al., 2018), grain size (e.g. Qiang et al., 2015; Cai et al., 2016), mineral compositions (e.g. Rathnayake and Schwab, 2016). Therefore, any future investigation into the role of physiochemical properties influencing children's blood Pb is likely to enhance understanding of the effects current mining emissions versus those held in soils as legacy deposits, which have been subject to weathering a modification over time.

Furthermore, as noted in Chapter Four, Aboriginal children have had higher geometric mean blood Pb concentrations (Aboriginal: 7.4 μg/dL; non-Aboriginal: 6.2 μg/dL) over the last two decades. Interestingly, this disparity has widened recently (2012-2015) (e.g. Aboriginal: 9.3 μg/dL and non-Aboriginal children: 4.9 μg/dL in 2015), which may in part due to the greater participation of all children in blood screening resulting in a more accurate picture of exposures across the community (Lesjak and Jones, 2016). However, the precise mechanisms responsible for this disparity remain poorly understood, particularly in Australia, where there has been limited investigation of this phenomenon. In the USA, it has been established previously from several studies blood Pb levels are elevated in the following communities in the following order African-American > Hispanic > white (Caucasian) American (Lanphear et al., 2002; Jones et al., 2009; White et al., 2016).

Previous studies conducted outside of Australia demonstrate that racial/ethnic disparities in childhood Pb poisoning can be influenced by a range of factors including biological, behavioural and socio-economic ones (Lanphear et al., 1996; Malcoe et al., 2002; Krieger et al., 2005; Jones et al., 2009; Ngueta, 2014; Moody et al., 2016; White et al., 2016). More detailed studies about mechanisms of racial/ethnic disparities in childhood Pb poisoning would provide insight as to why Aboriginal children have higher blood Pb exposure risks in Australia, which could be used to apply more targeted, effective intervention strategies. Although a range of contamination controls have been implemented in Broken Hill since early 1990s (c.f. section 7.7 of this thesis; Kristensen et al., 2015; Perilya Limited, 2017), there remains a considerable

amount of Pb being still emitted into the ambient environment from Broken Hill Pb and Zn mining operations resulting in contamination of aerosols and deposited dusts (Chapter Three; Figure 7-1). The incomplete control of contamination in Broken Hill highlights a clear need to implement and actively enforce more stringent emission management strategies. Any such strategies should be coupled to a lowering of environmental contaminant benchmark standards, to reduce exposure risk in the community in future. Lower standards might include for example dust deposition limits and no spikes of Pb in air. Following the implementation of any new contamination controls, a critical step would should include an evaluation of effectiveness on both the ambient levels of Pb in the environment and also in children's blood.

7.10 References

ABC News, 2003. Air pollution breach baffle miner. http://www.abc.net.au/news/2003-08-01/air-pollution-breach-baffles-miner/1458054 (accessed 28.05.16)

Abraham, J., Dowling, K., Florentine, S., 2017. Controlled burn and immediate mobilization of potentially toxic elements in soil, from a legacy mine site in Central Victoria, Australia. Science of the Total Environment 616-617, 1022-1034.

Albalak, R., McElroy, R. H., Noonan, G., Buchanan, S., Jones, R. L., Flanders, D. W., 2003. Blood lead levels and risk factors for lead poisoning among children in a Mexican smelting community. Archives of Environmental Health 58, 172-183.

Aschengrau, A., Beiser, A., Bellinger, D., Copenhafer, D., Weitzman, M., 1997. Residential lead-based-paint hazard remediation and soil lead abatement: their impact among children with mildly elevated blood lead levels. American Journal of Public Health 87, 1698-1702.

Australian Government, 2017. Australian Early Development Census (AEDC)—Data Guidelines. Department of Education and Training. http://www.aedc.gov.au/resources/detail/aedc-data-guidelines-2017 (accessed 21.01.18).

Baghurst, P. A., Tong, S. L., McMichael, A. J., Robertson, E. F., Wigg, N. R., Vimpani, G. V., 1992. Determinants of blood lead concentrations to age 5 years in a birth cohort study of children living in the lead smelting city of Port Pirie and surrounding areas. Archives Environmental Health 47, 203-210.

Baghurst, P. A., McMichael, A. J., Wigg, N. R., Vimpani, G. V., Robertson, E. F., Roberts, R. J., Tong, S. L., 1992. Environmental Exposure to Lead and Children's Intelligence at the Age of Seven Years — The Port Pirie Cohort Study. New England Journal of Medicine 327, 1279-1284.

Bellinger, D. C., 2012. A Strategy for Comparing the Contributions of Environmental Chemicals and Other Risk Factors to Neurodevelopment of Children. Environmental Health Perspectives 120, 501-507.

Berglund, A. M. M., Ingvarsson, P. K., Danielsson, H., Nyholm, N. E. I., 2010. Lead exposure and biological effects in pied flycatchers (*Ficedula hypoleuca*) before and after the closure of a lead mine in northern Sweden. Environmental Pollution 158, 1368-1375.

Bono, R., Pignata, C., Scursatone, E., Rovere, R., Natale, P., Gilli, G., 1995. Updating about Reductions of Air and Blood Lead Concentrations in Turin, Italy, Following Reductions in the Lead Content of Gasoline. Environmental Research 70, 30-34.

Boreland, F., Lesjak, M., Lyle, D., 2009. Evaluation of home lead remediation in an Australian mining community. Science of the Total Environment 408, 202-208.

Boreland, F., Lyle, D. M., Wlodarczyk, J., Balding, W. A., 2006. Lead Dust in Broken Hill Homes: Relationship between House Dust and Children's Blood Lead Levels. Environmental Health 6, 15-24.

Broken Hill Environmental Lead Program, 2016. STEERING COMMITTEE ANNUAL REPORT 2015-2016. http://leadsmart.nsw.gov.au/wp-content/uploads/2017/03/DOC17-125421-02-Attachment-B-Broken-Hill-Environmental-Lead-Program-BHELP-Steering-

Committee-Annual-Report-2015-2016.pdf (accessed 14.01.18).

Budtz-Jørgensen, E., Bellinger, D., Lanphear, B., Grandjean, P., 2013. An International Pooled Analysis for Obtaining a Benchmark Dose for Environmental Lead Exposure in Children. Risk Analysis 33, 450-461.

Burns, J. M., Baghurst, P. A., Sawyer, M. G., McMichael, A. J., Tong, S., 1999. Lifetime Low-Level Exposure to Environmental Lead and Children's Emotional and Behavioural Development at Ages 11–13 Years: The Port Pirie Cohort Study. American Journal of Epidemiology 149, 740-749.

Cai, M., McBride, M. B., Li, K., 2016. Bioaccessibility of Ba, Cu, Pb, and Zn in urban garden and orchard soils. Environmental Pollution 208, 145-152.

Calderón, J., Navarro, M. E., Jimenez-Capdeville, M. E., Santos-Diaz, M. A., Golden, A., Rodriguez-Leyva, I., Borja-Aburto, V., Diaz-Barriga, F., 2001. Exposure to arsenic and lead and neuropsychological development in Mexican children. Environmental Research 85, 69-76.

Cao, S., Duan, X., Zhao, X., Wang, B., Ma, J., Fan, D., Sun, C., Wei, F., Jiang, G., 2014. Isotopic ratio based source apportionment of children's blood lead around coking plant area. Environment International 73, 158-166.

Canfield, R. L., Henderson, C. R., Cory-Slechta, D. A., Cox, C., Jusko, T., Lanphear, B., 2003. Intellectual Impairment in Children with Blood Lead Concentrations below 10 μg per Deciliter. The New England Journal of Medicine 348, 1517-1526.

Carrizales, L., Razo, I., Téllez-Hernández, J. I., Torres-Nerio, R., Torres, A., Batres, L. E., Cubillas, A., Díaz-Barriga, F., 2006. Exposure to arsenic and lead of children living near a copper-smelter in San Luis Potosi, Mexico: Importance of soil contamination for exposure of children. Environmental Research 101, 1-10.

CBH Resources Limited, 2012. Environment Management Strategy V2. https://www.google.com.au/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwjE-pKzj-PYAhVONbwKHdNFAfsQFggnMAA&url=http%3A%2F%2Fwww.cbhresources.com.au%2Ffiles%2F2613%2F4508%2F4197%2FEnvironment_Management_Strategy_Jun2012_V2.docx&usg=AOvVaw1nUV4aeoOktPbjw6tOoLO7 (accessed 19.01.18).

Centers for Disease Control and Prevention (CDC), 2012. Low Level Lead Exposure Harms Children: A Renewed Call for Primary Prevention. https://www.cdc.gov/nceh/lead/acclpp/final_document_030712.pdf (accessed 18.12.17).

Cho, S. C., Bhang, S. Y., Hong, Y. C., Shin, M. S., Kim, B. N., Kim, J. W., Yoo, H. J., Cho, I. H., Kim, H. W., 2010. Relationship between Environmental Phthalate Exposure and the Intelligence of School-Age Children. Environmental Health Perspectives 118, 1027-1032.

Ciesielski, T., Bellinger, D. C., Schwartz, J., Hauser, R., Wright, R. O., 2013. Associations between cadmium exposure and neurocognitive test scores in a cross-sectional study of US adults. Environmental Health 12: 13. https://doi.org/10.1186/1476-069X-12-13.

Cooksley, N. A. J. B., Atkinson, D., Marks, G. B., Toelle, B. G., Reeve, D., Johns, D. P., Abramson, M. J., Burton, D. L., James, A. L., Wood-Baker, R., Walters, E. H., Buist, A. S.,

Maguire, G. P., 2015. Prevalence of airflow obstruction and reduced forced vital capacity in an Aboriginal Australian population: The cross-sectional BOLD study. Respirology 20, 766-774.

Csavina, J., Field, J., Taylor, M. P., Gao, S., Landázuri, A., Betterton, E. A., Sáez, A. E., 2012. A review on the importance of metals and metalloids in atmospheric dust and aerosol from mining operations. Science of the Total Environment 433, 58-73.

Dalton, C. B., Bates, L. I., 2005. Impact of closure of a large lead-zinc smelter on elevated blood lead levels of children in adjacent suburbs, Boolaroo, Australia. Environmental Exposure and Health 85, 377–387.

Davidson, P. W., Myers, G. J., Weiss, B., 2004. Mercury Exposure and Child Development Outcomes. Pediatrics 113, 1023-1029.

Davis, J. J., Morrison, A. L., Gulson, B. L., 2016. Uncovering pathways of metal contamination with microscopic techniques and lead isotopic tracing. Australian Journal of Earth Sciences 63, 795-803.

do Nascimento, S. N., Barth, A., Göethel, G., Baierle, M., Charão, M. F., Brucker, N., Moro, A., Bubols, G. B., Sobreira, J. S., Sauer, E., Rocha, R., Gioda, A., Dias, A. C., Salles, J. F., Garcia, S. C., 2015. Cognitive deficits and ALA-D-inhibition in children exposed to multiple metals. Environmental Research 136, 387-395.

Dobson, A. W., Erikson, K. M., Aschner, M., 2004. Manganese Neurotoxicity. Annals of the New York Academy of Sciences 1012, 115-128.

Dong, C., Taylor, M. P., Kristensen, L. J., Zahran, S., 2015. Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes. Environmental Pollution 207, 345-356.

Driussi, C., Jansz, J., 2006. Pollution minimisation practices in the Australian mining and mineral processing industries. Journal of Cleaner Production 14, 673-681.

Dudka, S., Adriano, D. C., 1997. Environmental Impacts of Metal Ore Mining and Processing: A review. Journal of Environmental Quality 26, 590-602.

Earl, R., Burns, N., Nettelbeck, T., Baghurst, P. 2016. Low-level environmental lead exposure still negatively associated with children's cognitive abilities. Australian Journal of Psychology 68, 98-106.

Edwards, S. C., Jedrychowski, W., Butscher, M., Camann, D., Kieltyka, A., Mroz, E., Flak, E., Li, Z., Wang, S., Rauh, V., Perera, F., 2010. Prenatal Exposure to Airborne Polycyclic Aromatic Hydrocarbons and Children's Intelligence at 5 Years of Age in a Prospective Cohort Study in Poland. Environmental Health Perspectives 118, 1326-1331.

Ejaredar, M., Nyanza, E. C., Eycke, K. T., Dewey, D., 2015. Phthalate exposure and childrens neurodevelopment: A systematic review. Environmental Research 142, 51-60.

Ericson, B., 2014. Mitigation of Acute Lead Exposures in Dong Mai Village, Vietnam—Final Report. http://www.pureearth.org/wp-content/uploads/2014/01/Dong-Mai-Final-Report.pdf (accessed 03.01.18).

Ericson, B., Duong, T. T., Keith, J., Nguyen, T. C., Havens, D., Daniell, W., Karr, C. J., Hai, D. N., Tung, L. V., Ha, T. T. N., Wilson, B., Hanrahan, D., Croteau, G., Taylor, M. P., 2018. Improving human health outcomes with a low-cost intervention to reduce exposures from lead acid battery recycling: Dong Mai, Vietnam. Environmental Pollution 161, 181-187.

Evens, A., Hryhorczuk, D., Lanphear, B. P., Rankin, K. M., Lewis, D. A., Forst, L., Rosenberg, D., 2015. The impact of low-level lead toxicity on school performance among children in the Chicago Public Schools: a population-based retrospective cohort study. Environmental Health 14:21. https://doi.org/10.1186/s12940-015-0008-9.

Fujimori, T., Taniguchi, M., Agusa, T., Shiota, K., Takaoka, M., Yoshida, A., Terazono, A., Ballesteros Jr, F. C., Takigami, H., 2018. Effect of lead speciation on its oral bioaccessibility in surface dust and soil of electronic-wastes recycling sites. Journal of Hazardous Materials 341, 365-372.

Gascon, M., Fort, M., Martínez, D., Carsin, A., Forns, J., Grimalt, J. O., Marina, L. S., Lertxundi, N., Sunyer, J., Vrijheid, M., 2012. Polybrominated Diphenyl Ethers (PBDEs) in Breast Milk and Neuropsychological Development in Infants. Environmental Health Perspectives 120, 1760-1765.

Gavin, H. 2000. Pollution prevention and cleaner production in the mining industry: an analysis of current issues. Journal of Cleaner Production 8, 119-126.

Gould, E., 2009. Childhood lead poisoning: conservation estimates of the social and economic benefits of lead hazard control. Environmental Health Perspectives 117, 1162-1167.

Gulson, B. L., Davis, J. J., Mizon, K. J., Korsch, M. J., Bawden-Smith, J., 1995. Sources of lead in soil and dust and the use of dust fallout as a sampling medium. Science of the Total Environment 166, 245-262.

Gulson, B. L., Denton, G., Gardner, B., 1997. Lead isotopic analyses of aerosol particulates from filters and ceilings dust from Mount Isa. CSIRO Division of Exploration and Mining.

Gulson, B. L., Pisaniello, D., McMichael, A. J., Mizon, K. J., Korsch, M. J., Luke, C., Ashbolt, R., Pederson, D. G., Vimpani, G., Mahaffey, K. R., 1996. Stable lead isotope profiles in smelter and general urban communities: a comparison of environmental and blood measures. Environmental Geochemistry and Health 18, 147-163.

Gulson, B. L., Mizon, K. J., Davis, J. D., Palmer, J. M., Vimpani, G., 2004. Identification of sources of lead in children in a primary zinc-lead smelter environment. Environmental Health Perspectives 112, 52-60.

Gulson, B. L., Mizon, K. J., Korsch, M. J., Howarth, D., 1996. Non-orebody sources are significant contributors to blood lead of some children with low to moderate lead exposure in a major lead mining community. Science of the Total Environment 181, 223-230.

Gulson, B. L., Mizon, K. J., Law, A. J., Korsch, M, J., Davis, J. J., 1994. Source and Pathways of Lead in Humans from the Broken Hill Mining Community – An Alternative Use of Exploration Methods. Economic Geology 89, 889 – 908.

Gulson, B. L., Mizon, K., Taylor, A., Korsch, M., Davis, J. M., Louie, H., Wu, M., Gomez, L., Antin, L., 2014. Pathways of Pb and Mn observed in a 5-year longitudinal investigation in

young children and environmental measures from an urban setting. Environmental Pollution 191, 38-49.

Gulson, B. L., Taylor, A., 2017. A simple lead dust fall method predicts children's blood lead level: New evidence from Australia. Environmental Research 159, 76-81.

Han, Z., Bi, X., Li, Z., Yang, W., Wang, L., Yang, H., Li, F., Ma, Z., 2012. Occurrence, speciation and bioaccessibility of lead in Chinese rural household dust and the associated health risk to children. Atmospheric Environment 46, 65-70.

Hanna-Attisha, M., LaChance, J., Sadler, R. C., Schnepp, A. C., 2016. Elevated Blood Lead Levels in Children Associated With the Flint Drinking Water Crisis: A Spatial Analysis of Risk and Public Health Response. American Journal of Public Health 106, 283-290.

Harvey, P. J., Rouillon, M., Dong, C., Handley, H. K., Taylor, M. P., Tyson, E., Tennant, P., Telfer, V., Trinh, R., Geochemical sources, forms and phases of soil contamination in an industrial city. Science of the Total Environment 584-585, 505-514.

Harvey, P. J., Taylor, M. P., Kristensen, L. J., Grant-Vest, S., Rouillon, M., Wu, L., Handley, H. K., 2016. Evaluation and assessment of the efficacy of an abatement strategy in a former lead smelter community, Boolaroo, Australia. Environmental Geochemistry and Health 38, 941-954.

Hunt, A., Johnson, D. L., Griffith, D. A., 2006. Mass transfer of soil indoors by track-in on footwear. Science of the Total Environment 370, 360-371.

Humphries, K., 2015. NSW Government Commits More than $13 Million to Reduce Lead Levels at Broken Hill. Media release: Kevin Humphries MP Minister for Natural Resources, Lands and Water Minister for Western NSW, 13th February 2015. https://www.brokenhill.nsw.gov.au/sites/brokenhill/files/public/images/documents/brokenhill/News/Stokes%20Skinner%20Humphries%20med%20rel%20-%20NSW%20Govt%20commits%20more%20than%2013%20million%20to%20reduce%20lead%20levels%20at%20Broken%20Hill.pdf (accessed 03.01.18).

Hwang, Y. H., Ko, Y., Chiang, C. D., Hsu, S. P., Lee, Y. H., Yu, C. H., Chiou, C. H., Wang, J. D., Chuang, H. Y., 2004. Transition of cord blood lead level, 1985–2002, in the Taipei area and its determinants after the cease of leaded gasoline use. Environmental Research 96, 274-282.

Jacobs, D. E., Clickner, R. P., Zhou, J. Y., Viet, S. M., Marker, D. A., Rogers, J. W., Zeldin, D. C., Broene, P., Friedman, W., 2002. The prevalence of lead-based paint hazards in U.S. housing. Environmental Health Perspectives 110, A599-A606.

Jamieson, H. E., 2014. The Legacy of Arsenic Contamination from Mining and Processing Refractory Gold Ore at Giant Mine, Yellowknife, Northwest Territories, Canada. Reviews in Mineralogy and Geochemistry 79, 533-551.

Janu, E. K., Annabattula, B. I., Kumariah, S., Zajaczkowska, M., Whitehall, J. S., Edwards, M. J., Lujic, S., Masters, I. B., 2014. Paediatric hospitalisations for lower respiratory tract infections in Mount Isa. Medical Journal of Australia 200, 591-594.

Jayaratne, E. R., Johnson, G. R., McGarry, P., Cheung, H. C., Morawska, L., 2011. Characteristics of airborne ultrafine and coarse particles during the Australian dust storm of

23 September 2009. Atmospheric Environment 45, 3996-4001.

Jones, R. L., Homa, D. M., Meyer, P. A., Brody, D. J., Caldwell, K. L., Pirkle, J. L., Brown, M. J., 2009. Trends in Blood Lead Levels and Blood Lead Testing Among US Children Aged 1 to 5 Years, 1988-2004. Pediatrics 123, e376-e385.

Jusko, T. A., Henderson, C. R., Lanphear, B. P., Cory-Slechta, D. A., Parsons, P. J., Canfield, R. L., 2008. Blood Lead Concentrations <10 μg/dL and Child Intelligence at 6 Years of Age. Environmental Health Perspectives 116, 243-248.

Kim, B. N., Cho, S. C., Kim, Y., Shin, M. S., Yoo, H. J., Kim, J. W., Yang, Y. H., Kim, H. W., Bhang, S. Y., Hong, Y. C., 2009. Phthalates Exposure and Attention-Deficit/Hyperactivity Disorder in School-Age Children. Biological Psychiatry 66, 958-963.

Konoha, K., Sadakane, Y., Kawahara, M., 2006. Zinc Neurotoxicity and its Role in Neurodegenerative Diseases. Journal of Health Science 52, 1-8.

Krieger, N., Chen, J. T., Waterman, P. D., Rehkopf, D. H., Subramanian, S. V., 2005. Painting a Turer Picture of US Socioeconomic and Racial/Ethnic Health Inequalities: The Public Health Disparities Geocoding Project. American Journal of Public Health 95, 312-323.

Kristensen, L. J., Taylor, M. P., 2016. Unraveling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. Environmental Geochemistry and Health 38, 1015-1027.

Kristensen, L. J., Taylor, M. P., Flegal, A. R., 2017. An odyssey of environmental pollution: The rise, fall and remobilisation of industrial lead in Australia. Applied Geochemistry 83, 3-13.

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

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

Laidlaw, M. A., Filippelli, G. M., 2008. Resuspension of urban soils as a persistent source of lead poisoning in children: A review and new directions. Applied Geochemistry 23, 2021-2039.

Laidlaw, M. A. S., Mohmmad, S. M., Gulson, B. L., Taylor, M. P., Kristensen, L. J., Birch, G., 2017. Estimates of potential childhood lead exposure from contaminated soil using the US EPA IEUBK Model in Sydney, Australia. Environmental Research 156, 781-790.

Laidlaw, M. A. S., Zahran, S., Pingitore, N., Clague, J., Devlin, G., Taylor, M. P., 2014. Identification of lead sources in residential environments: Sydney Australia. Environmental Pollution 184, 238-246.

Laidlaw, M. A. S., Zahran, S., Mielke, H. W., Taylor, M. P., Filippelli, G. M., 2012. Re-suspension of lead contaminated urban soil as a dominant source of atmospheric lead in Birmingham, Chicago, Detroit and Pittsburgh, USA. Atmospheric Environment 49, 302-310.

Landrigan, P. J., Gehlbach, S. H., Rosenblum, B. F., Shoults, J. M., Candelaria, R. M., Barthel, W. F., Liddle, J. A., Smrek, A. L., Staehling, N. W., Sanders, J. F., 1975. Epidemic Lead Absorption near an Ore Smelter — The Role of Particulate Lead. New England Journal of Medicine 292, 123-129.

Landrigan, P. J., Baker Jr, E. L., Feldman, R. G., Cox, D. H., Eden, K. V., Orenstein, W. A., Mather, J. A., Yankel, A. J., von Lindern, I. H., 1976. Increased lead absorption with anemia and slowed nerve conduction in children near a lead smelter. Journal of Pediatrics 89, 904-910.

Lanphear, B. P., 2015. The Impact of Toxins on the Developing Brian. Annual Review of Public Health 36, 211-230.

Lanphear, B. P., Emond, M., Jacobs, D. E., Weitzman, M., Tanner, M., Winter, N. L., Yakir, B., Eberly, S., 1995. A Side-by-Side Comparison of Dust Collection Methods for Sampling Lead-Contaminated House Dust. Environmental Research 68, 114-123.

Lanphear, B. P., Horung, R., Ho, M., Howard, C. R., Eberle, S., Knauf, K., 2002. Environmental lead exposure during early childhood. The Journal of Pediatrics 40, 40-47.

Lanphear, B. P., Horung, R., Khoury, J., Yolton, K., Baghurst, P., Bellinger, D. C., Canfield, R. L., Dietrich, K. N., Born, R., Greene, T., Rothenberg, S. J., Needleman, H. L., Schnaas, L., Wasserman, G., Graziano, J., Roberts, R., 2005. Low-Level Environmental Lead Exposure and Children's Intellectual Function: An International Pooled Analysis. Environmental Health Perspectives 113, 894-899.

Lanphear, B. P., Matte, T. D., Rogers, J., Clickner, R. P., Dietz, B., Bornschein, R. L., Succop, P., Mahaffey, K. R., Dixon, S., Galke, W., Rabinowitz, M., Farfel, M., Rohde, C., Schwartz, J., Ashley, P., Jacobs, D. E., 1998. The contribution of lead-contaminated house dust and residential soil to children's blood lead levels. A pooled analysis of 12 epidemiologic studies. Environmental Research 79, 51-68.

Lanphear, B. P., Roghmann, K. J., 1997. Pathways of Lead Exposure in Urban Children. Environmental Research 74, 67-73.

Lanphear, B. P., Succop, P., Roda, S., Henningsen, G., 2003. The Effect of Soil Abatement on Blood Lead Levels in Children Living near a Former Smelting and Milling Operation. Public Health Reports 118, 83-91.

Lanphear, B. P., Weitzman, M., Eberly, S., 1996. Racial Differences in Urban Children's Environmental Exposures to Lead. American Journal of Public Health 86, 1460-1463.

Layton, D. W., Beamer, P. I., 2009. Migration of Contaminated Soil and Airborne Particulates to Indoor Dust. Environmental Science & Technology 43, 8199-8205.

Leighton, J., Klitzman, S., Sedlar, S., Matte, T., Cohen, N. L., 2003. The effect of lead-based paint hazard remediation on blood lead levels of lead poisoned children in New York City. Environmental Research 92, 182-190.

Lesjak, M., Jones, T., 2016. Lead Health Report 2015 – Children less than 5 years old in Broken Hill. Population Health Unit, NSW Government, Western NSW & Far West Local Health District. http://leadsmart.nsw.gov.au/wp-content/uploads/2016/12/Broken-Hill-Lead-Health-Report-2015-children-aged-0%E2%80%934.pdf (accessed 26.07.17)

Levallois, P., St-Laurent, J., Gauvin, D., Courteau, M., Prévost, M., Campagna, C., Lemieux, F., Nour, S., D'Amour, M., Rasmussen, P. E., 2014. The impact of drinking water, indoor dust and paint on blood lead levels of children aged 1–5 years in Montréal (Québec, Canada). Journal of Exposure Science & Environmental Epidemiology 24, 185-191.

Li, X., Felix, O. I., Gonzales, P., Saez, A. E., Ela, W. P., 2016. Reconciling PM_{10} analyses by different sampling methods for Iron King Mine tailings dust. Reviews on Environmental Health 31, 37-41.

Lidsky, T. I., Schneider, J. S., 2003. Lead neurotoxicity in children: basic mechanisms and clinical correlates. Brian 126, 5-19.

Lillo, J., Oyarzun, R., Eesbri, J., Garcia-Lorenzo, M., & Higueras, P., 2015. Pb–Zn–Cd–As pollution in soils affected by mining activities in central and southern Spain: A scattered legacy posing potential environmental and health concerns. In Jiménez, E., Cabañas, B., & Lefebvre, G. (Eds.), Environment, energy and climate change I. Berlin: Springer.

Lin, S., Wang, X., Yu, I. T., Tang, W., Miao, J., Li, J., Wu, S., Lin, X., 2011. Environmental Lead Pollution and Elevated Blood Lead Levels Among Children in a Rural Area of China. American Journal of Public Health 101, 834-841.

Liu, J., Li, L., Wang, Y., Yan, C., Liu, X., 2013. Impact of Low Blood Lead Concentrations on IQ and School Performance in Chinese Children. PloS ONE 8, e65230. https://doi.org/10.1371/journal.pone.0065230.

Lottermoser, B. G., 2002. Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia. Mineralogical Magazine 66, 475-490.

Malcoe, L. H., Lynch, R. A., Keger, M. C., Skaggs, V. J., 2002. Lead sources, behaviors, and socioeconomic factors in relation to blood lead of native american and white children: a community-based assessment of a former mining area. Environmental Health Perspectives 110, 221-231.

Martin, R., Dowling, K., Pearce, D. C., Florentine, S., Bennett, J. W., Stopic, A., 2016. Size-dependent characterisation of historical gold mine wastes to examine human pathways of exposure to arsenic and other potentially toxic elements. Environmental Geochemistry and Health 38, 1097-1114.

Mathee, A., Röllin, H., Levin, J., Naik, I., 2007. Lead in Paint: Three Decades Later and Still a Hazard for African Children? Environmental Health Perspectives 115, 321-322.

McCrindle, J., Green, D., Sullivan, M., 2017. The Association between Environmental Lead Exposure and High School Educational Outcomes in Four Communities in New South Wales, Australia. International Journal of Environmental Research and Public Health 14, 1395.

McLaine, P., Navas-Acien, A., Lee, R., Simon, P., Diener-West, M., Agnew, J., 2013. Elevated Blood Lead Levels and Reading Readiness at the Start of Kindergarten. Pediatrics 131, 1081-1089.

McMichael, A. J., Baghurst, P. A., Robertson, E. F., Vimpani, G. V., Wigg, N. R., 1985. The Port Pirie cohort study. Blood lead concentrations in early childhood. Medical Journal of Australia 143, 499-503.

McMichael, A. J., Baghurst, P. A., Wigg, N. R., Vimpani, G. V., Robertson, E. F., Roberts, R. J., 1988. Port Pirie Cohort Study: Environmental Exposure to Lead and Children's Abilities at the Age of Four Years. New England Journal of Medicine 319, 468-475.

Meeker, J. D., Ferguson, K. K., 2011. Relationship between Urinary Phthalate and Bisphenol A Concentrations and Serum Thyroid Measures in U.S. Adults and Adolescents from the National Health and Nutrition Examination Survey (NHANES) 2007–2008. Environmental Health Perspectives 119, 1396-1402.

Mielke, H. W., Berry, K. J., Mielke, P. W., Powell, E. T., Gonzales, C. R., 2005. Multiple metal accomulation as a factor in learning achievement within various New Orleans elementary school communities. Environmental Research 97, 67-75.

Mielke, H. W., Gonzales, C. R., Powell, E. T., Mielke Jr, P. W., 2016. Spatiotemporal dynamic transformations of soil lead and children's blood lead ten years after Hurricane Katrina: New grounds for primary prevention. Environment International 94, 567-575.

Mielke, H. W., Reagan, P. L., 1998. Soil is an important pathway of human lead exposure. Enviornmental Health Perspectives 106, 217-229.

Moody, H., Darden, J. T., Pigozzi, B. W., 2016. The Racial Gap in Childhood Blood Lead Levels Related to Socioeconomic Position of Residence in Metropolitan Detroit. Sociology of Race and Ethnicity 2, 200-218.

Mount Isa Mines, 2017. How we manage air and water quality at Mount Isa Mines. http://www.mountisamines.com.au/en/publications/LeadPathways/4_Mount%20Isa%20Mines%20-%20Community%20Update%20Feb%2017%20FINAL.pdf (accessed 03.01.17).

Mudd, G. M., Jowitt, S. M., Werner, T. T., 2017. The world's lead-zinc mineral resources: Scarcity, data, issues and opportunities. Ore Geology Reviews 80, 1160-1190.

National Academies of Sciences, Engineering, and Medicine, 2017. Investigation Strategies for Lead-Source Attribution at Superfund Sites Associated with Mining Activities. The National Academics Press, Washington, DC.

National Environment Protection Measure (NEPM), 2013. Schedule B1: Guideline on Investigation Levels For Soil and Groundwater. https://www.legislation.gov.au/Details/F2013C00288/Html/Volume_2 (accessed 08.01.18).

National Pollutant Inventory (NPI), 2017. 2015/2016 data within Australia—Lead & compounds from Facilities (Industry). http://www.npi.gov.au/npidata/action/load/emission-by-facility-result/criteria/substance/52/destination/ALL/source-type/INDUSTRY/subthreshold-data/Yes/substance-name/Lead%2B%2526%2Bcompounds/year/2016 (accessed 20.09.17).

Ngueta, G., 2014. Racial disparities in children’s blood lead levels: Possible implication of divalent metal transporter 1. Medical Hypotheses 82, 71-73.

Nichani, V., Li, W. I., Smith, M. A., Noonan, G., Kulkarni, M., Kodavor, M., Naeher, L. P., 2006. Blood lead levels in children after phase-out of leaded gasoline in Bombay, India. Science of the Total Environment 363, 95-106.

NSW EPA, 2016. Fact Sheet: Old Lead Paint. http://www.epa.nsw.gov.au/resources/pesticides/lead-old-paint-fact-sheet-150700.pdf (accessed 11.12.17).

NSW EPA, 2017. Notice of variation of Licence No. 2688. http://app.epa.nsw.gov.au/prpoeoapp/ViewPOEONotice.aspx?DOCID=-1&SYSUID=1&LICID=1545186 (accessed 19.01.18).

NSW Government, 2010. Environmental compliance and performance report: Management of dust from coal mines. http://www.epa.nsw.gov.au/your-environment/air/regional-air-quality/minimising-particulate-pollution-coal-mines (accessed 30.11.17).

NSW Health, 2015. Blood Lead Screening in North Lake Macquarie, 2015. http://www.hnehealth.nsw.gov.au/hneph/EnvironmentalHealth/Documents/blood-lead-screening-2015.pdf (accessed 25.12.17).

Noller, B., T., Zheng, J., Huynh, T., Ng, J., Diacomanolis, V., Taga, R., Harris, H., 2017. Lead Pathways Study-Air: Health Risk Assessment of Contaminants to Mount Isa City. http://www.mountisamines.com.au/en/publications/LeadPathways/Lead%20Pathways%20Study%20Air%20Report.pdf (accessed 11.12.17).

Nussbaumer-Streit, B., Yeoh, B., Griebler, U., Pfadenhauer, L. M., Busert, L. K., Lhachimi, S. K., Lohner, S., Gartlehner, G., 2016. Household interventions for preventing domestic lead exposure in children (Review). Cochrane Database of Systematic Reviews, Art. No.: CD006047.

O'Bryant, S. E., Edwards, M., Menon, C. V., Gong, G., Barber, R., 2011. Long-Term Low-Level Arsenic Exposure Is Associated with Poorer Neuropsychological Functioning: A Project FRONTIER Study. International Journal of Environmental Research and Public Health 8, 861-874.

Ordóñez, A., Álvarez, R., Loredo, J., 2014. Soil pollution related to the mercury mining legacy at Asturias (Northern Spain). International Journal of Mining, Reclamation and Environment 28, 389-396.

Perera, F., Vishnevetsky, J., Herbstman, J. B., Calafat, A. M., Xiong, W., Rauh, V., Wang, S., 2012a. Prenatal Bisphenol A Exposure and Child Behavior in an Inner-City Cohort. Environmental Health Perspectives 120, 1190-1194.

Perera, F. P., Tang, D., Wang, S., Vishnevestsky, J., Zhang, B., Diaz, D., Camann, D., Rauh, V., 2012b. Prenatal Polycyclic Aromatic Hydrocarbon (PAH) Exposure and Child Behavior at Age 6–7 Years. Environmental Health Perspectives 120, 921-926.

Pestana, M. H. D., Formoso, M. L. L., 2003. Mercury contamination in Lavras do Sul, south Brazil: a legacy from past and recent gold mining. Science of the Total Environment 307, 125-140.

Peterson, B. S., Rauh, V. A., Bansal, R., Hao, X., Toth, Z., Nati, G., Walsh, K., Miller, R. L., Arias, F., Semanek, D., Perera, F., 2015. Effects of Prenatal Exposure to Air Pollutants

(Polycyclic Aromatic Hydrocarbons) on the Development of Brain White Matter, Cognition, and Behavior in Later Childhood. JAMA Psychiatry 72, 531-540.

Perilya Limited, 2017. Environment. http://www.perilya.com.au/health--safety--environment/environment (accessed 03.01.18).

Pirkle, J. L., Brody, D. J., Gunter, E. W., Kramer, R. A., Paschal, D. C., Flegal, K. M., Matte, T. D., 1994. The Decline in Blood Lead Levels in the United States—The National Health and Nutrition Examination Surveys (NHANES). JAMA 272, 284-291.

Qiang, L., Liu, J., Wang, Q., Zou, M., 2015. Grain-size distribution and heavy metal contamination of road dusts in urban parks and squares in Changchun, China. Environmental Geochemistry and Health 37, 71-82.

Qiu, K., Xing, W., Scheckel, K. G., Cheng, Y., Zhao, Z., Ruan, X., Li, L., 2016. Temporal and seasonal variations of As, Cd and Pb atmospheric deposition flux in the vicinity of lead smelters in Jiyuan, China. Atmospheric Pollution Research 7, 170-179.

Ramsey, K. A., Foong, R. E., Sly, P. D., Larcombe, A. N., Zosky, G. R., 2013. Early Life Arsenic Exposure and Acute and Long-term Responses to Influenza A Infection in Mice. Environmental Health Perspectives 121, 1187-1193.

Rasmussen, P. E., Beauchemin, S., Chénier, M., Levesque, C., MacLean, L. C. W., Marro, L., Jones-Otazo, H., Petrovic, S., McDonald, L. T., Gardner, H. D., 2011. Canadian House Dust Study: Lead Bioaccessibility and Speciation. Environmental Science & Technology 45, 4959-4965.

Rathnayake, S., Schwab, A. P., 2016. Chemical and mineralogical characterization of arsenic, lead, cadmium and zinc in a smelter contaminated soil, in: Bhattacharya, P., Vahter, M., Jarsjö, J., Kumpiene, J., Ahmad, A., Sparrenbom, C., Jacks, G., Donselaar, E. M., Bundschuh, J., Naidu, R. (Eds.), Arsenic Research and Global Sustainability. Taylor & Francis Group, London, pp. 181-182.

Rauh, V., Arunajadai, S., Horton, M., Perera, F., Hoepner, L., Barr, D. B., Whyatt, R., 2011. Seven-Year Neurodevelopmental Scores and Prenatal Exposure to Chlorpyrifos, a Common Agricultural Pesticide. Environmental Health Perspectives 119, 1196-1201.

Rosner, D., Markowitz, G., 2005. Standing Up to the Lead Industry: An Interview with Herbert Needleman. Public Health Reports 120, 330-337.

Rouillon, M., Harvey, P. J., Kristensen, L. J., George, S. G., Taylor, M. P., 2017. VegeSafe: A community science program measuring soil-metal contamination, evaluating risk and providing advice for safe gardening. Environmental Pollution 222, 557-566.

Roze, E., Meijer, L., Bakker, A., Van Braeckel, K. N. J. A., Sauer, P. J. J., Bos, A. F., 2009. Prenatal Exposure to Organohalogens, Including Brominated Flame Retardants, Influences Motor, Cognitive, and Behavioral Performance at School Age. Environmental Health Perspectives 117, 1953-1958.

SA Government, 2017. A review of air quality impacts and regulation—South Australian mining and extractives industry. https://sarigbasis.pir.sa.gov.au/WebtopEw/ws/samref/sarig1/image/DDD/RB201600005.pdf (accessed 30.11.17).

SA Health, 2013. 2013 Port Pirie Soil Lead Concentration Report—prepared for the Port Pirie Regional Council. http://www.sahealth.sa.gov.au/wps/wcm/connect/fe9ace8040cc6bd396eeb66c5432000f/2013+Port+Pirie+Soil+Lead+Concentrations+Report+%28web%29.pdf?MOD=AJPERES&CACHEID=fe9ace8040cc6bd396eeb66c5432000f (accessed 15.11.2017).

Safruk, A. M., McGregor, E., Whitfield Aslund, M. L., Cheung, P. H., Pinsent, C., Jackson, B. J., Hair, A. T., Lee, M., Sigal, E. A., 2017. The influence of lead content in drinking water, household dust, soil, and paint on blood lead levels of children in Flin Flon, Manitoba and Creighton, Saskatchewan, Science of The Total Environment 593, 202-210.

Sanders, A. P., Henn, B. C., Wright, R. O., 2015. Perinatal and Childhood Exposure to Cadmium, Manganese, and Metal Mixtures and Effects on Cognition and Behavior: A Review of Recent Literature. Current Environmental Health Reports 2, 284-294.

Schoof, R. A., Johnson, D. L., Handziuk, E. R., Landingham, C. V., Feldpausch, A. M., Gallagher, A. E., Dell, L. D., Kephart, A., 2016. Assessment of blood lead level declines in an area of historical mining with a holistic remediation and abatement program. Environmental Pollution 150, 582-591.

Schuhmacher, M., Bellés, M., Rico, A., Domingo, J. L., Corbella, J., 1996. Impact of reduction of lead in gasoline on the blood and hair lead levels in the population of Tarragona Province, Spain, 1990-1995. Science of the Total Environment 184, 203-209.

Schwarz, K., Pouyat, R. V., Yesilonis, I., 2016. Legacies of Lead in Charm City's Soil: Lessons from the Baltimore Ecosystem Study. International Journal of Environmental Research and Public Health 13, 209.

Skalny, A. V., Zhukovskaya, E. V., Kireeva, G. N., Skalnaya, M. G., Grabesklis, A. R., Radysh, I. V., Shakieva, R. A., Nikonorov, A. A., Tinkov, A. A., Whole blood and hair trace elements and minerals in children living in metal-polluted area near copper smelter in Karabash, Chelyabinsk region, Russia. Environmental Science and Pollution Research, https://doi.org/10.1007/s11356-016-7876-6.

Smargiassi, A., Kosatsky, T., Hicks, J., Plante, C., Armstrong, B., 2009. Risk of asthmatic episodes in children exposed to sulfur dioxide stack emissions from a refinery point source in Montreal, Canada. Environmental Health Perspectives 117, 653-659.

Soto-Jiménez, M. F., Flegal, A. R., 2011. Childhood lead poisoning from the smelter in Torreón, México. Environmental Research 111, 590-596.

Spear, M., Thomas, R., Shrader-Frechette, K., 2015. Commentary: Flawed Science Delays Smelter Cleanup and Worsens Health. Accountability in Research 22, 41-60.

Stovern, M., Guzmán, H., Rine, K. P., Felix, O., King, M., Ela, W. P., Betterton, E. A., Sáez, A. E., 2016. Windblown Dust Deposition Forecasting and Spread of Contamination around Mining Tailings. Atmosphere 7, doi:10.3390/atmos7020016.

Sullivan, M., 2014. Tainted Earth: Smelters, Public Health and the Environment. Rutgers University Press, New Brunswick, US.

Sullivan, M., Green, D., 2016. Misled about lead: an assessment of online public health education material from Australia's lead mining and smelting towns. Environmental Health 15:1. https://doi.org/10.1186/s12940-015-0085-9.

TA Luft, 2002. Technical Instructions on Air Quality Control. In: First General Administration Regulation Pertaining the Federal Immission Control Act. http://www.bmub.bund.de/fileadmin/bmu-import/files/pdfs/allgemein/application/pdf/taluft_engl.pdf (accessed 10.03.15).

Tang, D., Lee, J., Muirhead, L., Li, T. Y., Qu, L., Yu, J., Perera, F., 2014. Molecular and Neurodevelopmental Benefits to Children of Closure of a Coal Burning Power Plant in China. PLoS ONE 9, e91966. https://doi.org/10.1371/journal.pone.0091966.

Taylor, M. P., 2012. Lead poisoning of Port Pirie children: a long history of looking the other way. http://theconversation.com/lead-poisoning-of-port-pirie-children-a-long-history-of-looking-the-other-way-8296 (accessed 18.09.17).

Taylor, M. P., 2015. Atmospherically deposited trace metals from bulk mineral concentrate port operations. Science of the Total Environment 515-516, 143-152.

Taylor, M. P., Camenzuli, D., Kristensen, L. J., Forbes, M., 2013. Environmental lead exposure risks associated with children's outdoor playground. Environmental Pollution 178, 447-454.

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

Taylor, M. P., Davis, P. J., Kristensen, L. J., Csavina, J. L., 2014b. 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.

Taylor, M. P., Dong, C., Harvey, P., 2017. Mount Isa contamination 'within guidelines' but residents told to clean their homes. https://theconversation.com/mount-isa-contamination-within-guidelines-but-residents-told-to-clean-their-homes-72862 (accessed 15.01.18).

Taylor, M. P., Schniering, C., 2010. The public minimization of the risks associated with environmental lead exposure and elevated blood lead levels in children, Mount Isa, Queensland, Australia. Archives of Environmental & Occupational Health 65, 45-48.

Taylor, M. P., Zahran, S., Kristensen, L., Rouillon, M., 2015. Evaluating the efficacy of playground washing to reduce environmental metal exposures. Environmental Pollution 202. 112-119.

Telmer, K., Bonham-Carter, G. F., Kliza, D. A., Hall, G. E. M., 2004. The atmospheric transport and deposition of smelter emissions: evidence from the multi-element geochemistry of snow, Quebec, Canada. Geochimica et Cosmochimica Acta 68, 2961-2980.

Tirima, S., Bartrem, C., von Lindern, I., von Braun, M., Lind, D., Anka, S. M., Abdullahi, A., 2016. Environmental Remediation to Address Childhood Lead Poisoning Epidemic due to Artisanal Gold Mining in Zamfara, Nigeria. Environmental Health Perspectives 124, 1471-1478.

Tong, S., Baghurst, P. A., McMichael, A., Sawyer, M., Mudge, J., 1996. Lifetime exposure to environmental lead and children's intelligence at 11-13 years: the Port Pirie cohort study. BMJ 312, 1569.

Vahidnia, A., van der Voet, G. B., de Wolff, F. A., 2007. Arsenic neurotoxicity − A review. Human & Experimental Toxicology 26, 823-832.

Valeri, L., Mazumdar, M. M., Bobb, J. F., Henn, B. C., Rodrigues, E., Sharif, O. I. A., Kile, M. L., Quamruzzaman, Q., Afroz, S., Golam, M., Amarasiriwardena, C., Bellinger, D. C., Christiani, D. C., Coull, B. A., Wright, R. O., 2017. The Joint Effect of Prenatal Exposure to Metal Mixtures on Neurodevelopmental Outcomes at 20–40 Months of Age: Evidence from Rural Bangladesh. Environmental Health Perspectives 125, https://doi.org/10.1289/EHP614.

Varrica, D., Dongarrà, G., Alaimo, M. G., Monna, F., Losno, R., Sanna, E., De Giudici, G., Tamburo, E., 2018. Lead isotopic fingerprint in human scalp hair: The case study of lglesias mining district (Sardinia, Italy). Science of the Total Environment 613-614, 456-461.

van Alphen, M., 1991. The history of smelting and ore dressing in Broken Hill and the potential for mine derived lead contamination in Broken Hill. Unpublished report.

von Lindern, I., Spalinger, S., Petroysan, V., von Braun, M., 2003. Assessing remedial effectiveness through the blood lead: soil/dust lead relationship at the Bunker Hill Superfund Site in the Silver Valley of Idaho. Science of the Total Environment 303, 139-170.

von Lindern, I., Spalinger, S., Stifelman, M. L., Stanek, L. W., Bartrem, C., 2016. Estimating Children's Soil/Dust Ingestion Rates through Retrospective Analyses of Blood Lead Biomonitoring from the Bunker Hill Superfund Site in Idaho. Environmental Health Perspectives 124, 1462-1470.

Wang, B., Du, Y., 2013. Cadmium and Its Neurotoxic Effects. Oxidative Medicine and Cellular Longevity 2013, Article ID 898034, http://dx.doi.org/10.1155/2013/898034.

Wang, J., Hu, Z., Chen, Y., Chen, Z., Xu, S., 2013. Contamination characteristics and possible sources of PM10 and PM2.5 in different functional areas of Shanghai, China. Atmospheric Environment 68, 221-229.

Wasserman, G. A., Liu, X., Parvez, F., Ahsan, H., Factor-Litvak, P., Ahsan, H., Levy, D., Kline, J., van Geen, A., Mey, J., Slavkovich, V., Siddique, A. B., Islam, T., Graziano, J. H., 2011. Arsenic and manganese exposure and children's intellectual function. NeuroToxicology 32, 450-457.

Wasserman, G. A., Liu, X., Parvez, F., Factor-Litvak, P., Kline, J., Siddique, A. B., Shahriar, H., Uddin, M. N., van Geen, A., Mey, J. L., Balac, O., Graziano, J. H., 2016. Child Intelligence and Reductions in Water Arsenic and Manganese: A Two-Year Follow-up Study in Bangladesh. Environmental Health Perspectives 124, 1114-1120.

Webster, A. E., 2006. The geology of the Broken Hill lead−zinc−silver deposit, New South Wales, Australia. CODES ARC Centre of Excellence in Ore Deposits, University of Tasmania.

Weitzman, M., Aschengrau, A., Bellinger, D., Jones, R., Hamlin, J.S., Beiser, A., 1993. Lead-contaminated soil abatement and urban children's blood lead levels. JAMA 269, 1647-1654.

White, B. M., Bonilha, H. S., Ellis, C. Jr., 2016. Racial/Ethnic Differences in Childhood Blood Lead Levels Among Children <72 Months of Age in the United States: a Systematic Review of the Literature. Journal of Racial and Ethnic Health Disparities 3, 145-153.

Wietlisbach, V., Rickenbach, M., Berode, M., Guillemin, M., Time Trend and Determinants of Blood Lead Levels in a Swiss Population over a Transition Period (1984-1993) from Leaded to Unleaded Gasoline Use. Environmental Research 68, 82-90.

Wigg. N. R., McMichael, A. J., Baghurst, P. A., Roberton, E. F., Roberts, R. J., 1988. Port Pirie Cohort Study: Childhood blood lead and neuropsychological development at age two years. Journal of Epidemiology and Community Health 42, 213-219.

Willmore, A., Sladden, T., Bates, L., Dalton, C. B., 2006. Use of a geographic information system to track smelter-related lead exposures in children: North Lake Macquarie, Australia, 1991–2002. International Journal of Health Geographics 5: 30. https://doi.org/10.1186/1476-072X-5-30.

World Health Organization, 2010. Childhood Lead Poisoning. http://www.who.int/ceh/publications/leadguidance.pdf (accessed 08.01.18).

Wright, R. O., Amarasiriwardena, C., Woolf, A. D., Jim, R., Bellinger, D. C., 2006. Neuropsychological correlates of hair arsenic, manganese, and cadmium levels in school-age children residing near a hazardous waste site. Neurotoxicology 27, 210-216.

Wu, L., Taylor, M. P., Handley, H. K., Wu, M., 2016. Australian atmospheric lead deposition reconstructed using lead concentrations and isotopic compositions of archival lichen and fungi. Environmental Pollution 678-687.

Yang, K., Cattle, S. R., 2015. Bioaccessibility of lead in urban soil of Broken Hill, Australia: A study based on in vitro digestion and the IEUBK model. Science of the Total Environment 538, 922-933.

Yeoh, B., Woolfenden, S., Lanphear, B., Ridley, G., Livingstone, N., Jorgensen, E., 2014. Household interventions for preventing domestic lead exposure in children. Cochrane Database of Systematic Reviews, Art. No.: CD006047. doi: 10.1002/14651858.CD006047.pub4.

Young, A. R. M., Bryant, E. A., Winchester, H. P. M., 1992. The Wollongong lead study: an investigation of the blood lead levels of pre-school children and their relationship to soil lead levels. Australian Geographer 23, 121-132.

Young, T. M., Heeraman, D. A., Sirin, G., Ashbaugh, L. L., 2002. Resuspension of Soil as a Source of Airborne Lead near Industrial Facilities and Highways. Environmental Science & Technology 36, 2484-2490.

Zahran, S., Laidlaw, M. A. S., McElmurry, S. P., Filippelli, G. M., Taylor, M., 2013. Linking Source and Effect: Resuspended Soil Lead, Air Lead, and Children's Blood Lead Levels in Detroit, Michigan. Environmental Science & Technology 47, 2839-2845.

Zahran, S., Mielke, H. W., Weiler, S., Hempel, L., Berry, K. J., Gonzales, C. R., 2012. Associations between standardized school performance tests and mixtures of Pb, Zn, Cd, Ni, Mn, Cu, Cr, Co, and V in community soils of New Orleans. Environmental Pollution 169, 128-135.

Zahran, S., Mielke, H. W., Weiler, S., Gonzales, C. R., 2011. Nonlinear associations between blood lead in children, age of child, and quantity of soil lead in metropolitan New Orleans. Science of the Total Environment 409, 1211-1218.

Zhang, H., Yolton, K., Webster, G. M., Sjödin, A., Calafat, A. M., Dietrich, K. N., Xu, Y., Xie, C., Braun, J. M., Lanphear, B. P., Chen, A., 2017. Prenatal PBDE and PCB Exposures and Reading, Cognition, and Externalizing Behavior in Children. Environmental Health Perspectives 125, 746-752.

Zhang, R., Liu, C., Zhou, G., Sun, J., Liu, N., Hsu, P. C., Wang, H., Qiu, Y., Zhao, J., Wu, T., Zhao, W., Cui, Y., 2017. Morphology and property investigation of primary particulate matter particles from different sources. Nano Research, https://doi.org/10.1007/s12274-017-1724-y.

Zhou, X., Taylor, M. P., Davies, P. J., Prasad, S., 2017. Identifying sources of environmental contamination in European honey bees (*Apis mellifera*) using trace elements and lead isotopic compositions. Environmental Science and Technology, Accepted Manuscript, https://doi.org/10.1021/acs.est.7b04084.

Chapter 8: Conclusions

This thesis employed a multiple lines of evidence approach to identify the sources, causes and human health impact of Pb contamination in the city of Broken Hill, NSW. The results of laboratory analyses, including metal concentrations, Pb isotopic compositions, chemical compositions and morphological characteristics of contaminated particulates, showed that contemporary dust Pb deposits were the primary route of exposure. Further, the study data clearly supports the contention that contemporary dust contamination in Broken Hill originates from current mining activities and not from weathering or legacy sources. Generalised linear regression modelling demonstrated that contemporary dust Pb loading ($\mu g/m^2/day$) increased with ore production and decreased with distance away from current active mining operations. While this is not unexpected for a Pb mining operation with significant point source emissions (estimated at 28,000 kg of Pb in 2015/2016), the results provide clear evidence for intervention strategies as part of the NSW Government's Broken Hill Environmental Lead Program.

In addition to the effects of ongoing emissions to the environment in Broken Hill, soil Pb contamination from historical mining and smelting activities was assessed. The statistical analyses based upon the Broken Hill dataset comprising >30,000 blood and environmental Pb data covering a 25–year period showed that both soil and dust Pb are contributors to blood Pb exposure. However, for the first time, this research was able to differentiate soil and dust as separate sources of blood Pb exposure, with the ultimate aim of being able to identify the primary targets, using evidence based conclusions, for remediation. In order to differentiate these known likely sources of exposure, the thesis applied a novel approach of using two natural experiments: (a) prevailing wind direction conditions in Broken Hill; (b) the massive 2009 desert dust storm that affected Broken Hill and NSW more broadly. The depositions from this storm sourced from the adjacent desert area (i.e. Lake Eyre Basin) were dominated by crustal elemental oxides of Al, Si and Fe,[1] with low level of Pb concentrations[2] moderating local residual soil Pb contamination in Broken Hill. Analyses of the most recent period (2011–2015) of the available dataset showed that contemporary blood Pb outcomes in Broken Hill are determined by:

(a) an individuals' geographic location with respect to the prevailing wind direction (i.e.

[1] Aryal, R., Kandel, D., Acharya, D., Chong, M. N., Beecham, S., 2012. Unusual Sydney dust storm and its mineralogical and organic characteristics. Environmental Chemistry 9, 537-546.

[2] Gunawardena, J., Ziyath, A. M., Bostrom, T. E., Bekessy, L. K., Ayoko, G. A., Egodawatta, P., Goonetilleke, A., 2013. Characterisation of atmospheric deposited particles during a dust storm in urban areas of Eastern Australia. Science of the Total Environment 461-462, 72-80.

those with consistently higher blood Pb levels resided downwind of the prevailing northerly winds in Broken Hill)

(b) the volume of current mining emissions and ore production rates

(c) dust Pb depositions with soil Pb providing a small, but clear contribution to exposures.

Previous claims that dust Pb contamination and elevated blood Pb are due to natural weathering, recycling of legacy Pb in soil or from other contamination sources (e.g. leaded petrol, Pb-based paints, legacy emissions) were not supported by the data analysis. The promulgation of these as sources of contamination has stymied effective intervention in Broken Hill and has left the community ill-informed about the source, cause and risks of Pb exposure associated with living in the city. Looking forward, in terms of the future community exposure reduction program in Broken Hill, it is clear that the reduction of ongoing emissions is a critical step in limiting exposures in the wider population. Moreover, the data shows clearly that interventions should be specifically targeted at mitigating exposure in children aged 12–36 months, especially those that are of Aboriginal descent. As part of any future mitigation strategy, capping contaminated household soil and addressing building condition and infrastructure (e.g. peeling paint in older homes, poorly sealed ceilings and windows) would also be critical, particularly in older buildings.

More broadly, this research has demonstrated that the adverse impacts of environmental metal(loid)s contamination on children's health (e.g. cognitive and behavioural development) are also observed in the other major Australian mining and smelting communities of Port Pirie and Mount Isa.

This highlights a clear need to identify major contamination sources to direct effective community exposure reduction programs. Communities that have been subject to a history of ore processing will typically have a range of potential contaminant sources that need to be delineated in terms of their risk to human health. The absence of comprehensive information about contamination sources and their specific contribution is likely to result in mis-directed or ineffective intervention strategies, pushing the burden of responsibility on to residents rather than it being addressed at its origin. In this regard, this thesis reinforces the importance of primary prevention by controlling emissions at their source to prevent unnecessary exposures in communities adjoining mining and smelting operations.

Appendix

Appendix

The Appendix contains one paper (Paper Six) published in the peer-reviewed journal *Environmental Pollution* and two co-authored online articles relating pollution matters at Broken Hill and Mount Isa published in *The Conversation* (Article One and Article Two). These works are included as part of the body of research work completed during the candidature of this PhD thesis.

The *Environmental Pollution* paper evaluates the *in-situ* versus *ex-situ* use of field portable X-ray Fluorescence (pXRF) for metal-contaminated site assessment. The study also assesses the advantages of increased sampling to increase the confidence of decision making for a lower cost. It compares the cost of using pXRF against traditional approaches that involve field work followed by laboratory processing of samples for trace elements concentrations via ICP-MS. This pXRF study provided technical insight into the utility of applying rapid field analytical methods as were used for a proportion of the Broken Hill soil samples included the study presented in Chapter Six.

Subsequent to the publication of Paper Five (*Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes*), Article One was written and published for broader dissemination of our study findings about the adverse impacts of environmental Pb contamination on children in Broken Hill. Article Two builds on a significant body of work coming out of Professor Mark P. Taylor's research group in relation to the disputes over contamination sources in the mining and smelting community of Mount Isa. It was published in response to the release of Glencore's Mount Isa Mines Ltd report on airborne contamination in the city. Its purpose was to highlight company's flawed Pb exposure mitigation advice arising from the report's findings that contamination was coming off the mine lease. This advice amounted to recommending that parents that they should keep their homes clean, with insufficient focus on emission control on the sources of Pb coming from the mine lease and its operations. The publication of the two online articles increase the awareness of the wider community about contamination issues in mining and smelting communities and synthesize detailed research to make its findings more accessible.

Appendix

Appendix A: Paper Six

Appendix B: Online Article 1

Appendix C: Online Article 2

Appendix D: Supplementary Information for Chapter One
Supplementary Document S1
Supplementary Table S2

Appendix E: Supplementary Information for Paper One
Supplementary Table S1
Supplementary Table S2
Supplementary Table S3
Supplementary Table S4
Supplementary Table S5
Supplementary Figure S6
Supplementary References

Appendix F: Supplementary Information for Paper Two
Supplementary Data 1
Supplementary Data 2
Supplementary Data 3
Supplementary Data 4

Appendix G: Supplementary Information for Paper Three
Supplementary Figure S1
Supplementary Table S2
Supplementary Document S3
Supplementary Figure S4
Supplementary Figure S5
Supplementary Figure S6
Supplementary References

Appendix H: Supplementary Information for Paper Four
Supplementary Table S1
Supplementary Figure S2
Supplementary Table S3
Supplementary References

Appendix I: Supplementary Information for Paper Five
Supplementary Table S1
Supplementary Table S2
Supplementary Figure S3
Supplementary Table S4
Supplementary Table S5
Supplementary Figure S6
Supplementary Table S7
Supplementary Figure S8
Supplementary Table S9

Supplementary Table S10
Supplementary Table S11
Supplementary Table S13
Supplementary Table S14
Supplementary Table S15
Supplementary Table S16
Supplementary References

Appendix J: Ethics approval documents
Supplementary Document S1
Supplementary Document S2

Appendix A

Environmental Pollution 229 (2017) 780 789

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Reducing risk and increasing confidence of decision making at a lower cost: *In-situ* pXRF assessment of metal-contaminated sites.☆

Marek Rouillon [a, *], Mark P. Taylor [a, b], Chenyin Dong [a]

[a] Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, Sydney, NSW 2109, Australia
[b] The Energy and Environmental Contaminants Research Centre, Department of Environmental Sciences, Faculty of Science and Engineering, Macquarie University, Sydney, NSW 2109, Australia

ARTICLE INFO

Article history:
Received 20 April 2017
Received in revised form
2 June 2017
Accepted 6 June 2017
Available online 28 June 2017

Keywords:
Metal-contamination
Site assessment
Field portable XRF spectrometry
In-situ pXRF
Measurement uncertainty

ABSTRACT

This study evaluates the *in situ* use of field portable X ray Fluorescence (pXRF) for metal contaminated site assessments, and assesses the advantages of increased sampling to reduce risk, and increase con fidence of decision making at a lower cost. Five metal contaminated sites were assessed using both *in situ* pXRF and *ex situ* inductively coupled plasma mass spectrometry (ICP MS) analyses at various sampling resolutions. Twenty second *in situ* pXRF measurements of Mn, Zn and Pb were corrected using a subset of parallel ICP MS measurements taken at each site. Field and analytical duplicates revealed sampling as the major contributor (>95% variation) to measurement uncertainties. This study shows that increased sampling led to several benefits including more representative site characterisation, higher soil metal mapping resolution, reduced uncertainty around the site mean, and reduced sampling un certainty. Real time pXRF data enabled efficient, on site decision making for further judgemental sam pling, without the need to return to the site. Additionally, *in situ* pXRF was more cost effective than the current approach of *ex situ* sampling and ICP MS analysis, even with higher sampling at each site. Lastly, a probabilistic site assessment approach was applied to demonstrate the advantages of integrating estimated measurement uncertainties into site reporting.

1. Introduction

Land contamination is a ubiquitous, worldwide problem resulting from various industrial activities such as chemical manufacturing, mining, and metal refining (Bastos et al., 2012; Vacca et al., 2012). Metal and metalloid contaminants (hereafter referred to as metals) often accumulate in high concentrations in soils, posing potential health risks to humans and biota if left un managed (Boon and Ramsey, 2010). Government bodies limit the maximum acceptable concentration of contaminants in soils for the land's current or intended use, in an effort to minimise risks associated with exposure (Brevik, 2013). For instance in New South Wales (NSW), Australia, contaminated sites are overseen and regulated, in part, by the state Environment Protection Authority (NSW EPA, 2015). If contamination is observed or suspected, there is a duty to report by the polluter or land owner to the NSW EPA under Section 60 of the *Contaminated Land Management Act 1997* (NSW), when certain notification triggers are met. For both on site and off site soil contamination, two notification triggers exist that target the site and samples, specifically (NSW EPA, 2015):

(1) "The 95% upper confidence limit on the arithmetic average concentration of a contaminant in or on soil is equal to or above the Health Investigation Level and/or Health Screening Level for that contaminant for the current or approved use of the respective on site land …"
(2) "The concentration of a contaminant in an individual soil sample is equal to or more than 250% of the Health Investi gation Level and/or Health Screening Level for that contaminant for the current or approved use of the respec tive on site land … and a person has been or foreseeably will be exposed to the contaminant or a by product of the contaminant."

Similar notification triggers are used worldwide, with contam ination being typically assessed using *ex situ* sampling and wet chemistry analyses such as Inductively Coupled Plasma Mass

☆ This paper has been recommended for acceptance by Dr. J. Rinklebe.
* Corresponding author.
E-mail address: marek.rouillon@mq.edu.au (M. Rouillon).

http://dx.doi.org/10.1016/j.envpol.2017.06.020
0269-7491/

Abbreviations

CI	Confidence interval
CRM	Certified reference material
Ha	Hectare
HIL	Health investigation level
ICP–MS	Inductively Coupled Plasma Mass Spectrometry
Mn	Manganese
NSW EPA	New South Wales Environmental Protection Authority
Pb	Lead
pXRF	Field portable X ray Fluorescence
RANOVA	Robust Analysis of Variance
RP	Relative proximity
s_{anal}	Analytical standard deviation
$s_{geochem}$	Geochemical standard deviation
s_{meas}	Measurement standard deviation
s_{samp}	Sampling standard deviation
U_{anal}	Analytical uncertainty
U_{meas}	Measurement uncertainty
U_{samp}	Sampling uncertainty
UCL	Upper confidence limit
Zn	Zinc

Spectrometry (ICP–MS) (e.g. US EPA, 2002). Soil metal contamination is characteristically heterogeneous and may require many samples to adequately characterise a site. For example, the 95% upper confidence limit (UCL) used in notification trigger 1, is influenced strongly by the number of samples taken to calculate the mean. Calculation of the UCL with fewer samples decreases the confidence in accurately locating the mean due to an increased confidence interval (CI) (Boon and Ramsey, 2010). Inversely, an increased number of samples is likely to increase the confidence in locating the mean by decreasing the CI. Infield sampling is typically constrained due to the cost of individual analyses charged by commercial laboratories (Ramsey and Boon, 2012).

The use of *in situ* measurement techniques for soil metals, such as field portable X ray Fluorescence (pXRF), have been increasingly applied as screening tools for the presence of trace metals due to their rapid, simple and inexpensive operation (e.g. Argyraki et al., 1997; Bernick et al., 1995; Boon and Ramsey, 2012; Carr et al., 2008; Clark et al., 1999; Higueras et al., 2012; Horta et al., 2015; Kalnicky and Singhvi, 2001; Parsons et al., 2013; Paulette et al., 2015; Peinado et al., 2010; Radu et al., 2013; Ran et al., 2014; Taylor et al., 2004, 2005; Vanhoof et al., 2004; Weindorf et al., 2013). *In situ* pXRF for assessing contaminated sites has some advantages over *ex situ* laboratory analyses including the low cost of ownership and operation and instantaneous on site estimates of metals (Ramsey and Boon, 2012; Weindorf et al., 2014). The ability to guide field based decision making, such as identification of contaminant hot spots and delineation of contaminant zones at low cost is indispensable for ensuring representative assessments of metal contaminated sites (Melquiades and Appoloni, 2004). However, the difficulties of deriving analytical quality control on field samples, higher pXRF detection limits and limited training of operators when compared to *ex situ* laboratory techniques are also well known (Peinado et al., 2010). The mismatch between field samples (unprepared, heterogeneous surface soils) and reference materials (dried, homogenous powders) makes quantification of analytical bias challenging (Boon and Ramsey, 2012). Moreover, the widespread screening use of pXRF (e.g. Restriction of Hazardous Materials, Bosco, 2013) have largely underplayed and inappropriately informed users in regards to its analytical capabilities.

Measurement techniques are most effectively employed when their advantages are fully utilised and the drawbacks are mitigated where possible. With this in mind, this study evaluates the potential integration of *in situ* pXRF for the assessment of metal contaminated sites. Hence, the aims of this paper are therefore to:

1. Assess the reliability of *in situ* pXRF data compared to *ex situ* commercial ICP–MS analysis.
2. Determine error contributions from sampling and analysis towards measurement uncertainty.
3. Evaluate the advantages of increased sampling using *in situ* pXRF and its impact on decision making.
4. Estimate the overall costs involved for *in situ* and *ex situ* measurement approaches.
5. Demonstrate the advantages of integrating measurement uncertainty into site reporting.

2. Methods

2.1. Site selection and sampling design

Five metal contaminated sites of varying sizes and land uses in NSW, Australia, were selected for this study (Table 1). Sites 1 and 3 were located near a former zinc/lead (Zn/Pb) smelter, whose surrounding suburbs were subject to decades of slag material distribution and metal rich atmospheric depositions (Batley, 1992; Harvey et al., 2016; Morrison and Gulson, 2007). Site 2 was located at a primary school in inner city Sydney, where seven decades of leaded petrol emissions, coupled to the use of Pb based paint since the 19th century have contaminated the surrounding environment (Kristensen, 2015; Rouillon et al., 2017). Sites 4 and 5 were located in a mining city where >100 years of Zn/Pb mining and early smelting have contaminated city soils with Zn– and Pb–rich emissions (Dong et al., 2015; Kristensen and Taylor, 2016).

All five sites were measured systematically in a grid pattern using the minimum recommended resolution for both the current regulatory approach of *ex situ* sampling and ICP–MS analysis (NSW EPA, 1995) and a proposed *in situ* pXRF measurement approach (Table 1). Similar analytical and statistical approaches to metal contaminated site assessments exist around the world, yet for the purpose of this comparative study, the current regulatory practice of sampling and off site laboratory measurements, set by the NEPM (2013) and the NSW EPA (1995), are compared against an *in situ* pXRF method. A pilot study was conducted at a small (0.04 ha), geochemically heterogeneous site and determined 30 samples as a reliable and robust minimum for estimating a site mean (cf. Student, 1908) (Supplementary Fig. 1). An increased sampling resolution was used for *in situ* pXRF measurements to assess the benefits of increased sampling at metal contaminated sites. After the measurement of surface soil contamination using a systematic assessment approach (pXRF Phase 1), a second phase of measurements was undertaken halfway between targets of interest (e.g. where sample concentration > guideline) and adjacent samples (pXRF Phase 2). This second phase (judgemental sampling) utilised the advantages of real time pXRF data which assisted in identifying hot spots without the need to return to the site.

2.2. In situ pXRF measurement approach

Sites were measured *in situ* at the minimum resolution specified in Table 1, using an Olympus Delta Premium XRF Analyser fitted

Table 1
Minimum sampling resolution for the current regulatory approach (NSW EPA, 1995) and proposed *in-situ* pXRF approach per given site size. *The number of samples taken at Site 4 was 36 for ICP MS and 46 for pXRF Phase 1.

Site number	Land use type	Size (ha)	Current minimum samples (ICP MS)	Proposed minimum samples for *in-situ* pXRF (pXRF Phase 1)	Systematic + judgemental sampling for *in-situ* pXRF (pXRF Phase 1 + 2)
1	Empty house lot	0.1	6	30	64
2	School grounds	0.6	15	30	76
3	Recreational park	1.0	21	30	61
4	Sports field	2.2	*35	*45	83
5	Recreational park	2.8	40	50	90

with a 50 kV, 4 W Ta anode X ray tube and a silicon drift detector. Measurement targets were pre determined and marked with flags. Grasses and debris were removed where necessary to expose the surface soil layer, which was compacted prior to pXRF analysis. The pXRF measurement window was cleaned with KimWipes between samples to mitigate cross contamination. Samples were measured for 20 s on Beam II (40 kV) using the proprietary soil mode for manganese (Mn), Zn, and Pb concentrations. Despite being measured most accurately on Beam III (15 kV), Mn was included in this assessment to ascertain if elements can be measured accurately on other X ray beams that are not intended for its measurement. The pXRF was protracted from the operator via an extension pole to minimise radiation exposure associated with pXRF operation (Rouillon et al., 2015) and to provide ergonomic *in situ* measurements.

Recommended operational procedures were followed (cf. Rouillon and Taylor, 2016), including daily measurements of an energy calibration check, measurements of a silicate (SiO_2) blank and National Institute of Standards and Technology certified reference materials (CRMs: NIST 2709a, 2710a, 2711a) throughout the measurement process. Instrument detection limits for Mn, Zn and Pb measurements were 9.1, 5.1 and 3.0 mg/kg respectively, while the mean relative standard deviation for these elements were 0.8, 0.8 and 1.8% (Rouillon and Taylor, 2016). Mean pXRF recoveries were 102% (Mn), 99% (Zn) and 99% (Pb) for *ex situ* measurements, however these are not likely to be representative of *in situ* mea surements. Hence, the analytical bias of *in situ* pXRF measurements were corrected using ICP–MS analysis (Section 2.5).

2.3. ICP–MS analysis

Sites were sampled and measured by ICP–MS at the minimum resolution specified in Table 1. Surface soils were collected at 0–2 cm depth and analysed for total acid extractable metal con centrations at the National Measurement Institute at North Ryde, Australia. Approximately 0.5 g of sample was digested in 3 mL of 10 M HCL and 3 mL of 16 M HNO_3, and measured using an Agilent 7900 ICP–MS for Mn, Zn and Pb concentrations (NMI, 2014). Six procedural blanks returned concentrations <0.5 mg/kg for all ele ments. Laboratory control spikes were 99%, 105% and 102%, while matrix control spikes were 93–106%, 97–112% and 83–116% for Mn, Zn and Pb respectively. Duplicate analyses were 0–39% (Mn), 0.1–27% (Zn) and 0.1–18% (Pb).

2.4. Sampling, analytical and measurement uncertainty

The simplest and most cost efficient method for estimating sampling and analytical precision, and ultimately measurement uncertainty is using a balanced duplicate method (Supplementary Fig. 2) (Ramsey et al., 1992, 2002). Ten to 15% ($n \geq 3$) of samples from each site were randomly selected for duplicate sampling and analysis for both *in situ* pXRF and ICP–MS measurement ap proaches. Duplicate samples (S1, S2) were taken at 10% of the mean grid spacing distance between targets at 90° orientation from each other. Duplicate analyses (A1, A2) were conducted for each dupli cate sample. The variation between sample duplicates demon strates sampling ambiguity, including small scale heterogeneity of the sample and precisely locating the sample target. The variation between analyses of the same sample duplicate provides variation of the analytical process and technique. To estimate individual contributions to variance and uncertainty, duplicates data were analysed using robust analysis of variance (RANOVA). Robust ANOVA was selected over standard ANOVA to down weigh the effect of outliers in the frequency distribution, and provide more reliable estimates of variances (Ramsey and Ellison, 2007). Calcu lation of measurement uncertainty via RANOVA is further explained and demonstrated in Boon and Ramsey (2010). Analytical bias was not included in variance estimates given the disparity between soil reference materials (dry/small particles) and the field sample (wet/varying particle size).

2.5. In situ pXRF data correction

To correct for analytical bias and moisture content, parallel measurements of both *in situ* pXRF and ICP–MS were conducted at the same sample targets (T) used for duplicate analyses at each site. This form of pXRF data adjustment has previously been applied in *in situ* vs. *ex situ* measurement comparisons (e.g. Ramsey and Boon, 2012). The sample was first measured by pXRF, then sampled directly under the measurement window location by inserting a 35 mm open ended XRF cup 2 cm into the soil. This was done to ensure the sample measured by *in situ* pXRF was as close to the 'same' sample measured by ICP–MS as possible. Prior to pXRF data correction, ICP–MS data was converted from 'dry weight' to 'as received' basis using moisture content (%) estimated by the com mercial laboratory (Supplementary Table 1). A Deming regression was used to plot both measurement techniques with pXRF placed on the x–axis, and ICP–MS on the y–axis. Rotational (slope, m) and translational (intercept, b) bias were corrected for *in situ* pXRF data by solving for 'y' in 'y mx + b'.

3. Results and discussion

3.1. Corrected in situ pXRF data

Calculating *in situ* pXRF analytical bias using CRMs is not rec ommended due to the clear disparity between the quality of field sample (wet, coarse, heterogeneous soil) and CRMs (dry, fine and homogeneous soil). Hence, 20 s *in situ* pXRF measurements were corrected at each site using ICP–MS data, provided the relationship

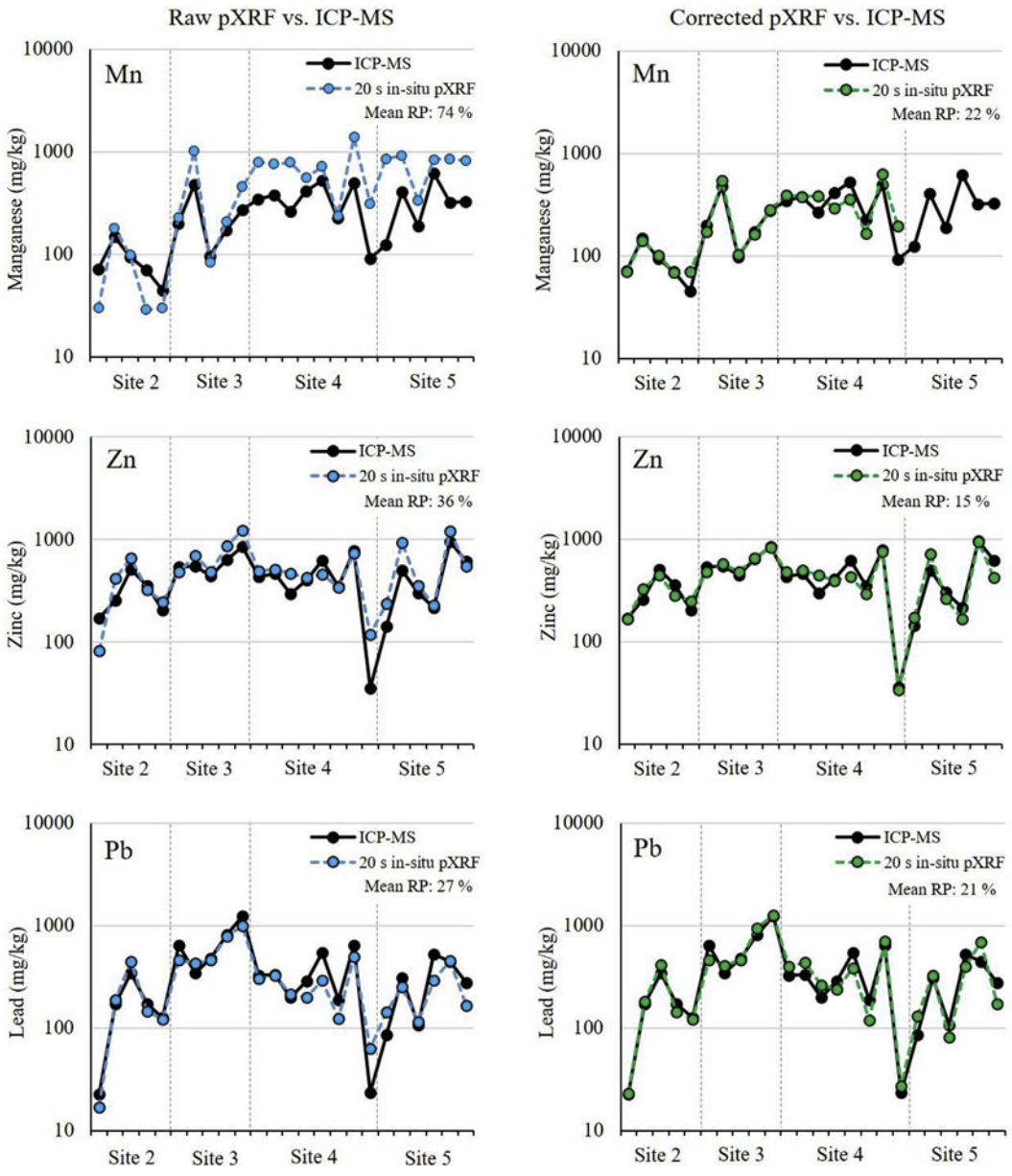


Fig. 1. Point by point graphs of 20 s *in-situ* pXRF measurements against ICP MS data at four metal-contaminated at Sites 2 5. Impact of *in-situ* pXRF data adjustment using ICP MS data is demonstrated between pre- and post-correction rows. Relative proximity (RP) gives an indication of pXRF inaccuracy when compared to a reference value (ICP MS data) and is calculated by RP (absolute (100 recovery value).

between pXRF and ICP–MS measurements were systematic (Regression plots are provided in Supplementary Fig. 3). The moisture content of soil samples were estimated by the commercial laboratory prior to ICP–MS analysis and are presented alongside pre and post correction pXRF data in Supplementary Table 1. Sites 2–5 were comprised largely of a single soil matrix, and achieved strong correlations between the two measurement techniques (Fig. 1). Due to the presence of multiple matrices at Site 1 (silicate based soils and glassy black slag particles), *in situ* pXRF did not generate a systematic relationship with ICP–MS data, and were not corrected. The low number of data correction samples at this site (n 5), combined with the marked small–scale heterogeneity of each sample are likely contributors to the weak correlation. Despite efforts of sampling for ICP–MS analysis from directly under the pXRF measurement window, the issue of mis representation when comparing measurements from different techniques remained. Samples sent for ICP–MS analysis were not homogenised in the field, nor homogenised prior to measurement by the commercial laboratory to reflect standard commercial practice. Homogenisation of these samples would have likely improved comparisons between the analytical techniques.

Relative proximity (RP absolute (100–(pXRF value/ICP–MS value))) is a useful indicator of inaccuracy as it demonstrates the proportional difference away from the reference value (Rouillon and Taylor, 2016). After pXRF data correction, the mean RP improved from 74% to 22% for Mn (Sites 2–4), 36%–15% for Zn and from 27% to 21% for Pb measurements (Fig. 1). *In situ* pXRF Mn measurements were not corrected at Site 5 due to poor, non systematic correlation with ICP–MS measurements (r^2 0.153). The large improvement in Mn RP at Sites 2–4 is likely due to its measurement on a non primary X ray beam (40 kV instead of 15 kV). The poor correlation between raw pXRF and ICP–MS for Mn

concentrations suggest *in situ* pXRF measurement using a primary X ray beam is required to guide judgemental sampling. Raw pXRF measurements of Zn and Pb were not markedly different from ICP–MS values for the majority of samples, justifying their use to guide judgemental sampling. Using ICP–MS data as reference values, mean *in situ* pXRF recoveries were 109% (Mn), 101% (Zn) and 103% (Pb) across Sites 2–5, validating the use of *in situ* pXRF when the data is corrected with laboratory analyses. Moreover, 20 s *in situ* pXRF measurements enabled the inclusion of numerous additional inexpensive on site measurements.

3.2. Sampling and analysis in measurement uncertainty

Contributions towards measurement uncertainty (U_{meas}) were estimated using RANOVA analysis (Supplementary Table 2). Vari ance between field duplicate sets (s_{samp}) reveal soil heterogeneity at sample locations, and the contaminant concentration range that a user may encounter when attempting to locate the sample. Variance between analytical sets (s_{anal}) reveals the imprecision of repeat measurements for a specific analytical method. *In situ* pXRF duplicate analyses were typically more precise than the ICP–MS method across the five sites, largely because ICP–MS analytical duplicates were split prior to sample digestion, rather than at the end of the sample preparation process. Estimated sampling and analytical contributions towards site measurement uncertainties are summarised in Table 2. High sample and site heterogeneity at Site 1 contributed to large measurement uncertainties for all three contaminants assessed. Sampling uncertainty contributed more than 99% of the total measurement uncertainty at Site 1, high lighting the need for an increased sampling resolution at hetero geneous sites (Table 2). Theoretically, increasing the sampling resolution by a factor of n will reduce the sampling uncertainty by $1-(1/\sqrt{n})$ (Gy, 1979). However in practice this was not always achieved, *in situ* pXRF measurements (n 30) were five times the sampling resolution of *ex situ* ICP–MS measurements (n 6) for Site 1, yet uncertainties still remained high. Probable explanations include the contaminant distribution was not uniformly hetero geneous across the site and/or because *in situ* pXRF duplicate sampling occurred at more heterogeneous areas.

Sampling (U_{samp}) was the primary contributor to measurement uncertainty at the other four sites, regardless of measurement approach (Table 2). Despite the application of consistent duplicate sampling approaches, estimated measurement uncertainties varied considerably between the two techniques (e.g. U_{meas} for Site 5 Pb: ICP–MS–31.6%, pXRF–103%). Duplicate sampling was not system atically distributed across each site, but were selected randomly prior to visiting each site. Given the heterogeneity of soil contam ination at the sites, it is possible that this could have skewed un certainty estimates, particularly where by chance, selected samples were grouped in an unrepresentative area of the site. Further, the low number of duplicate samples (10–15%, n $\geq$ 3) used for esti mating measurement uncertainty at each site may not have been sufficient. Boon and Ramsey (2010, 2012) used a minimum of eight duplicate samples for estimating measurement uncertainty, how ever such a protocol was difficult to apply when the minimum regulatory sampling requirement for a 0.1 ha site is only six samples (NSW EPA, 1995).

3.3. Advantages of increased sampling

Increased site sampling has several benefits including: genera tion of more representative site data, a better understanding of contaminant distribution, reducing the probability of missing contaminant hot spots, increased confidence of site mean report ing, and a reduction in sampling uncertainty (Gy, 1979) (Fig. 2). Increased sampling was undertaken using *in situ* pXRF to assess these benefits and its impact on site decision making. For example, soil Pb concentrations at Site 2 are compared using the minimum sampling resolution specified in Table 1 for both measurement approaches (i.e. a 0.6 ha area with 15 samples for ICP–MS as per the NSW EPA (1995) guideline vs. 30 pXRF samples) (Fig. 3). Both measurement approaches generated similar soil Pb maps, with higher soil Pb concentrations found towards the south west (SW) side of the site (Fig. 3). Increased sampling by *in situ* pXRF identi fied the same proportion (20%) of samples over the relevant health investigation level (HIL) of 300 mg/kg as the ICP–MS approach, but at twice the resolution, increasing the confidence that this was a true estimate. Real time pXRF data enabled efficient judgemental sampling around samples with soil Pb concentrations >300 mg/kg (Fig. 3). These additional data were critical for revealing the extent of higher Pb concentrations towards the SW edge of the site. *In situ* pXRF has the clear benefits of enabling the investigator to make informed decisions with respect to the need for additional judge mental sampling, without the need to return to the site, potentially saving both time and costs when compared to *ex situ* sampling approaches.

Table 2
Summary of sampling, analytical and measurement uncertainties (%) of soil Mn, Zn and Pb concentrations at five metal-contaminated sites. Both *ex-situ* ICP MS and *in-situ* pXRF measurement approaches are presented. Values in **bold** represent >95% variance contribution towards measurement uncertainties. Values with an asterisk (*) represent uncorrected *in-situ* pXRF data.

	ICP MS				pXRF			
		Sampling	Analysis	Measurement		Sampling	Analysis	Measurement
Mn	Site 1	**221**	16.4	222	Site 1	*__248__	*8.4	*249
	Site 2	15.4	11.4	19.2	Site 2	19.3	5.1	20.0
	Site 3	6.5	14.1	15.5	Site 3	49.6	16.7	52.3
	Site 4	51.4	17.3	54.2	Site 4	**63.0**	8.9	63.6
	Site 5	42.3	13.0	44.3	Site 5	*54.3	*15.9	*56.6
Zn	Site 1	**221**	9.4	221	Site 1	*__190__	*5.6	*190
	Site 2	2.3	**8.4**	8.7	Site 2	**36.1**	4.1	36.3
	Site 3	15.1	8.4	17.3	Site 3	19.6	6.1	20.5
	Site 4	**51.4**	9.7	52.3	Site 4	53.8	16.8	56.4
	Site 5	**65.9**	11.1	66.8	Site 5	**59.0**	10.1	59.8
Pb	Site 1	**178**	9.7	179	Site 1	*__190__	*5.4	*190
	Site 2	**65.0**	13.1	66.3	Site 2	**102**	2.9	102
	Site 3	21.6	14.4	25.9	Site 3	72.1	22.2	75.4
	Site 4	66.1	17.1	68.3	Site 4	**58.3**	5.8	58.6
	Site 5	28.4	13.7	31.6	Site 5	**102**	10.5	103

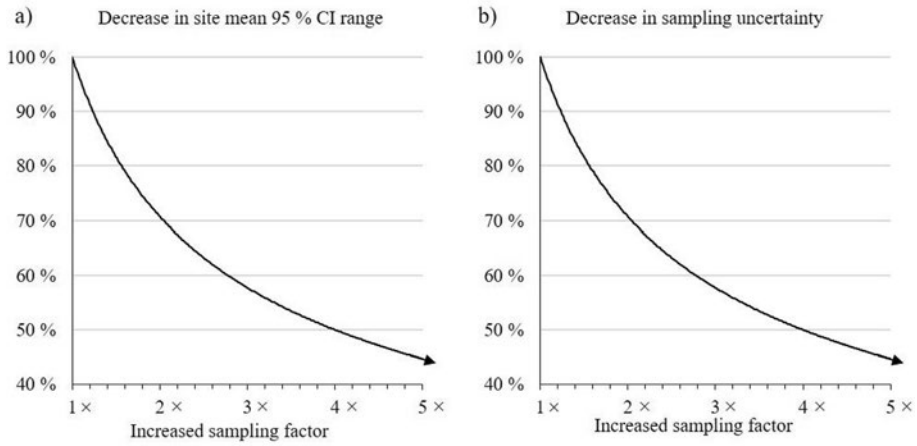


Fig. 2. Impact of increased sampling on both the a) 95% confidence interval around a site mean, and b) sampling uncertainty. Assuming site mean and standard deviation remain constant, an increase in sampling by a factor of 3 (i.e. from 20 to 60 samples) reduces the confidence interval range and sampling uncertainty by 1 $(1/\sqrt{3})$ 42%. Reduction of sampling uncertainty from increased sampling was adapted from Gy (1979).

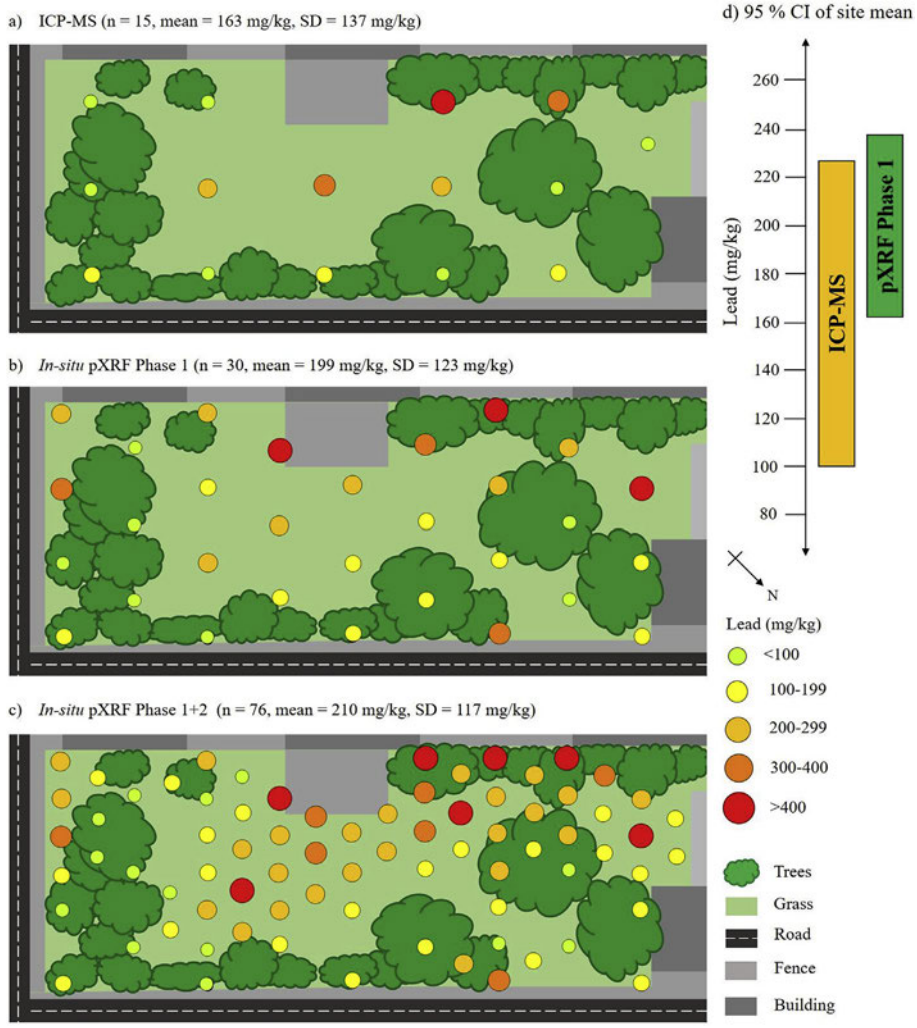


Fig. 3. Systematic spatial distribution of soil lead concentrations at Site 2 for a) ICP MS measurements (n 15) and b) *in-situ* pXRF Phase 1 measurements (n 30). c) Real time pXRF data (Phase 1 + 2) enabled efficient judgemental sampling directly after *in-situ* pXRF Phase 1. d) Uncertainty (95% CI) on the site mean is compared for ICP MS and *in-situ* pXRF Phase 1 measurement approaches.

In NSW the duty to notify contamination under the *Contaminated Land Management Act 1997* (NSW), is required where the upper confidence limit (95% CI) of a site mean is equal to, or exceeds the relevant HIL for the respective land use (NSW EPA, 2015). The 95% CI of a site mean is calculated using four variables: mean, student's t statistic, standard deviation and the number of samples:

$$CI \quad \mu \pm t\ (\sigma/\sqrt{n})$$

where CI confidence interval, μ arithmetic mean, t student's t statistic (level of significance and n−1 degrees of freedom), σ standard deviation and n number of samples. For sites with a coefficient of variation >1.2, refer to Procedure G of NSW EPA (1995). Coefficient of variation is the ratio of the standard deviation against the mean, and is calculated as CV $(\sigma/\mu) \times 100$.

Assuming the mean and standard deviation of a site remain constant, increasing the number of samples by a factor of n should theoretically reduce the 95% CI range by $1-(1/\sqrt{n})$. To demonstrate this, the minimum sampling resolution for ICP−MS (n 15) and *in situ* pXRF (n 30) approaches are compared at Site 2 (Fig. 3). Sampling was increased by a factor of two, hence the anticipated decrease in site mean CI range was $1-(1/\sqrt{2})$ 29%. The mean CI range of ICP−MS and *in situ* pXRF approaches were 124 mg/kg and 77 mg/kg Pb, respectively, resulting in a decrease of the site CI range by 38% (Fig. 3). The two measurement approaches resulted in similar UCL values of 225 mg/kg (ICP−MS) and 238 mg/kg (pXRF), both less than the soil Pb HIL guideline of 300 mg/kg. The second notification trigger (an individual soil sample being equal to or greater than 250% of the relevant HIL guideline) was also not met, with maximum Pb concentrations of 472 mg/kg and 493 mg/kg for ICP−MS and pXRF approaches respectively, meaning that in this case, neither approach was sufficient to trigger the duty to report.

Calculation of the UCL with low sample numbers expands the 95% confidence interval, and may erroneously extend the UCL above a HIL guideline. Subsequently, this may lead to a false positive i.e. a decision that the site should undergo further investigation (NEPM, 2013) and/or remediation. Misclassification of sites is more likely to occur where site assessments rely on small sample numbers because they fail to accurately represent the real site mean. Thus, small sample numbers can result in higher sampling uncertainty and consequently, a reduced confidence end users may have in reporting the site mean (Fig. 2). Alternatively, site assessments with high sample numbers reduce sample uncertainty and consequently reduce the likelihood of site misclassification due to increased confidence in reporting a site mean. For example, a 50% reduction in sampling uncertainty and site mean confidence range requires a four fold increase in sampling resolution (Fig. 2). This can prove costly using the current approach of *ex situ* sampling and wet chemistry analyses because a large percentage of costs relates to laboratory fees. Yet ultimately, improvements to site characterisation do not relate to the selection of analytical technique (ICP−MS or pXRF), but rather is primarily impacted by the number of samples collected.

3.4. Cost effectiveness of in situ pXRF site assessments

Increased sampling involves extra costs regardless of the analytical technique due to field labour and analytical costs. Yet, unlike wet chemistry analyses, *in situ* pXRF has practically no analytical costs in terms of instrument operation or field consumables. The primary costs of *in situ* pXRF relate to field labour and analysis of a subset of samples by a commercial laboratory using ICP−MS. The total costs involved for both *in situ* pXRF and *ex situ* sampling and ICP−MS analysis for the minimum sampling (Table 1) of metal contaminated sites were estimated using assumptions of individual costs (Fig. 4). Variables include field labour (AU$150/hour), commercial ICP−MS analysis (AU$22.60/sample), time between samples and for *ex situ* soil sampling (45 s/sample), time for *in situ* pXRF measurements (20 s/sample), time and costs for parallel sampling for *in situ* pXRF data correction and ownership of an environmental pXRF unit (AU$83/site). Field portable XRF ownership cost (AU$40,000) was split over the mean lifetime of a pXRF (7 years), under the assumption that it is utilised for a site assessment twice every working week. Total cost estimations do not include duplicate sampling and analysis, which would vary based on the number of duplicates taken.

In situ pXRF assessment of metal contaminated sites were more cost efficient, even with increased sampling, than the current approach of *ex situ* sampling and ICP−MS analysis (Fig. 4). Sampling resolution of both systematic and judgemental *in situ* pXRF phases were greater than the minimum sampling requirements for the ICP−MS approach (Table 1), and subsequently generated more information per site. This explains why *in situ* pXRF Phase 1 (n 30) and 1 + 2 (n 64) at the smallest site (Site 1) were more expensive than the ICP−MS approach (n 6). Both measurement approaches are compared for soil Zn concentrations and overall costs at Site 4 (Fig. 4, Supplementary Fig. 4). Real time *in situ* pXRF data identified slightly higher metal concentrations at the oval border, which guided further same day judgemental sampling towards street corners. When compared to *ex situ* sampling and ICP−MS analysis, *in situ* pXRF provided more than twice (2.3 times) as many site measurements for Site 4 at approximately half the cost (AU$466 vs. AU$880) (Fig. 4).

It is also possible to utilise the savings accrued using a pXRF for site assessment costs towards reducing uncertainties. For example, for the same cost as the ICP−MS approach at Site 4 (AU$880), the application of *in situ* pXRF will enable systematic assessment at >4.5 times the resolution (165 vs. 36 samples), reducing both sampling and site mean uncertainty by >50% (Fig. 2). This is important as sampling typically contributes the greatest error towards measurement uncertainty (see Section 3.2). Through

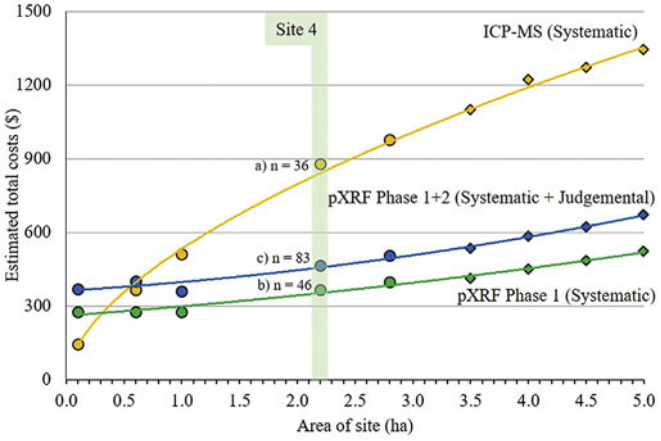


Fig. 4. Estimated total costs for the characterisation of metal-contaminated sites at the minimum sampling resolution for ICP MS and *in-situ* pXRF. Cost assumptions include: labour call out rate $150/hour, *in-situ* pXRF measurement 20 s, pXRF ownership cost $83/assessment, time between samples 45 s, commercial laboratory eight element analysis $22.60/sample. The cost of duplicate sampling to establish measurement uncertainty was not included given that this would vary according to the number of duplicate samples being taken. Circles are estimated costs from the five-metal contaminated sites in this study, while diamonds are projected costs for sites larger than 3 ha. The number of samples used to characterise Zn concentrations at Site 4 are shown for a) the ICP MS approach (n 36), b) pXRF Phase 1 (n 46), and c) pXRF Phase 1 + 2 (n 83).

increased sampling achieved by applying a cheaper, but ultimately equally reliable analytical technique, large measurement uncertainties associated with field heterogeneity can be more adequately addressed.

3.5. Shift towards probabilistic classification of sites

The current approach of metal contaminated site characterisation compares soil metal concentrations to the relevant HIL guidelines (NSW EPA, 2015), under the notion that individual measurements are correct. Every measurement is incorrect to some extent due to uncertainty contributions from both field sampling and analysis (Boon and Ramsey, 2010). In cases where field and analytical duplicates are taken, measurement variation is typically presented separately from the primary findings in a Quality Assurance/Quality Control section. Given the typically heterogeneous nature of metal contaminated sites, this variation should ideally be presented as a part of the primary findings to reduce the risk of site misclassification.

Integration of measurement uncertainty into site reporting, also known as probabilistic classification, was first suggested by Ramsey and Argyraki (1997). Probabilistic classification includes the estimated measurement uncertainty (%) of a site and places it around each sample concentration, enabling the investigator to report with 95% confidence that a sample falls within a concentration range (Boon and Ramsey, 2010). This concentration range (C) is then compared to the relevant guideline (G), and placed in one of four categories:

- Definitely under guideline – Probability of C > G (<2.5%)
- Possibly over guideline – Probability of C > G (2.5–50%)
- Probably over guideline – Probability of C > G (50–97.5%)
- Definitely over guideline – Probability of C > G (>97.5%)

To illustrate this probabilistic approach, soil Pb concentrations from Site 4 were plotted in increasing order with and without the estimated measurement uncertainty of 58.6% (Fig. 5). A deterministic (non uncertainty) approach identified 72% of samples below the HIL guideline of 600 mg/kg Pb for public open spaces such as sporting fields (NEPM, 2013). The application of a probabilistic approach identifies uncertainties around each measurement and classifies samples based on the probability they exceed the guideline value. Only 47% of samples had measurement uncertainty ranges below the guideline, which signifies to the investigator a >97.5% probability these samples do not exceed the guideline (Fig. 5). Comparatively, a larger proportion of samples exceeded the guideline using the current approach (28%) than a probabilistic approach (5%), due to the exclusion of field and analytical variation. Clearly, this might lead to a false positive scenario, i.e. a decision that determines a site is contaminated to the extent that it warrants remediation.

Reducing the risk of both site and sample misclassification is perhaps the most important advantage of a probabilistic approach (Boon and Ramsey, 2010). Conversely, it also increases the proportion of samples that are 'possibly' or 'probably' over a guideline. This knowledge gap can be addressed through increased sampling to reduce the estimated measurement uncertainty of a site, which would in turn reduce the uncertainty range around each sample. The confidence level of reporting (i.e. 90, 95 or 99%) and classification categories (e.g. definitely over guideline) can also be modified for specific data quality objectives. Nevertheless, probabilistic reporting of metal contaminated sites demonstrates that the investigator understands the true variation of measurements at a site, and can tailor their findings accordingly. This enables investigators to make more robust decisions by lowering the risk of site misclassification.

4. Potential limitations of *in-situ* pXRF

1) This study evaluated *in situ* pXRF measurements directly on wet, unprepared soils. Moisture content can impact the accuracy of pXRF measurements, particularly on elements with low

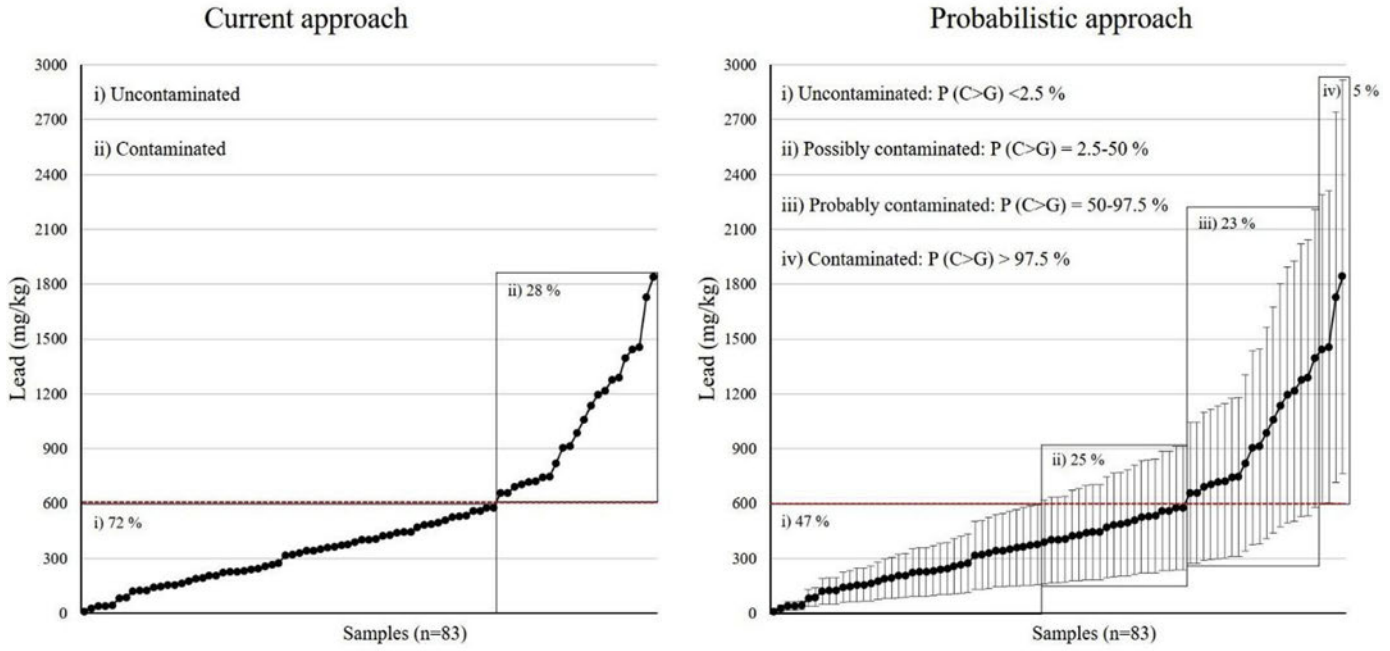


Fig. 5. Comparison between the current approach and probabilistic *in-situ* pXRF approach to metal-contaminated soil classification for Pb concentrations at Site 4. Measurement uncertainty was estimated to be 58.6% (Table 2), and represents the error bars around each sample. The Australian health investigation level (HIL C) for sports fields is 600 mg/kg for Pb and is represented by the dotted red line. P Probability of, C concentration of sample, G guideline.

atomic numbers (Bastos et al., 2012). Estimated moisture con tent (%) was used from the subset of ICP–MS measurements at each site to adjust the wet chemistry data to an 'as received' basis (Weindorf et al., 2012). This was done to compare and correct accurately for any analytical bias between the two measurement techniques, and to represent actual exposures that could potentially be experienced by an organism (Ramsey and Boon, 2012).

2) Environmental investigations measure surface and subsurface soils to ascertain the distribution of contaminants across a site and down the soil profile. This study did not investigate sub surface soil metal concentrations, yet measurements of auger soils could be expedited using similar *in situ* pXRF protocols. Although further research is required to ascertain if *in situ* pXRF can be applied to subsurface soils, there is no clear technical barrier for that to not be the case.
3) *In situ* pXRF data at Site 1 did not correlate strongly with ICP–MS data due to the presence of multiple matrices in the soil (silicate based soils and glassy black slag particles). As a result, these samples were subject to light sample preparation steps, including drying and gently crushing using a mortar and pestle, and were re measured by pXRF through a polyethylene bag. As expected, correlation with ICP–MS data improved significantly (Supplementary Figures 3 and 5) suggesting some sample preparation may be required when multiple matrices are pre sent on site.
4) An important limitation of the application of *in situ* pXRF is that it can only be addressing inorganic contamination. By compar ison, *ex situ* analysis of soils allows for samples to be split and subject to a variety of metal and non metal contaminants such as hydrocarbons, organics and persistent chemicals, which are also common co contaminants at sites. It is possible that future developments to pXRF may be capable of non metal contami nant screening via add on accessories. For example, *in situ* soil screening of total petroleum hydrocarbons (CSIRO, 2012) and asbestos (Thermo Scientific, 2011) exist, however these are measured using separate analysers.

5. Conclusions and recommendations

In situ pXRF was demonstrated to be a powerful and cost effective tool for metal contaminated site assessments when complemented with ICP–MS data. Twenty second *in situ* pXRF measurements were corrected using parallel ICP–MS data, allow ing for accurate, rapid and inexpensive high resolution sampling. Field and analytical duplicates revealed sampling as the primary contributor to high measurement uncertainties, regardless of analytical technique. Increased sampling generated more repre sentative site data, higher resolution contaminant mapping, increased confidence in reporting site means and decreased un certainty related to sampling. Real time pXRF data also has the clear benefit over *ex situ* ICP–MS analysis by enabling effective judge mental sampling for detecting contaminant hot spots. The *in situ* pXRF assessment method proposed here was also usually more cost efficient than the current approach of *ex situ* sampling and ICP–MS analysis, despite increased sampling by pXRF. Finally, integrating measurement uncertainty into site reporting data can lower the risk of site misclassification.

Every analytical technique have advantages and disadvantages associated with their application. This study targeted the advan tages of *in situ* pXRF, while simultaneously addressing the short falls of its use. Understanding the analytical capabilities and limitations of *in situ* pXRF allowed for effective and reliable assessment of metal contaminated sites. However, further work is required to demonstrate if other environmentally significant con taminants (e.g. nickel, arsenic and mercury) can be assessed using the methods described in this paper. The proposed *in situ* pXRF method is a cost effective alternative to wet chemistry analysis, capable of lowering misclassification risks and generating higher confidence in site data when compared to the data from the current regulatory practice in NSW, Australia. Supplementing slower and more expensive analytical methods (ICP–MS) with a rapid and cheaper analytical technique (pXRF) should be considered for metal contaminated site assessments in other regulatory jurisdic tions in Australia and around the world. This is particularly relevant where high soil metal heterogeneity requires the use of many samples for site characterisation.

Acknowledgements

The authors thank Olympus Australia and the National Mea surement Institute for contributing funding towards this research. For technical support and discussions, we thank Sam Habib, Andrew Taylor and Jake Jarvinen (Olympus Australia), Andrew Evans and Shiva Prasad (National Measurement Institute) and Paul Harvey, Peyton Lisenby and Rory Williams (Macquarie University). Marek Rouillon is funded by an Australian Physiotherapy Associa tion. Chenyin Dong is funded by an International Macquarie Uni versity Research Excellence Scholarship (iMQRES No. 2014098).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.06.020.

References

Argyraki, A., Ramsey, M.H., Potts, P.J., 1997. Evaluation of portable x-ray fluorescence instrumentation for in situ measurements of lead on contaminated land. Ana- lyst 122, 743 749.
Bastos, R.O., Melquiades, F.L., Biasi, G.E., 2012. Correction for the effect of soil moisture on in situ XRF analysis using low-energy background. X-ray Spectrom. 41, 304 307.
Batley, G., 1992. Investigation report CET/LHIR077. Leachability of lead and other trace metals from lead-zinc smelter slag. Commonw. Sci. Industrial Res. Organ. Div. Coal Energy Technol. Centre Adv. Anal. Chem. 1 10.
Bernick, M.D., Kalnicky, D.J., Prince, G., Singhvi, R., 1995. Results of field-portable X- ray fluorescence analysis of metal contaminants in soil and sediment. J. Hazard. Mater. 43, 101 110.
Boon, K.A., Ramsey, M.H., 2010. Uncertainty of measurement or of mean value for the reliable classification of contaminated land. Sci. Total Environ. 409, 423 429.
Boon, K.A., Ramsey, M.H., 2012. Judging the fitness of on-site measurements by their uncertainty, including contribution from sampling. Sci. Total Environ. 419, 196 207.
Bosco, G.L., 2013. James L. Waters Symposium 2012 Report. Development and application of portable, hand-held X-ray fluorescence spectrometers. Trends Anal. Chem. 45, 121 134.
Brevik, E.C., 2013. Soils and human health: an overview. In: Brevik, E.C., Burgess, L.C. (Eds.), Soils and Human Health. CRC Press, Boca Raton, pp. 59 82.
Carr, R., Zhang, C., Moles, N., Harder, M., 2008. Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. Environ. Geochem. Health 30, 45 52.
Clark, S., Menrath, W., Chen, M., Roda, S., Succop, P., 1999. Use of a field portable X- ray fluorescence analyzer to determine the concentration of led and other metals in soil samples. Ann. Agric. Environ. Med. 6, 27 32.
Commonwealth Scientific and Industrial Research Organisation (CSIRO), 2012. Portable Device Detects Soil Contamination. News. Ziltek. http://www.ziltek.com.au/pdf/CSIRO%20News%20Release%20-%20Portable%20device%20detects%20soil%20contamination.pdf (accessed 21 March 2017).
Dong, C., Taylor, M.P., Kristensen, L.J., Zahran, S., 2015. Environmental contamination in an Australian mining community and potential influences on early childhood health and behavioural outcomes. Environ. Pollut. 207, 345 356.
Gy, P., 1979. Sampling of Particulate Materials Theory and Practice. Elsevier, Amsterdam, pp. 1 450.
Harvey, P.J., Taylor, M.P., Kristensen, L.J., Grant-Vest, S., Rouillon, M., Wu, L., Handley, H.K., 2016. Evaluation and assessment of the efficacy of an abatement strategy in a former lead smelter community, Boolaroo, Australia. Environ. Geochem. Health 38 (4), 941 954.

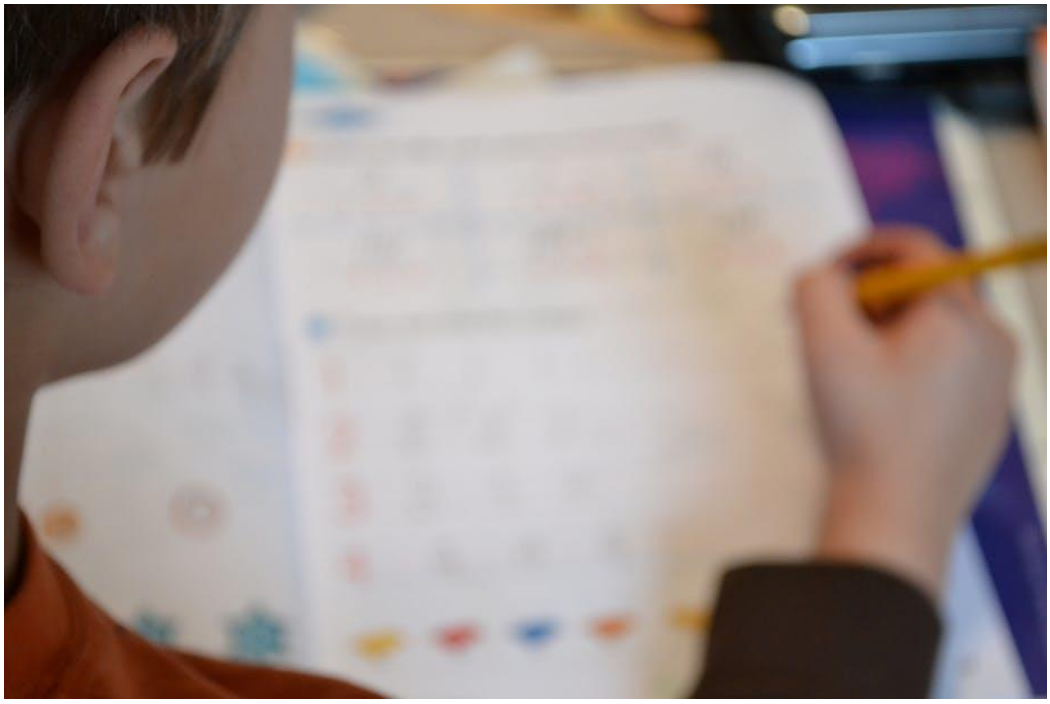
Higueras, P., Oyarzun, R., Iraizoz, J.M., Lorenzo, S., Esbri, J.M., Martinez-Coronado, A., 2012. Low-cost geochemical surveys for environmental studies in developing countries: testing a field portable XRF instrument under quasi-realistic conditions. J. Geochem. Explor. 113, 3 12.
Horta, A., Malone, B., Stockmann, U., Minasny, B., Bishop, T.F.A., McBratney, A.B., Pallasser, R., Pozza, L., 2015. Potential integrated field spectroscopy and spatial analysis for enhanced assessment of soil contamination: a prospective review. Geoderma 241 242, 180 209.
Kalnicky, D.J., Singhvi, R., 2001. Field portable XRF analysis of environmental samples. J. Hazard. Mater. 93 122.
Kristensen, L., 2015. Quantification of atmospheric lead emissions from 70 years of leaded petrol consumption in Australia. Atmos. Environ. 111, 195 201.
Kristensen, L.J., Taylor, M.P., 2016. Unravelling a 'miner's myth' that environmental contamination in mining towns is naturally occurring. Environ. Geochem. Health 38 (4), 1015 1027.
Melquiades, F.L., Appoloni, C.R., 2004. Application of XRF and field portable XRF for environmental analysis. J. Radioanalytical Nucl. Chem. 262 (2), 533 541.
Morrison, A.L., Gulson, B.L., 2007. Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. Sci. Total Environ. 382, 30 42.
National Measurement Institute (NMI), 2014. Method NT2.49: Determination of Acid Extractable Elements in Soils, Sediments, Sludges and Solid Waste. Inorganic Section. National Measurement Institute, Sydney.
National Environmental Protection Measure (NEPM), 2013. Schedule B1: Guideline on Investigation for Soil and Groundwater, p. 57. Available at: http://www.scew.gov.au/system/files/resources/93ae0e77-e697-e494-656f-afaaf9fb4277/files/schedule-b1-guideline-investigation-levels-soil-and-groundwater-sep10.pdf (accessed 29 January 2017).
New South Wales Environmental Protection Authority (NSW EPA), 1995. Sampling Design Guidelines. Contaminated Sites. http://www.epa.nsw.gov.au/resources/clm/95059sampgdlne.pdf (accessed 02 March 2017).
New South Wales Environmental Protection Authority (NSW EPA), 2015. Guidelines on the Duty to Report Contamination under the Contaminated Land Management Act 1997. http://www.epa.nsw.gov.au/resources/clm/150164-report-land-contamination-guidelines.pdf (accessed 04 March 2017).
Parsons, C., Grabulosa, E.M., Pili, E., Floor, G.H., Roman-Ross, G., Charlet, L., 2013. Quantification of trace arsenic in soils by field-portable X-ray fluorescence spectrometry: considerations for sample preparation and measurement conditions. J. Hazard. Mater. 262, 1213 1222.
Paulette, L., Man, T., Weindorf, D.C., Person, T., 2015. Rapid assessment of soil and contaminant variability via portable X-ray fluorescence spectroscopy: copsa Mica Romania. Geoderma 243 244, 130 140.
Peinado, F.M., Ruano, S.M., Gonzalez, M.G.B., Molina, C.E., 2010. A rapid field procedure for screening trace elements in polluted soil using portable X-ray fluorescence (PXRF). Geoderma 190, 76 82.
Radu, T., Gallagher, S., Byrne, B., Harris, P., Coveney, S., McCarron, S., McCarthy, T., Diamond, D., 2013. Portable x-ray fluorescence as a rapid technique for surveying elemental distributions in soil. Spectrosc. Lett. Int. J. Rapid Commun. 46 (7), 516 526.
Ramsey, M.H., Argyraki, A., 1997. Estimation of measurement uncertainty from field sampling: implications for the classification of contaminated land. Sci. Total Environ. 198, 243 257.
Ramsey, M.H., Boon, K.A., 2012. Can *in situ* geochemical measurements be more fit-for-purpose than those made *ex situ*? Appl. Geochem. 27, 969 976.
Eurachem, Eurolab, Citac, Nordtest, AMC Guide. In: Ramsey, M.H., Ellison, S.L.R. (Eds.), 2007. Measurement Uncertainty Arising from Sampling: a Guide to Methods and Approaches, ISBN 978 0 948926 26 6, pp. 1 103.
Ramsey, M.H., Thompson, M., Hale, M., 1992. Objective evaluation of precision requirements for geochemical analysis using robust analysis of variance. J. Geochem. Explor. 44, 23 36.
Ramsey, M.H., Taylor, P.D., Lee, J., 2002. Optimized contaminated land investigation at minimum overall cost to achieve fitness-for-purpose. J. Environ. Monit. 4, 809 814.
Ran, J., Wang, D., Wang, C., Zhang, G., Yao, L., 2014. Using portable X-ray fluorescence spectrometry and GIS to assess environmental risk and identify sources of trace metals in soils of peri-urban areas in the Yangtze Delta region, China. Environ. Sci. Process. Impacts 16, 1870 1877.
Rouillon, M., Taylor, M.P., 2016. Can field portable X-ray Fluorescence (pXRF) produce high quality data for application in environmental contamination research? Environ. Pollut. 214, 255 264.
Rouillon, M., Kristensen, L.J., Gore, D.B., 2015. Handheld x-ray fluorescence spectrometers: radiation exposure risks of matrix-specific measurement scenarios. Appl. Spectrosc. 69 (7), 815 822.
Rouillon, M., Harvey, P., Kristensen, L., George, S., Taylor, M.P., 2017. VegeSafe: a community science program measuring soil-metal contamination, evaluating risk and providing advice for safe gardening. Environ. Pollut. 222, 557 566.
Student, 1908. Probable error of a correlation coefficient. Biometrika 6 (2 3), 302 310.
Taylor, P.D., Ramsey, M.H., Potts, P.J., 2004. Balancing measurement uncertainty against financial benefits: comparison of in situ and ex situ analysis of contaminated land. Environ. Sci. Technol. 38, 6824 6831.
Taylor, P.D., Ramsey, M.H., Potts, P.J., 2005. Spatial contaminant heterogeneity: quantification with scale of measurement at contrasting sites. J. Environ. Monit. 7, 1364 1370.
Thermo Scientific, 2011. Thermo Scientific MicroPHAZIR AS, Handheld Asbestos Analyzer. Product Specification. https://www.thermofisher.com.au/Uploads/file/Environmental-Industrial/Environmental-Monitoring-Safety/Industrial-Hygiene-Instruments/MicroPhazir-Asbestos-Analyser-TFS.pdf (accessed 21 March 2017).
United States Environmental Protection Agency (US EPA), 2002. Calculating Upper Confidence Limits for Exposure Point Concentrations at Hazardous Waste Sites. United States Environmental Protection Agency, Washington, D.C, pp. 1 32.
Vacca, A., Bianco, M.R., Murolo, M., Violante, P., 2012. Heavy metals in contaminated soils of the Rio Sitzerri floodplain (Sardinia, Italy): characterisation and impact of pedodiversity. Land Degrad. Dev. 23, 350 364.
Vanhoof, C., Corthouts, V., Tirez, K., 2004. Energy-dispersive X-ray fluorescence systems as analytical tool for assessment of contaminated soils. J. Environ. Monit. 6, 344 350.
Weindorf, D.C., Zhu, Y., Chakraborty, S., Bakr, N., Huang, B., 2012. Use of portable X-ray fluorescence spectrometry for environmental quality assessment of peri-urban agriculture. Environ. Monit. Assess. 184, 217 227.
Weindorf, D.C., Paulette, L., Man, T., 2013. In-situ assessment of metal contamination via portable X-ray fluorescence spectroscopy: zlatna, Romania. Environ. Pollut. 182, 92 100.
Weindorf, D.C., Bakr, N., Zhu, Y., 2014. Chapter one: advances in portable x-ray fluorescence (pXRF) for environmental, pedological, and agronomic applications. Adv. Agron. 128, 1 45.

Appendix B

The Conversation

Australian children exposed to toxic mining metals do worse at school

Taylor, M. P., **Dong, C.,** Kristensen, L., Zahran, S.



Children living closest to the mines had the lowest literacy and numeracy scores. Katherine Clark/Flickr, CC BY-NC-ND

Children in mining and smelting towns who are exposed high levels of lead, arsenic and cadmium are more than twice as likely to have developmental disorders than the national average. They also perform lower than neighbouring peers on school tests, our research, published today in the journal Environmental Pollution, reveals.

Children living closest to Broken Hill's lead and zinc mine who had the highest levels of exposure to toxic air, dust and soils consistently had the lowest literacy and numeracy scores in years three and five. We found similar results in Australia's two other major lead mining and smelting cities: Mount Isa and Port Pirie.

Exposure to lead and other toxic metals during early childhood can harm the growing brain. Progress is now being made to reduce exposure in the three mining towns. But for children already exposed, the damage cannot be reversed.

Long-known harms

Broken Hill in western New South Wales, has been home to continuous lead mining since 1884. One of the first reports suggesting that ore extraction and processing (including smelting in the early days) caused poisoning was published in 1893.

A systematic, annual program of testing children's blood lead showed a generally decreasing level between 1991 and 2009. However, after 2010 the trend was reversed. By 2014, one in five children exceeded the already too-high blood-lead goal of ten micrograms per decilitre (10 μg/dL). Levels above this value were investigated.

While some of the apparent rise in children with high blood levels may be due to greater participation in NSW Health's annual monitoring, the result clearly reflects the persistence and pervasiveness of the environmental lead exposure problem in the city.

In May 2015, the National Health and Medical Research Council (NHMRC) lowered the childhood blood lead intervention level from ten to five micrograms per decilitre. This reflects the global view that there is no minimum safe level of exposure.

This new guideline means around 50% of children under five years old in Broken Hill have a blood lead in excess of the new intervention value. A similar percentage of children in Port Pirie and Mount Isa are also affected. These children are at risk of permanent damage to the brain.

Indigenous children typically have higher blood lead exposures than Caucasian children so are at greater risk.

How does lead affect the brain?

Lead is a neurotoxin, which means that when it is absorbed, inhaled or ingested, it can affect the development of the child's nervous system.

The effects of lead exposure are greatest in unborn children and those aged under five years. This is because their growing nervous and skeletal systems require high levels of calcium to develop and function properly. Lead (Pb^{2+}) mimics calcium (Ca^{2+}), so children living in a lead-rich environments are at risk of absorbing lead in place of calcium.

Previous research focused only on lead exposure in Broken Hill, but our recent research revealed that other trace metals and metalloids were also abundant in easily accessible dust

deposits in children's playgrounds. Of these, arsenic and cadmium cause similar neurological, developmental and other health problems.

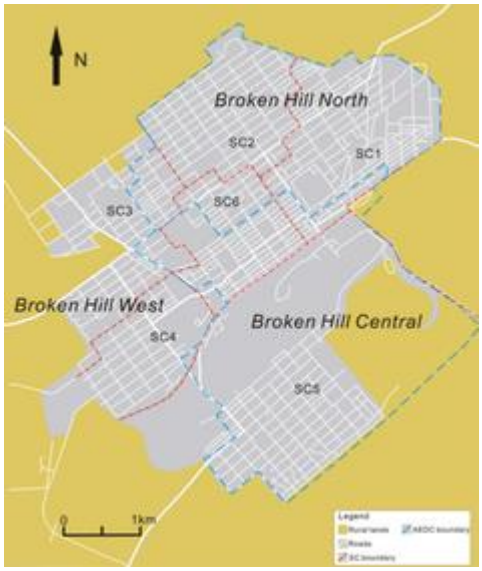
Impact on school performance

Our latest research examined arsenic, cadmium and lead in aerosols, dusts and surface soils in Broken Hill and their impact on children's behaviour and educational performance.

We used the publicly available National Assessment Program – Literacy and Numeracy (NAPLAN) and Australian Early Development Census (AEDC) data for Broken Hill children. NAPLAN evaluates children in years three, five, seven and nine for reading, narrative writing, spelling, grammar and punctuation and numeracy. AEDC assesses children in their first year of school for their physical health and well-being, social competence, emotional maturity, language and cognitive skills, communication skills and general knowledge.

We focused our analysis on primary school children and assumed they attended the school in their catchment. We took into account that the city's Catholic schools draw children from across Broken Hill but excluded children who reside on remote sheep or cattle stations. We also took into account differences in socioeconomic status.

What did we find?

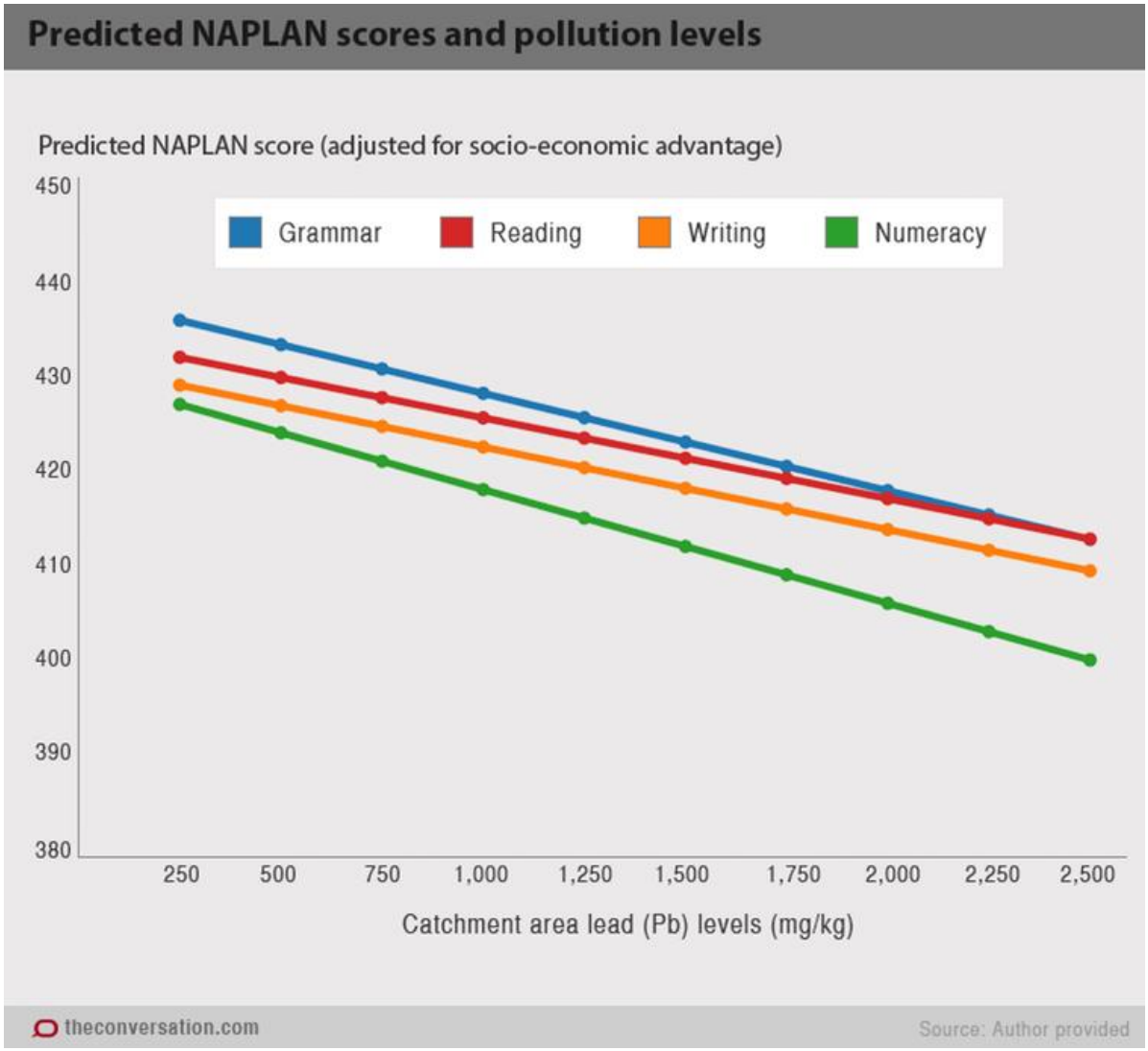


Blue lines: AEDC local communities; red lines: primary school catchment areas. Dong. C. et al. 2015. Environmental Pollution.

Children from school catchment five (SC5) had the highest levels of contamination and the worst NAPLAN and AEDC outcomes. Children in school catchment three (SC3) – which had the lowest soil arsenic, cadmium and lead concentrations – performed better (see below).

Children from Broken Hill central area (encompassing school catchments five and six) – the area with the highest environmental contamination – were 2.6 times more likely to have vulnerabilities in two or more of the AEDC developmental areas.

This graph shows the modelled relations between soil lead levels in Broken Hill and NAPLAN scores.



Predicted NAPLAN school scores (adjusted for socioeconomic advantage) versus soil levels.

The relationship is similar for arsenic and cadmium: NAPLAN scores decrease with increasing soil metal values.

The difference between children attending schools in areas with the maximum soil lead risks compared to the lower soil lead risk is a loss of 20 NAPLAN points (or about 5%). After adjusting for socioeconomic disadvantage, the difference is around 60 points (or about 14%).

We found a similar phenomenon in Australia's other two main smelting and mining communities of Port Pirie and Mount Isa. These impacts are consistent with other similar studies in the United States and a recent study of Port Pirie and Broken Hill children.

Reducing exposure

Industry and government must ensure blood lead levels are as low as possible and that all modifiable toxic exposures are prevented. And they're making some progress.

At Broken Hill, the New South Wales Government announced in February funded a five-year A$13 million program to address the issue of lead contamination and elevated blood lead levels among local children.

In South Australia, the A$500 million Port Pirie transformation project will see a cleaner smelter and remediation of contamination in the city in years to come.

At Mount Isa, the Glencore owned mining company will have spent more than A$600 million on a range of environmental improvements by the end of 2016.

Hopefully, these investments will result in better outcomes for the next generation of children growing up in these toxic metal-rich communities – and we'll be keeping an eye on the efficacy of the programs.

However, it's very likely that the current environmental regulatory limits will not be strict enough to prevent the significant exposures identified in our study from reoccurring.

Appendix C

The Conversation

Mount Isa contamination ‘within guidelines’ but residents told to clean their homes

Taylor, M. P., **Dong, C.,** Harvey, P.

After an 11-year wait, Mount Isa Mines has released the official report into the lead contamination that has blighted the city for decades.

The report, commissioned by the mine’s owner, Glencore, and produced by researchers at the University of Queensland, says that household dust contaminated by airborne lead from the mining and smelting operations is the dominant source of the city’s exposure.

In some aspects this marks an important shift in the industry’s acceptance of the problem. Yet the report goes on to argue that Mount Isa residents are nevertheless responsible for keeping themselves, their houses and their children free from dust, thus putting the onus back on them to avoid exposure to the contamination.

A history of excuses

This is the latest iteration in the decade-long evolution of Mount Isa Mines’ arguments rebutting research that linked the contamination to its mining and smelting operations.

Back in 2007, when owned by Xstrata, Mount Isa Mines stated that the contamination was “naturally occurring”. We have previously termed this the “miner’s myth” – the idea that contamination surrounding a mine is a product of natural geology and weathering rather than the mining activity itself.

Before Mount Isa Mines was taken over by Glencore in 2013, the company admitted that Mount Isa was affected by “industrial mineralisation” (industry-speak for contamination from emissions), but also said that the contamination was partly due to natural sources in the city’s soils and rocks.

We and our colleagues have produced more than 20 studies documenting environmental contamination and its management in the Mount Isa region, dating back to 2005 when the Leichhardt River, which supplies drinking water to Mount Isa, was found to be contaminated with lead and other metals. Since then, we have detailed contamination in local sediments, water

and soils, and used isotope fingerprinting to pinpoint the likely source; none of this research was mentioned in the new report.

Despite the welcome admission that the company is indeed contaminating Mount Isa, the report caveats this by saying that the risk of direct inhalation of lead emitted into the air is low. It states that exposure arises mainly when children are exposed to lead-contaminated surfaces in their homes – chiefly carpets. For Mount Isa families, these comments do not fully encapsulate the real challenges they face in protecting themselves and their families.

Passing the buck

The report offers the following advice to residents attempting to keep their exposure as low as possible:

- keep a "clean home environment"
- consider replacing carpets with timber or other hard floors, and clean them with phosphate-based agents
- wash childrens' hands frequently and before meals, and encourage very young children not to suck non-food items
- wash all homegrown fruit and vegetables, and peel root vegetables, before cooking and/or eating.

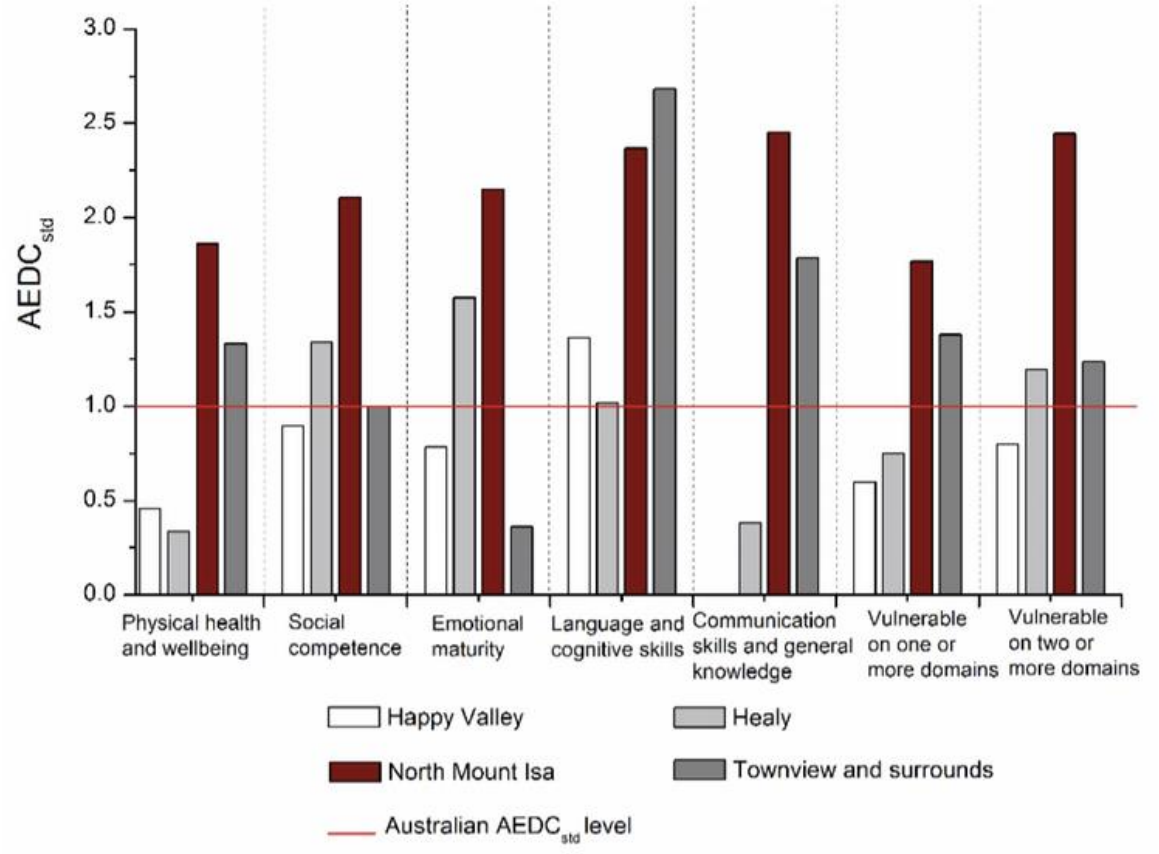
The implied argument is essentially that, despite the contamination, if you do the right thing (such as keeping your house clean) there is no problem.

The obvious rebuttal to this is that if there were no industrial lead in the community, there would be no problem at all. The root cause of the issue is not the natural hand-to-mouth behaviours of children but the pervasive, persistent and permanent arsenic, cadmium and lead contamination that penetrates everything they touch: clothes, toys, food, floors and furnishings.

The rates of lead dust deposition are such that that people living closest to the smelters would have to wash their backyards and indoor surfaces several times a day to keep toxic dust levels within acceptable guidelines. Cleaning one's house more than once a day, especially if working or looking after little children, is nearly impossible to maintain even over a few days, never mind a lifetime. While the advice to keep houses, hands and surfaces is not unreasonable in itself, the evidence suggests that it is little use in preventing lead exposure.

How serious is the exposure?

Mount Isa's schoolchildren are performing well below the national average, according to standardised testing data from the first full year of school. Similar outcomes have been seen in Broken Hill, another of Australia's major lead mining towns. Children in North Mount Isa, the area nearest the smelter, did worse than in other areas of the city.



Educational testing outcomes in children from various areas of Mount Isa, compared with the national average. Author provided

Mount Isa's children have an average blood lead level of about 35 parts per billion – about three times higher than normal. A 2015 study of children from Broken Hill and Port Pirie showed that a increase in blood lead from 10 to 100 parts per billion can reduce IQ by 13.5 points. Relevantly, low exposures cause proportionally more harm, which is why it is important for children to be protected from any lead contamination at all.

The report is clear that exposure happens as a result of contamination released into the air, which later settles as dust:

The major source of lead exposure is via ingestion in the community and is from air particulates (<250µm diameter) that are on the ground from deposition as fallout.

However, it goes on to say that the mine cannot be directly faulted for this, because the average rate of airborne emissions is within the guidelines outlined in its environmental permit. The report suggests that its modelled blood lead values do not match the actual values on children because they may be exposing themselves to extra lead by ingesting dirt, or through other sources such as lead-based paint, leaded petrol, or lead-acid batteries.

But this rationale fails to take into account the short-term spikes in emissions, which cause depositions that accumulate in soils and dusts, which in turn cause elevated blood lead exposures in children. The question could easily be answered by comparing the isotopic composition of lead from blood samples with that from the mine's emissions. Disappointingly, the Glencore report did not undertake this critical analytical step to link environmental sources to actual exposures in children.

Another setback

Authorities have been aware of lead emissions from the Mount Isa smelter since the early 1930s. It was always a fanciful notion to suggest that emissions were not finding their way across the city and into homes, and that the contamination was somehow natural.

Intensive air monitoring in the community has continued for at least the past 40 years. Blood lead surveys and internal memos, along with environmental assessments from various government agencies, have provided significant prior knowledge of the nature, extent and cause of the problem. In 2010, Queensland's chief medical officer Jeanette Young told The Australian newspaper:

I do know the cause; it is emissions being released from the mine. If you think where it is coming from, it is coming from emissions from the smelter that are going up in the air and they are depositing across the town fairly evenly.

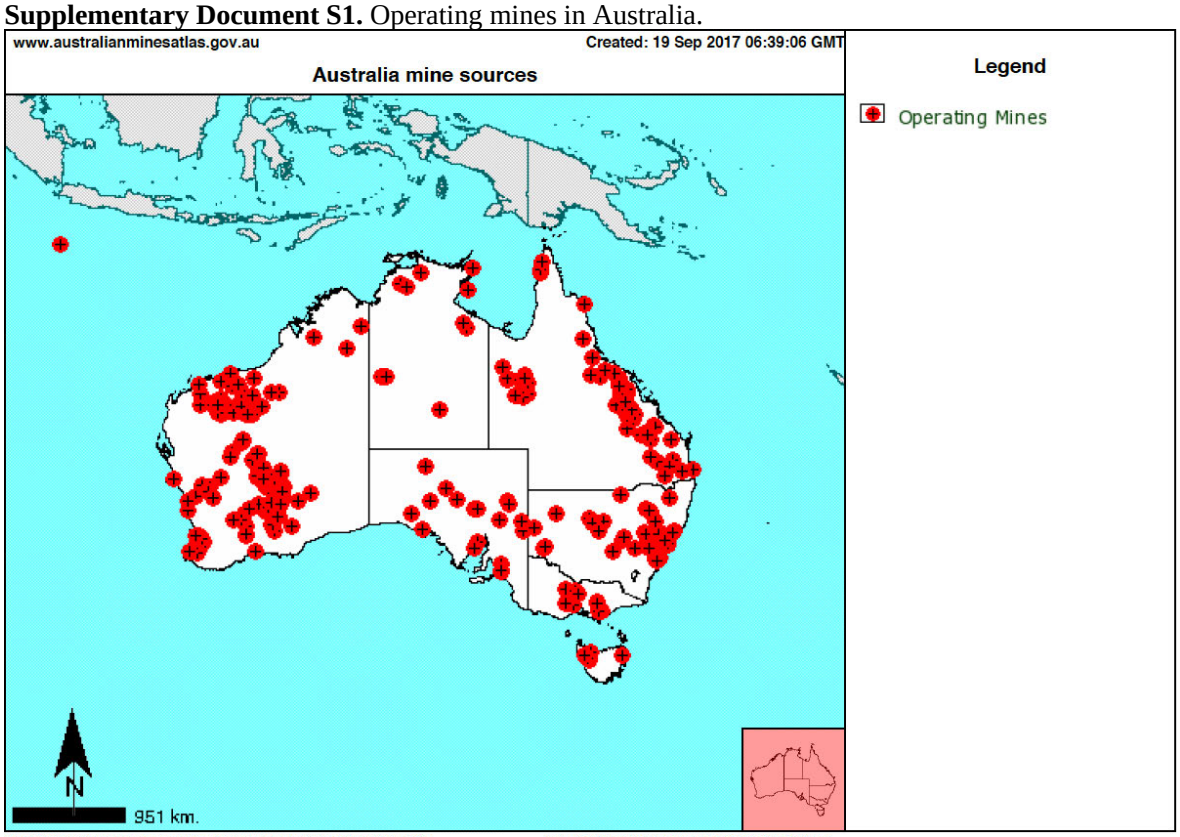
Thus, in this sense, the latest study merely represents confirmation of what many people already knew.

Yet despite this overdue acknowledgement of the problem, the report implies that Glencore is not taking full ownership of the issue. The overriding message to Mount Isa's residents is that it falls to them to keep themselves free from dangerous contamination.

In this sense, this is yet another setback in improving the living conditions for the community of Mount Isa, particularly young children who are the most vulnerable to the adverse and life-long effects of lead exposure.

Appendix D

Supplementary Document S1. Operating mines in Australia.



Supplementary Table S2. Soil Pb concentrations of the citywide footpath in the early 1990s.

Sample ID	Total Pb	60μm Pb	Sample ID	Total Pb	60μm Pb	Sample ID	Total Pb	60μm Pb
1	3900	5400	109	270	555	217	295	760
2	5160	9400	110	255	570	218	380	890
3	2140	5400	111	130	315	219	105	335
4	2490	8200	112	210	570	220	90	200
5	5580	11600	113	470	810	221	220	470
6	365	595	114	395	475	222	740	1220
7	10000	23800	115	375	680	223	100	105
8	10400	28400	116	640	2150	224	930	1440
9	5800	20600	117	115	260	225	100	215
10	3200	16200	118	130	265	226	715	1140
11	4880	9400	119	130	200	227	620	1180
12	3270	9400	120	415	680	228	105	550
13	1350	2500	121	830	1450	229	535	810
14	2080	4900	122	330	720	230	180	385
15	2750	6300	123	480	585	231	100	270
16	2220	5500	124	105	255	232	1255	7300
17	8720	14200	125	665	2250	234	240	695
18	10400	23200	126	315	825	235	135	885
19	111000	31000	127	405	645	236	300	505
20	3720	10000	128	285	345	237	460	1180
21	1155	3450	129	1090	1450	238	435	1060
22	390	725	130	565	1300	239	265	3960
23	740	1650	131	290	430	240	355	435
24	1645	3750	132	225	360	241	740	980
25	820	2400	133	160	390	242	475	775
26	6020	13200	134	440	910	243	195	880
27	5850	12600	135	175	345	244	55	100
28	205	515	136	220	395	245	1150	3120
29	2950	4800	137	140	235	246	685	1280
30	1560	7800	138	35	50	247	405	905
31	1500	3500	139	520	730	248	660	1260
32	920	2600	140	765	800	249	770	1720
33	1815	5350	141	810	1650	250	285	510
34	1760	4150	142	115	180	251	35	55
35	665	2600	143	410	915	252	620	1600
36	1230	3000	144	60	80	253	285	410
37	130	990	145	180	325	254	515	1220
38	6510	11600	146	150	325	255	455	1360
39	925	1300	147	115	550	256	320	920
40	790	1400	148	215	500	257	850	2320
41	460	410	149	470	760	258	2425	4980
42	90	485	150	180	485	259	560	1060
43	535	1850	151	90	160	260	800	2080
44	135	605	152	635	1150	261	815	1100

45	105	220	153	180	485	262		105
46	1385	4300	154	460	1550	263	200	460
47	105	510	155	115	245	264	315	495
48	480	625	156	25	95	265	690	1540
49	260	460	157	110	240	266	285	890
50	1425	3600	158	320	630	267	595	340
51	340	525	159	490	2500	268	800	2240
52	300	1200	160	490	1200	269	195	740
53	685	1400	161	225	465	270	8570	8100
54	745	1400	162	135	300	271	170	650
55	2095	4000	163	125	290	272	1630	2560
56	530	1550	164	440	1150	273	340	245
57	330	855	165	110	220	274	1825	2540
58			166	80	195	275	35	90
59			167	40	75	276	1585	2820
60	855	1700	168	205	620	277	310	805
61	1275	2150	169	125	300	278	785	2580
62	840	2000	170	135	250	279	1615	2160
63	1240	3200	171	210	950	280	1095	915
64	685	2450	172	345	975	281	125	255
65	635	1850	173	210	420	282	260	845
66	1055	1900	174	55	40	283	195	255
67	125	205	175	555	1250	284	970	2300
68	460	1350	176	240	415	285	565	1520
69	1665	2800	177	395	680	286	295	625
70	1020	1850	178	15	20	287	1790	3280
71	360	1300	179	175	325	288	1430	2320
72	360	1300	180	20	35	289	2490	5300
73	1400	3550	181	85	290	290	4770	7500
74	1090	2200	182	450	1000	291	2570	3820
75	1465	2550	183	1170	1600	292	670	1100
76	95	605	184	55	170	293	1085	1700
77	405	950	185	505	735	294	10	20
78	405	955	186	2250	2100	295	575	1140
79	1055	2450	187	215	1020	296	300	500
80	280	675	188	385	1035	297	940	2840
81	470	2050	189	90	125	298	310	1300
82	550	1550	190	90	135	299	3350	7800
83	470	1700	191	290	570	300	2085	4740
84	250	585	192	110	260	301	985	1700
85	475	2050	193	160	450	302	3920	7500
86	250	510	194	130	285	303	640	1005
87	630	1400	195	190	425	304	340	820
88	420	840	196	440	895	305	25	55
89	140	280	197	165	355	306	510	555
90	170	440	198	240	490	307	125	240
91	485	965	199	185	320	308	20	35

92	105	80	200	195	385	309	20	40
93	1130	2300	201	220	675	310	75	145
94	75	175	202	280	795	311	390	665
95	815	2300	203	405	505	312	390	765
96	120	895	204	575	390	313	800	2980
97	335	760	205	225	785	314	1755	2820
98	280	625	206	560	1200	315	1555	2180
99	640	1600	207	105	115	316	590	2680
100	660	2150	208	400	1300	317	680	600
101	1240	2800	209	775	1500	318	565	735
102	150	430	210	885	1520	319	530	2260
103	320	760	211	2095	3220	320	4195	5440
104	135	640	212	230	855	321	505	2040
105	4895	5750	213	160	350	322	1610	2680
106	1690	4000	214	200	375	323	3160	3700
107	1010	1900	215	415	755	324	2975	5340
108	190	530	216	165	380			

Note: Total Pb: the Pb concentrations of fractions <2 mm; 60μm Pb: the Pb concentrations of fractions <60μm.

Appendix E

Supplementary Table S1. Reported estimates of atmospheric Pb emissions of Perilya Broken Hill Limited (NPI, 2016).

Years	Atmospheric Pb emissions (tonnes)
2002	0.79
2003	4.3
2004	4.2
2005	0.25
2006	0.51
2007	0.99
2008	0.68
2009	0.69
2010	11
2011	28
2012	26
2013	31
2014	29
Total	137.4

Supplementary Table S2. Contemporary dust Pb (total) loading values in Broken Hill from November 2014 to November 2015.

	D1 (μg/m^2/day)	D2 (μg/m^2/day)	D3 (μg/m^2/day)	D4 (μg/m^2/day)	D5 (μg/m^2/day)	D6 (μg/m^2/day)
Nov 2014	372.9	461.2	84.0	65.8	NA	NA
Dec 2014*	141.6	108.5	68.3	16.2	34.4	NA
Jan 2015*	65.8	341.7	96.7	26.5	30.3	203.2
Mar 2015*	98.0	359.4	96.3	20.3	38.6	29.9
Apr 2015	240.0	149.6	108.9	25.5	56.4	27.0
May 2015	277.6	220.5	31.0	25.8	1.5	NA
Jun 2015**	145.4	94.3	54.7	16.2	16.8	5.5
Jul 2015**	316.3	95.7	51.9	9.1	26.3	10.0
Aug 2015**	190.2	89.2	36.2	4.0	6.3	11.0
Sep 2015	140.9	321.6	77.3	34.4	40.4	36.9
Oct 2015	180.3	374.4	94.2	NA	54.0	43.4
Nov 2015	893.4	361.5	99.9	11.4	40.4	26.0
Averaged ± SD	255.2 ± 220.3	248.1 ± 135.8	74.9 ± 26.2	23.2 ± 16.7	31.4 ± 17.7	43.7 ± 61.2
Median	185.3	271.1	80.6	20.3	34.4	27.0
Distance (km)	0.5	1.5	3.0	3.7	4.3	6.0

Note: * summer months, ** winter months. Distance − distance of dust gauge site away from southern mining operation.
NA − no data due to dust gauge fall over or missing funnels.

Supplementary Table S3. Bioaccessibility (%) of the contemporary dust Pb in Broken Hill from November 2014 to November 2015.

	D1 (%)	D2 (%)	D3 (%)	D4 (%)	D5 (%)	D6 (%)
Nov 2014	92.3	82.6	80.7	74.0	NA	NA
Dec 2014*	80.7	68.3	83.0	74.7	78.4	NA
Jan 2015*	77.7	82.4	75.9	77.4	80.1	55.7
Mar 2015*	53.1	83.7	62.0	69.0	69.6	57.1
Apr 2015	82.0	64.4	78.7	67.8	81.2	51.8
May 2015	69.0	70.5	63.2	74.4	51.5	NA
Jun 2015**	87.3	83.7	23.2	76.5	79.1	62.4
Jul 2015**	41.9	64.1	77.6	53.8	58.9	51.1
Aug 2015**	84.2	71.2	57.5	47.5	55.9	53.1
Sep 2015	82.8	79.4	72.7	61.9	65.7	75.3
Oct 2015	84.7	72.4	62.6	NA	74.8	72.1
Nov 2015	59.3	63.8	57.6	54.4	62.5	55.0
Averaged ± SD	74.6 ± 15.5	73.9 ± 8.0	66.2 ± 16.4	66.5 ± 10.5	69.0 ± 10.3	59.2 ± 8.9
Median	81.3	71.8	68.0	69.0	69.7	55.7
Distance (km)	0.5	1.5	3.0	3.7	4.3	6.0

Note: NA − no data from this month due to dust gauge fall over or missing funnels.

Supplementary Table S4. Least Significant Difference (LSD) results of the averaged bioaccessibility comparison for the sites with difference distance away from the active mining operations.

	(I) Sites	(J) Sites	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
LSD	D1	D2	0.70833	5.00227	0.888	-9.2943	10.711
		D3	8.35833	5.00227	0.1	-1.6443	18.361
		D4	8.09242	5.1147	0.119	-2.135	18.3199
		D5	5.70152	5.1147	0.269	-4.526	15.929
		D6	15.29444*	5.40307	0.006	4.4903	26.0986
	D2	D1	-0.70833	5.00227	0.888	-10.711	9.2943
		D3	7.65	5.00227	0.131	-2.3527	17.6527
		D4	7.38409	5.1147	0.154	-2.8434	17.6116
		D5	4.99318	5.1147	0.333	-5.2343	15.2206
		D6	14.58611*	5.40307	0.009	3.782	25.3902
	D3	D1	-8.35833	5.00227	0.1	-18.361	1.6443
		D2	-7.65	5.00227	0.131	-17.6527	2.3527
		D4	-0.26591	5.1147	0.959	-10.4934	9.9616
		D5	-2.65682	5.1147	0.605	-12.8843	7.5706
		D6	6.93611	5.40307	0.204	-3.868	17.7402
	D4	D1	-8.09242	5.1147	0.119	-18.3199	2.135
		D2	-7.38409	5.1147	0.154	-17.6116	2.8434
		D3	0.26591	5.1147	0.959	-9.9616	10.4934
		D5	-2.39091	5.2247	0.649	-12.8383	8.0565
		D6	7.20202	5.50732	0.196	-3.8105	18.2146
	D5	D1	-5.70152	5.1147	0.269	-15.929	4.526
		D2	-4.99318	5.1147	0.333	-15.2206	5.2343
		D3	2.65682	5.1147	0.605	-7.5706	12.8843
		D4	2.39091	5.2247	0.649	-8.0565	12.8383
		D6	9.59293	5.50732	0.087	-1.4196	20.6055
	D6	D1	-15.29444*	5.40307	0.006	-26.0986	-4.4903
		D2	-14.58611*	5.40307	0.009	-25.3902	-3.782
		D3	-6.93611	5.40307	0.204	-17.7402	3.868
		D4	-7.20202	5.50732	0.196	-18.2146	3.8105
		D5	-9.59293	5.50732	0.087	-20.6055	1.4196

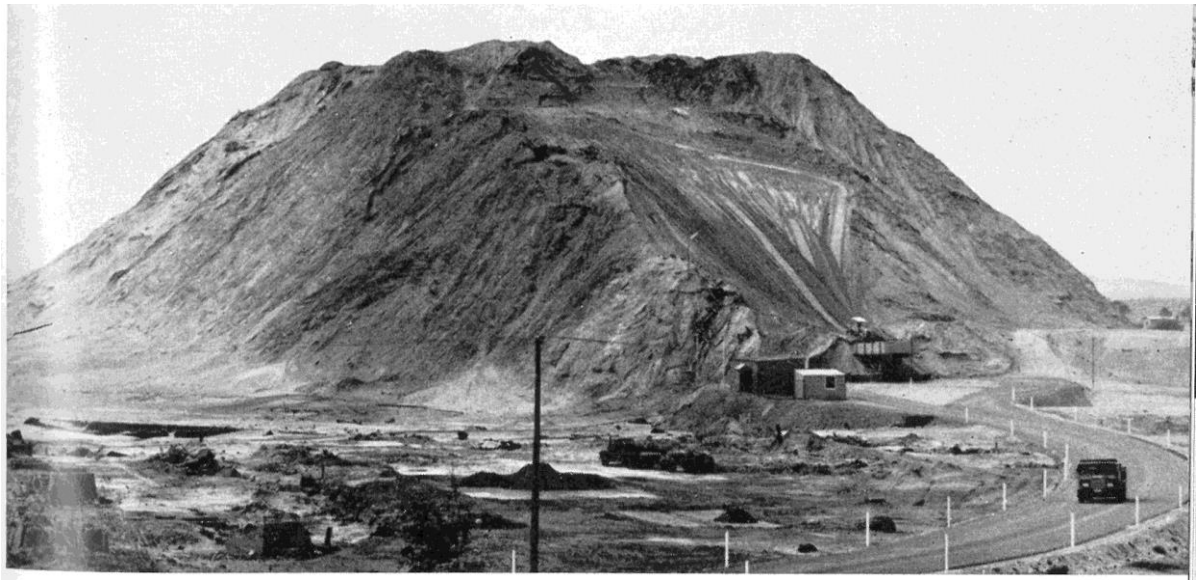
Note: * the mean difference is significant at the 0.05 level.

Supplementary Table S5. Chemical compositions of Pb bearing particles observed in dust gauge, tailings and gossan samples.

Site	ID of particle	Particle size (μm)	wt %			Atom percentage %		
			Pb	S	Fe+Mn	Pb	S	Fe+Mn
D1 (n=5)	1	27	61.1	8.1	ND	9.8	8.4	ND
	2	43	62.8	8.3	ND	10.4	8.8	ND
	3	25	45.9	6.0	ND	5.2	4.4	ND
	4	20	62.5	8.2	ND	10.2	8.7	ND
	5	25	53.8	7.1	ND	7.3	6.2	ND
D2 (n=4)	6	3.4	54.4	6.8	ND	7.2	5.8	ND
	7	26	49.2	6.1	ND	6.1	4.8	ND
	8	8.7	44.9	5.6	ND	5.1	4.0	ND
	9	10	25.6	3.8	ND	2.5	2.4	ND
D3 (n=3)	10	4	49.1	6.3	ND	6.7	5.5	ND
	11	1.6	53.2	ND	1.2	7.8	ND	0.6
	12	9	52.8	6.8	ND	6.8	5.7	ND
D4 (n=5)	13	5	68.5	8.8	ND	13.5	11.3	ND
	14	3	55.5	7.2	ND	7.5	6.3	ND
	15	3	41.4	5.4	0.3	4.4	3.7	0.1
	16	7	58.7	7.5	ND	8.7	7.2	ND
	17	5	54.7	7.0	ND	7.6	6.3	ND
D5 (n=4)	18	3	53.9	7.0	ND	7.4	6.3	ND
	19	9	72.1	9	ND	16.0	12.9	ND
	20	10	70.2	8.9	ND	14.6	11.9	ND
	21	5	51.9	6.5	0.7	6.8	5.5	0.4
D6 (n=3)	22	6	61.3	8.1	0.3	10.0	8.5	0.2
	23	3	59.8	7.8	0.6	9.6	8.1	0.3
	24	27	38.2	4.5	0.3	4.3	3.3	0.1
Gossan (n=3)	26	15	14.1	1.3	4.0	1.3	0.8	1.4
	27	10	25.4	2.9	15.2	3.1	2.3	6.8
	28	7	20.9	1.5	14.0	2.3	1.1	5.8
Tailings dump (n=4)	29	14	51.3	ND	0.5	6.8	ND	0.3
	30	15	61.7	ND	ND	10.4	ND	ND
	31	16	69.5	ND	ND	23.3	ND	ND
	32	14	55.4	ND	0.9	8.2	ND	0.5

Note: ND – not detected.

Supplementary Figure S6. Uncovered tailings mound produced from the central Broken Hill mine, known as Mount Hebbard (Blainey, 1968).



Supplementary References

NPI, 2016. The National Pollutant Inventory (NPI) data of Perilya Limited, Broken Hill; http://www.npi.gov.au/npidata/action/load/individual-facility-detail/criteria/state/NSW/year/2015/jurisdiction-facility/125 (accessed 23.07.2016).

Blainey, G. 1968. The Rise of Broken Hill. Macmillan of Australia: Melbourne.

Appendix F

Supplementary Data 1. Soil metal(loid) concentrations (pXRF derived) for public (Zone **A** S**B**; **A –** sampling zone number, **B** – sample site) and private (PRS**XY**; **X** – property code, **Y** – sample number on property) samples. All concentrations mg/kg except where * denotes wt%.

Sample	x co-ordinate	y co-ordinate	Ti	Cr	Mn	Fe*	Zn	As	Cd	Pb
Zone 1 S1	151.754117	-32.921500	4,770	130	1,120	3.51	520	41	<LOD	300
Zone 1 S2	151.757272	-32.917458	10,100	110	1,200	3.88	990	41	<LOD	590
Zone 1 S3	151.755289	-32.918547	3,750	77	820	2.58	800	18	<LOD	280
Zone 1 S4	151.752281	-32.918856	1,930	54	560	2.07	600	17	<LOD	250
Zone 1 S5	151.749133	-32.918808	4,710	120	1,470	3.53	2,010	56	<LOD	1,820
Zone 1 S6	151.745742	-32.914514	4,650	97	3,190	4.15	2,230	60	<LOD	1,310
Zone 1 S7	151.743853	-32.912803	5,130	190	2,110	5.97	1,990	69	<LOD	1,550
Zone 1 S8	151.746250	-32.911394	6,300	190	1,270	5.17	510	37	<LOD	340
Zone 1 S9	151.750283	-32.914881	4,750	170	2,090	5.30	2,660	180	<LOD	4,650
Zone 1 S10	151.753450	-32.916361	4,850	170	1,830	4.27	1,410	25	<LOD	500
Zone 1 S11	151.754900	-32.914300	3,670	59	500	2.20	270	9	<LOD	62
Zone 1 S12	151.753094	-32.910250	4,650	160	3,880	5.69	1,690	83	3	1,650
Zone 1 S13	151.759181	-32.909817	3,660	94	720	2.25	520	19	<LOD	160
Zone 1 S14	151.759392	-32.906031	7,030	260	3,580	10.30	9,470	87	10	1,120
Zone 1 S15	151.756672	-32.904525	5,480	180	1,450	5.22	2,010	55	6	730
Zone 1 S16	151.754450	-32.904392	2,800	90	1,600	3.18	630	17	<LOD	230
Zone 1 S17	151.755342	-32.907642	3,770	57	610	2.51	140	9	<LOD	35
Zone 1 S18	151.750922	-32.907825	3,940	110	1,120	3.39	2,000	130	<LOD	740
Zone 1 S19	151.750175	-32.904172	2,700	75	1,670	2.43	470	15	<LOD	150
Zone 1 S20	151.753067	-32.898278	5,500	210	4,490	14.17	5,090	130	16	2,060
Zone 1 S21	151.748775	-32.895000	3,810	230	3,410	9.71	1,910	35	4	590
Zone 1 S22	151.747103	-32.899675	5,160	200	2,450	9.51	1,230	50	<LOD	790
Zone 1 S23	151.745039	-32.903125	5,640	160	1,200	3.99	400	14	<LOD	240

Zone 1 S24	151.742175	-32.900814	3,900	140	1,040	3.30	1,070	25	<LOD	450
Zone 1 S25	151.744000	-32.896467	4,120	100	2,210	4.85	1,470	34	<LOD	640
Zone 1 S26	151.738069	-32.890289	3,520	92	1,040	3.39	680	12	<LOD	210
Zone 1 S27	151.734183	-32.891683	4,050	140	500	3.22	340	11	<LOD	110
Zone 1 S28	151.731650	-32.893592	6,150	220	1,240	4.08	610	23	<LOD	590
Zone 1 S29	151.727119	-32.889044	4,450	210	1,870	4.27	900	22	<LOD	450
Zone 2 S1	151.763972	-32.907889	6,290	160	1,810	4.80	690	24	<LOD	290
Sample	x co-ordinate	y co-ordinate	Ti	Cr	Mn	Fe*	Zn	As	Cd	Pb
Zone 2 S2	151.765667	-32.908611	4,920	81	1,980	3.94	830	29	<LOD	410
Zone 2 S3	151.766972	-32.907528	4,950	120	1,760	3.57	1,500	14	<LOD	270
Zone 2 S4	151.768639	-32.907889	13,700	710	3,630	17.08	12,100	200	7	2,550
Zone 2 S5	151.762028	-32.910972	5,130	92	546	2.82	140	6	<LOD	33
Zone 2 S6	151.764389	-32.910306	5,110	140	2,600	4.86	1,870	45	4	1,240
Zone 2 S7	151.766500	-32.910806	5,660	140	2,580	4.92	1,860	51	<LOD	1,240
Zone 2 S8	151.768417	-32.909250	5,670	350	3,110	7.18	2,570	61	6	930
Zone 2 S9	151.769806	-32.910778	6,560	330	2,370	4.15	1,130	23	<LOD	280
Zone 2 S10	151.762306	-32.912917	4,300	60	650	2.65	200	14	<LOD	57
Zone 2 S11	151.765167	-32.912889	5,200	130	2,100	4.39	3,050	69	<LOD	1,300
Zone 2 S12	151.767861	-32.912028	3,670	83	1,500	3.09	790	44	<LOD	400
Zone 2 S13	151.765417	-32.914111	3,690	110	1,540	3.00	1,010	32	<LOD	500
Zone 2 S14	151.768333	-32.914083	4,810	180	1,240	5.08	1,950	76	5	930
Zone 2 S15	151.761278	-32.915472	14,800	690	3,250	7.00	4,690	73	<LOD	900
Zone 2 S16	151.764556	-32.916500	4,950	120	1,230	3.54	1,040	36	<LOD	630
Zone 2 S17	151.765389	-32.919556	6,280	190	1,540	4.34	4,260	380	5	2,770
Zone 2 S18	151.766722	-32.918250	4,990	120	1,850	4.11	2,290	42	11	1,220
Zone 2 S19	151.766972	-32.917083	6,040	200	1,530	4.48	4,940	96	13	1,970
Zone 3 S1	151.760889	-32.923492	3,450	59	660	2.21	360	13	<LOD	190
Zone 3 S2	151.762344	-32.924817	4,310	69	1,260	3.69	640	74	<LOD	370
Zone 3 S3	151.765656	-32.925775	3,770	120	770	2.71	690	23	<LOD	220

Zone 3 S4	151.769256	-32.925933	5,110	88	840	3.58	390	44	<LOD	230
Zone 3 S5	151.771983	-32.926467	4,890	91	541	2.79	320	10	<LOD	230
Zone 3 S6	151.775775	-32.925344	3,030	38	790	1.70	240	10	<LOD	39
Zone 3 S7	151.780153	-32.925839	4,500	78	820	2.28	140	6	<LOD	45
Zone 3 S8	151.785872	-32.925525	4,490	88	300	2.03	96	6	<LOD	22
Zone 3 S9	151.789786	-32.924081	4,950	81	730	2.90	380	14	<LOD	150
Zone 3 S10	151.791397	-32.923228	5,740	92	580	2.80	180	9	<LOD	68
Zone 4 S1	151.787817	-32.926988	5,460	140	660	2.78	170	8	<LOD	27
Zone 4 S2	151.785853	-32.927366	4,160	72	360	2.22	250	19	<LOD	110
Zone 4 S3	151.783673	-32.928302	1,750	55	790	1.82	800	21	<LOD	270
Zone 4 S4	151.779448	-32.929244	4,810	68	370	2.03	290	23	<LOD	560
Sample	x co-ordinate	y co-ordinate	Ti	Cr	Mn	Fe*	Zn	As	Cd	Pb
Zone 4 S5	151.782722	-32.932442	5,910	130	680	5.14	220	56	<LOD	50
Zone 4 S6	151.778754	-32.931607	5,240	87	100	4.09	1,220	63	<LOD	3,450
Zone 4 S7	151.775584	-32.930542	3,870	94	660	2.50	170	5	<LOD	23
Zone 4 S8	151.776879	-32.929139	4,280	76	560	2.55	230	6	<LOD	75
Zone 4 S9	151.773684	-32.928170	4,400	74	430	2.12	280	7	<LOD	120
Zone 4 S10	151.770599	-32.929525	3,550	71	1,010	2.17	650	39	<LOD	720
Zone 4 S11	151.770951	-32.932130	8,890	140	280	1.67	98	25	<LOD	41
Zone 4 S12	151.767797	-32.930565	1,920	41	730	1.36	630	13	<LOD	360
Zone 4 S13	151.765789	-32.928902	6,590	160	920	3.27	510	13	<LOD	200
Zone 4 S14	151.766179	-32.927340	4,570	80	950	2.26	230	6	<LOD	150
Zone 4 S15	151.765789	-32.928902	5,390	100	830	3.29	300	23	<LOD	330
Zone 4 S16	151.762763	-32.926629	4,470	91	780	3.62	1,880	22	<LOD	620
Zone 4 S17	151.764658	-32.927587	5,760	110	860	3.58	510	17	<LOD	470
Zone 4 S18	151.789719	-32.926185	6,470	84	560	2.76	230	14	<LOD	69
Zone 4 S19	151.789625	-32.927671	5,880	130	540	2.96	130	9	<LOD	20
Zone 4 S20	151.785676	-32.925958	5,000	98	230	2.45	130	10	<LOD	120
Zone 4 S21	151.783617	-32.930237	5,970	110	540	2.83	460	21	<LOD	450

Zone 4 S22	151.777405	-32.930160	3,810	63	550	2.31	220	11	<LOD	83
Zone 4 S23	151.789632	-32.926502	6,340	93	740	3.41	150	7	<LOD	14
Zone 4 S24	151.784438	-32.927336	5,270	110	920	3.63	1,370	38	3	1,250
Zone 4 S25	151.770352	-32.928371	1,670	52	350	1.59	180	11	<LOD	53
Zone 5 S1	151.755858	-32.926782	3,870	63	780	2.64	420	12	<LOD	210
Zone 5 S2	151.755046	-32.927209	3,970	78	970	2.56	400	11	<LOD	120
Zone 5 S3	151.758133	-32.928261	3,500	96	1,100	2.34	540	18	<LOD	410
Zone 5 S4	151.754604	-32.930872	4,660	77	1,110	2.84	430	17	<LOD	220
Zone 5 S5	151.750771	-32.930600	2,320	77	580	1.84	280	8	<LOD	120
Zone 5 S6	151.753740	-32.933156	4,620	73	1,220	2.81	470	14	<LOD	240
Zone 5 S7	151.750693	-32.934451	4,970	80	700	2.59	280	36	<LOD	220
Zone 5 S8	151.750418	-32.937009	3,890	77	600	2.83	730	22	<LOD	560
Zone 5 S9	151.753171	-32.936175	4,590	68	600	2.34	330	83	<LOD	260
Zone 5 S10	151.755987	-32.938211	3,770	65	870	2.55	240	11	<LOD	180
Zone 5 S11	151.756269	-32.935044	3,440	74	980	2.07	680	13	<LOD	250
Sample	x co-ordinate	y co-ordinate	Ti	Cr	Mn	Fe*	Zn	As	Cd	Pb
Zone 5 S12	151.758250	-32.936281	4,250	86	600	2.53	600	33	<LOD	310
Zone 5 S13	151.760791	-32.937766	4,240	83	180	2.21	270	18	<LOD	440
Zone 5 S14	151.763637	-32.938862	4,790	74	750	2.42	550	42	<LOD	460
Zone 5 S15	151.763484	-32.935614	4,270	79	1,400	3.13	860	34	<LOD	590
Zone 5 S16	151.767670	-32.934845	4,290	57	320	2.06	190	15	<LOD	150
Zone 5 S17	151.765772	-32.934974	2,550	55	540	1.96	230	10	<LOD	140
Zone 5 S18	151.763240	-32.933954	5,360	88	590	2.85	190	10	<LOD	46
Zone 5 S19	151.762349	-32.931880	5,110	75	560	2.58	130	14	<LOD	71
Zone 5 S20	151.758135	-32.932137	3,610	83	1,480	3.08	780	47	<LOD	400
PRS1A	151.755494	-32.931677	2,900	85	760	1.97	640	33	<LOD	780
PRS1B	151.755494	-32.931677	3,940	83	670	2.07	530	39	<LOD	1,460
PRS1C	151.755494	-32.931677	2,520	80	700	2.10	500	25	<LOD	330
PRS2A	151.765575	-32.935832	5,440	73	330	2.09	610	39	<LOD	900

PRS2B	151.765575	-32.935832	5,230	89	460	2.28	400	21	<LOD	510
PRS2C	151.765575	-32.935832	4,140	100	490	2.33	2,090	85	<LOD	2,210
PRS3A	151.753439	-32.910121	4,470	97	790	2.99	880	25	<LOD	840
PRS3B	151.753439	-32.910121	5,670	120	790	3.61	1,030	48	<LOD	1,550
PRS3C	151.753439	-32.910121	5,460	120	1,850	4.32	1,130	63	<LOD	1,740
PRS3D	151.753439	-32.910121	6,790	220	2,220	5.61	6,240	85	3	3,420
PRS4A	151.750841	-32.914811	5,510	110	1,710	4.17	1,630	55	<LOD	1,730
PRS4B	151.750841	-32.914811	6,260	180	1,540	5.56	3,190	280	6	8,280
PRS4C	151.750841	-32.914811	6,610	390	1,650	6.48	8,570	280	5	11,600
PRS5A	151.765773	-32.935121	6,440	96	760	3.02	780	32	<LOD	960
PRS5B	151.765773	-32.935121	5,850	130	790	2.99	1,010	40	<LOD	1,690
PRS5C	151.765773	-32.935121	6,250	140	960	3.64	4,040	56	<LOD	2,090
PRS6A	151.765488	-32.935929	5,920	84	460	2.36	1,030	55	<LOD	1,190
PRS6B	151.765488	-32.935929	4,670	69	400	2.13	550	40	<LOD	740
PRS7A	151.753251	-32.911086	6,330	96	1,350	3.36	1,200	85	<LOD	2,830
PRS7B	151.753251	-32.911086	6,710	200	1,790	5.41	3,210	240	6	5,450
PRS8A	151.735041	-32.891055	4,690	140	650	3.90	1,880	24	<LOD	1,440
PRS8B	151.735041	-32.891055	3,690	110	590	3.47	710	19	<LOD	430
PRS8C	151.735041	-32.891055	4,340	130	600	2.89	660	32	<LOD	1,060
Sample	x co-ordinate	y co-ordinate	Ti	Cr	Mn	Fe*	Zn	As	Cd	Pb
PRS9A	151.733763	-32.891786	3,520	96	340	2.53	560	10	<LOD	110
PRS9B	151.733763	-32.891786	6,210	120	790	3.38	220	10	<LOD	42
PRS9C	151.733763	-32.891786	5,550	110	940	4.26	720	25	<LOD	180
PRS10A	151.747068	-32.899573	5,090	170	1,870	5.86	1,190	46	<LOD	1,170
PRS10B	151.747068	-32.899573	6,040	520	3,360	16.01	5,500	240	<LOD	7,640
PRS10C	151.747068	-32.899573	4,400	120	730	4.69	700	34	<LOD	530
PRS10D	151.747068	-32.899573	5,180	110	617	2.15	830	14	<LOD	510
PRS11A	151.747014	-32.899688	5,180	180	2,070	6.30	2,500	79	<LOD	2,340
PRS11B	151.747014	-32.899688	6,790	310	3,600	10.01	1,720	95	<LOD	2,520

PRS12A	151.765242	-32.917256	12,200	210	960	5.14	1,560	110	<LOD	1,370
PRS12B	151.765242	-32.917256	6,930	180	1,140	3.90	3,560	74	6	1,840
PRS13A	151.764114	-32.917046	2,920	140	740	2.35	1,380	34	<LOD	780
PRS13B	151.764114	-32.917046	4,260	170	970	3.56	3,210	62	9	1,240
PRS13C	151.764114	-32.917046	2,870	190	770	2.28	1,200	35	<LOD	610
PRS13D	151.764114	-32.917046	4,940	140	1,410	4.19	1,360	18	<LOD	400
PRS14A	151.764141	-32.917121	5,550	270	1,280	3.75	2,290	50	5	2,120
PRS14B	151.764141	-32.917121	5,720	180	1,200	3.05	1,420	35	<LOD	1,590
PRS14C	151.764141	-32.917121	5,690	300	960	3.14	2,060	64	<LOD	1,420
PRS14D	151.764141	-32.917121	6,360	410	1,790	5.96	2,800	150	<LOD	4,570
PRS15A	151.756360	-32.931232	4,040	87	700	2.34	1,160	20	<LOD	920
PRS15B	151.756360	-32.931232	2,720	98	910	1.94	793	16	<LOD	360
PRS15C	151.756360	-32.931232	4,690	81	670	2.69	1,320	22	<LOD	1,110
PRS16A	151.754543	-32.930401	4,950	2,400	480	5.59	140	18	<LOD	120
PRS16B	151.754543	-32.930401	3,190	580	500	2.62	420	16	<LOD	210
PRS16C	151.754543	-32.930401	2,880	65	590	2.09	200	21	<LOD	190
PRS17A	151.735603	-32.913977	4,810	98	660	2.66	1,230	42	<LOD	880
PRS17B	151.735603	-32.913977	5,170	160	930	3.98	3,850	160	4	1,450
PRS18A	151.737504	-32.891153	3,190	76	560	2.95	880	12	<LOD	430
PRS18B	151.737504	-32.891153	3,940	100	470	3.30	2,930	12	<LOD	1,230
PRS19A	151.758141	-32.911858	5,740	460	1,840	4.95	3,700	80	4	2,350
PRS19B	151.758141	-32.911858	6,200	160	910	3.22	1,970	30	<LOD	1,810
PRS20A	151.725239	-32.897365	6,350	170	1,100	4.24	2,600	28	<LOD	1,930
Sample	x co-ordinate	y co-ordinate	Ti	Cr	Mn	Fe*	Zn	As	Cd	Pb
PRS20B	151.725239	-32.897365	5,230	160	580	3.40	1,880	24	<LOD	1,020
PRS20C	151.725239	-32.897365	5,310	130	580	3.30	1,320	14	<LOD	830
PRS21A	151.747123	-32.940503	4,740	75	1,000	2.47	1,290	15	<LOD	980
PRS21B	151.747123	-32.940503	3,450	72	920	2.39	970	17	<LOD	1,180
PRS22A	151.711666	-32.926700	3,500	74	410	1.75	1,070	17	<LOD	1,360

PRS22B	151.711666	-32.926700	2,910	54	120	1.31	380	8	<LOD	150
PRS22C	151.711666	-32.926700	3,970	68	480	2.13	380	15	<LOD	170
PRS23A	151.784001	-32.903409	7,080	180	740	5.60	770	47	<LOD	790
PRS23B	151.784001	-32.903409	9,120	210	1,390	8.05	1,090	55	4	1,140
PRS23C	151.784001	-32.903409	6,650	170	1,130	5.23	830	38	<LOD	610
PRS23D	151.784001	-32.903409	5,060	110	990	3.73	820	24	<LOD	450
PRS23E	151.784001	-32.903409	7,320	330	2,130	14.78	3,840	130	4	3,420
Soil Depth Profile a (0 - 2 cm)	151.780194	-32.933708	6170	67	360	2.27	330	20	<LOD	160
Soil Depth Profile a (2 - 10 cm)	151.780194	-32.933708	6370	63	320	2.39	260	28	<LOD	150
Soil Depth Profile a (10 - 20 cm)	151.780194	-32.933708	6400	77	270	2.36	220	30	<LOD	150
Soil Depth Profile a (20 - 30 cm)	151.780194	-32.933708	8400	71	200	2.21	170	21	<LOD	150
Soil Depth Profile a (30 - 40 cm)	151.780194	-32.933708	1.18*	98	99	1.54	110	30	<LOD	88
Soil Depth Profile b (0 - 2 cm)	151.760230	-32.908183	6730	140	1400	4.69	1350	67	<LOD	600
Soil Depth Profile b (2 - 10 cm)	151.760230	-32.908183	6650	170	1500	5.01	1380	62	<LOD	640
Soil Depth Profile b (10 - 20 cm)	151.760230	-32.908183	7280	160	1100	4.62	1330	69	<LOD	390
Soil Depth Profile b (20 - 30 cm)	151.760230	-32.908183	8590	89	670	3.81	410	40	<LOD	150
Soil Depth Profile b (30 - 40 cm)	151.760230	-32.908183	9400	83	280	3.55	150	31	<LOD	66
Soil Depth Profile c (0 - 2 cm)	151.746483	-32.911400	3270	87	700	2.29	330	33	<LOD	250
Soil Depth Profile c (2 - 10 cm)	151.746483	-32.911400	2370	78	470	1.97	210	26	<LOD	110
Soil Depth Profile c (10 - 20 cm)	151.746483	-32.911400	3320	82	600	2.29	340	23	<LOD	210
Soil Depth Profile c (20 - 30 cm)	151.746483	-32.911400	8020	160	810	3.46	320	30	<LOD	200
Soil Depth Profile c (30 - 40 cm)	151.746483	-32.911400	6470	98	1400	3.79	470	32	<LOD	400
Soil Depth Profile d (0 - 2 cm)	151.758508	-32.932803	2640	67	790	1.96	270	29	<LOD	120
Soil Depth Profile d (2 - 10 cm)	151.758508	-32.932803	4270	89	750	2.59	370	36	<LOD	150
Soil Depth Profile d (10 - 20 cm)	151.758508	-32.932803	5460	78	450	2.94	240	85	<LOD	100
Soil Depth Profile d (20 - 30 cm)	151.758508	-32.932803	5860	77	270	2.47	150	44	<LOD	91
Soil Depth Profile d (30 - 40 cm)	151.758508	-32.932803	6450	56	210	1.9	110	32	<LOD	59
Sample	x co-ordinate	y co-ordinate	Ti	Cr	Mn	Fe*	Zn	As	Cd	Pb
Soil Depth Profile e (0 - 2 cm)	151.695386	-32.909801	3270	59	150	1.48	96	3	<LOD	41

Soil Depth Profile e (2 - 10 cm)	151.695386	-32.909801	3570	58	140	1.51	94	6	<LOD	39
Soil Depth Profile e (10 - 20 cm)	151.695386	-32.909801	3510	46	37	1.35	40	4	<LOD	17
Soil Depth Profile e (20 - 30 cm)	151.695386	-32.909801	4130	61	16	1.9	31	6	<LOD	14
Soil Depth Profile e (30 - 40 cm)	151.695386	-32.909801	5240	67	36	3.51	38	13	<LOD	15
Soil Depth Profile f (0 - 2 cm)	151.621760	-32.902235	2830	77	140	1.65	230	14	<LOD	150
Soil Depth Profile f (2 - 10 cm)	151.621760	-32.902235	3040	96	54	1.58	110	13	<LOD	88
Soil Depth Profile f (10 - 20 cm)	151.621760	-32.902235	3010	58	31	1.82	60	12	<LOD	35
Soil Depth Profile f (20 - 30 cm)	151.621760	-32.902235	3260	79	30	1.91	58	9	<LOD	29
Soil Depth Profile f (30 - 40 cm)	151.621760	-32.902235	3260	79	30	1.91	58	9	<LOD	29

Supplementary Data 2. Soil PAH concentrations (mg/kg) for the Newcastle city.

Sample	x co-ordinate	y co-ordinate	PAH 1	PAH 2	PAH 3	PAH 4	PAH 5	PAH 6	PAH 7	PAH 8	PAH 9	PAH 10	PAH 11	PAH 12	PAH 13	PAH 14	PAH 15	∑ PAH
Zone 5 S1	151.765942	-32.935172	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	2.2	2.1	0.8	0.7	1.4	1.0	0.6	<0.5	0.8	10
Zone 5 S4	151.751481	-32.936583	<0.5	<0.5	<0.5	<0.5	4.4	1.5	10	9.6	3.5	3.5	6.9	5.2	2.9	0.6	3.4	52
Zone 5 S5	151.755347	-32.931136	<0.5	<0.5	<0.5	<0.5	1.7	0.6	4.6	4.5	1.5	1.5	3.1	2.2	1.4	<0.5	1.6	23
Zone 2 S1	151.765858	-32.91974	<0.5	<0.5	<0.5	<0.5	2.4	0.7	6.9	6.4	2.4	2.1	4.5	3.3	2.0	<0.5	2.4	33
Zone 2 S2	151.765405	-32.914048	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	5.7	5.4	2.0	2.0	4.2	2.7	1.9	<0.5	2.2	28
Zone 2 S2**	151.765405	-32.914048	<0.5	<0.5	<0.5	<0.5	2.1	0.7	6.3	6.0	2.3	2.2	4.5	3.2	2.0	<0.5	2.4	32
Zone 2 S3	151.764169	-32.909803	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.7	1.6	0.6	0.6	1.5	1.0	0.7	<0.5	0.9	8.6
Zone 2 S4	151.766314	-32.910977	<0.5	0.9	<0.5	<0.5	3.8	1.4	10	10	4.0	3.8	7.3	5.4	3.1	0.7	3.5	54
Zone 1 S5	151.746816	-32.900268	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	5.4	5.3	2.0	2.0	4.4	2.9	2.0	<0.5	2.5	28
Zone 1 S2	151.750378	-32.914897	<0.5	<0.5	<0.5	<0.5	1.6	0.7	5.7	5.6	1.8	2.0	4.3	2.8	1.8	<0.5	2.0	28
Zone 1 S4	151.752958	-32.910561	<0.5	<0.5	<0.5	<0.5	1.9	0.6	5.5	5.3	1.7	1.8	3.7	2.7	1.6	<0.5	2.0	27
Zone 1 S7	151.734307	-32.891691	<0.5	0.8	<0.5	<0.5	8.2	2.4	20	18	7.3	7.5	14	9.8	6.1	1.4	7.6	103

Note: PAH: 1 – Naphthalene, 2 – Acenaphthylene, 3 – Acenaphthene, 4 – Fluorene, 5- Phenanthrene, 6 – Anthracene, 7 – Fluoranthene, 8 – Pyrene, 9 - Benz(a)anthracene, 10 – Chrysene, 11 - Benzo(b)&(k)fluoranthene, 12 - Benzo(a)pyrene, 13 - Indeno(1,2,3-cd)pyrene, 14 - Dibenzo(a,h)anthracene, 15 - Benzo(g,h,i)perylene. Soil samples: public (Zone **A** S**B**; **A –** sampling zone number, **B** – sample site).
Sample marked with ** is a field duplicate.

Supplementary Data 3. Lead isotope compositions for soils, slag and galena. Standard deviations determined from repeat analysis (10 analyses) of one sample. Soil samples: public (Zone **A** S**B**; **A –** sampling zone number, **B** – sample site), private (PRS**XY**; **X** – property code, **Y** – sample number on property) and depth (SDP**X X-Y** cm; where **X** is the depth profile number and **X-Y** is the depth).

Sample	**x co-ordinate**	**y co-ordinate**	**$^{208}Pb/^{207}Pb$** **+/- 0.004**	**$^{206}Pb/^{207}Pb$** **+/- 0.004**	**$^{206}Pb/^{204}Pb$** **+/- 0.091**
PRS4C	151.747014	-32.899688	2.400	1.114	17.483
PRS11A	151.747014	-32.899688	2.365	1.092	16.863
PRS8C	151.735041	-32.891055	2.402	1.126	17.483
PRS20C	151.725239	-32.897365	2.352	1.079	16.474
Zone 1 S20	151.753067	-32.898278	2.411	1.131	17.483
Zone 1 S9	151.750283	-32.914881	2.374	1.091	16.892
Zone 2 S17	151.755342	-32.907642	2.345	1.068	16.584
Zone 2 S4	151.768639	-32.907889	2.361	1.085	16.807
Zone 2 S4*	151.768639	-32.907889	2.365	1.117	17.513
Zone 2 S17**	151.755342	-32.907642	2.355	1.071	16.474
Slag 1	***	***	2.319	1.044	16.077
Slag 2	***	***	2.543	1.318	21.097
SDP b 30-40 cm	151.759338	-32.906211	2.384	1.099	16.949
SDP c 30-40 cm	151.747180	-32.911957	2.370	1.093	16.835
SDP d 30-40 cm	151.758508	-32.932803	2.406	1.124	17.544
SDP e 20-30 cm	151.695323	-32.910189	2.489	1.198	18.727
Wallaroo Galena	***	***	2.640	1.477	24.727
Broken Hill Galena	***	***	2.319	1.044	16.155

Note: *field duplicate; **laboratory duplicate; ***GPS co-ordinates not applicable.

Supplementary Data 4. Relative abundances of phases were estimated from XRD patterns using the relative intensity ratio (RIR) method.

Group	Phase	Chemical composition	PRS3B	PRS3D	PRS4C	PRS7A	Zone 1 S7	Zone 1 S9	Zone 2 S1	Zone 2 S4	Zone 2 S15
Silicates	Clinopyroxene	$(Ca,Mg,Fe,Al)_2Si_2O_6$		*	***		***	**			*
	Olivine	$(Ca,Fe,Mg)_2SiO_4$		*	*		*	***			
	Zircon	$ZrSiO_4$	*	tr	*	*	*		*	*	*
	Vesuvianite	$Ca_{10}(Mg,Fe)_2Al_4(SiO_4)_5(Si_2O_7)_2(OH,F$				**					
	Melilite	$Ca_2(Mg,Fe,Zn)Si_2O_7$				*			tr	*	
	Amorphous glass	Si-Ca-Fe		***	***	***	**	***		***	*
	Quartz	SiO_2	tr						*		*
Oxides	Hematite	Fe_2O_3	*	***	**	***	**	**	*	**	tr
	Spinel series	$(Fe,Zn,Mg)(Fe,Al,Cr)_2O_4$	*	*	*	*	tr	*	*	**	*
	Goethite	FeOOH						tr		tr	
	Wuestite	FeO								tr	
	Rutile	TiO_2	**	tr	tr		*	tr	*	tr	*
	Ilmenite	$FeTiO_3$	tr						***		tr
	Corundum	Al_2O_3	*								

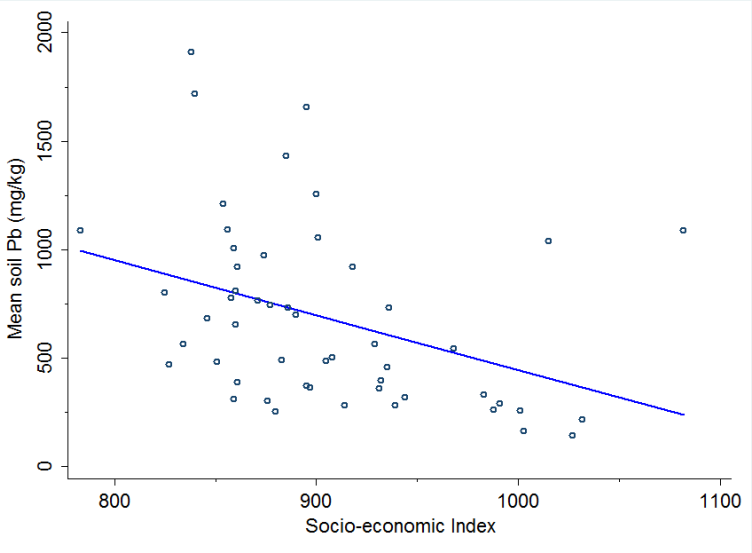
Note: *** abundant, ** common, * minor, tr trace

PRS3B – x co-ordinate: 151.754543; y co-ordinate: -32.930401
PRS3D – x co-ordinate: 151.747068; y co-ordinate: -32.899573
PRS4C – x co-ordinate: 151.750841; y co-ordinate: -32.914811
PRS7A – x co-ordinate: 151.753439; y co-ordinate: -32.910121
Zone 1 S7 – x co-ordinate: 151.743853; y co-ordinate: -32.912803
Zone 1 S9 – x co-ordinate: 151.750283; y co-ordinate: -32.914881
Zone 2 S1 – x co-ordinate: 151.761278; y co-ordinate: -32.915472

Zone 2 S4 – x co-ordinate: 151.768639; y co-ordinate: -32.907889
Zone 2 S15 – x co-ordinate: 151.761278; y co-ordinate: -32.915472

Appendix G

Supplementary Figure S1. Relationship between mean soil Pb of SA1 areas and socio-economic status (R^2=0.14, n=52, p<0.05).



Supplementary Table S2. Summary of mean soil Pb and socio-economic status by Aboriginality and age of house.

	Mean soil Pb (mg/kg)	SES
Aboriginal	765 (95% CI: 714, 816)	880 (95% CI: 877, 883)
non-Aboriginal	728 (95% CI: 708, 749)	892 (95% CI: 891, 894)
House built before 1940	884 (95% CI: 855, 913)	883 (95% CI: 882, 885)
House built after 1940	475 (95% CI: 456, 494)	905 (95% CI: 902, 907)

Supplementary Document S3. Comparison of socio-economic status between Aboriginal and non-indigenous homes (sourcing from NSW Government, 2017).

Tracking Aboriginal differences

In the table below, some indicators of community structure and well-being are calculated for Aboriginal people in Broken Hill. The difference or gap with non-Aboriginal people in Broken Hill is shown for 2011. Where Census data allows, changes in the Aboriginal rates are tracked over the decade.

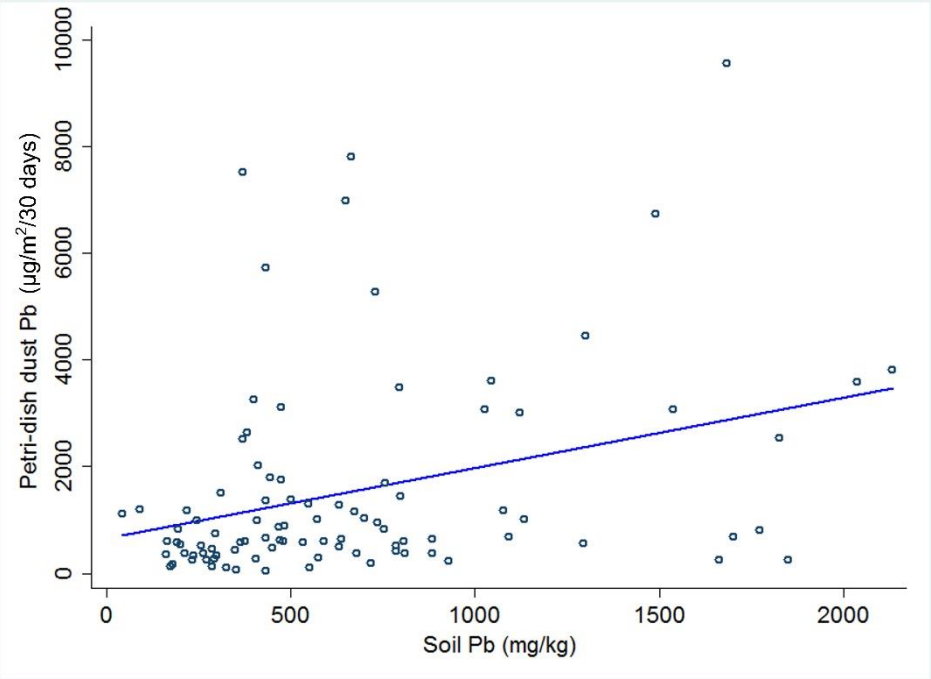
this colour indicates the rate was improving | this colour indicates the rate was fairly stable | this colour indicates the rate was worsening

Indicator	Rates in 2011			Change in Aboriginal rate	
	Aboriginal in Bkn Hill	non-Aboriginal in Bkn Hill *	Gap in 2011	2006-2011	2001-2006
home ownership % of households owning/buying their home	45%	77%	-32%	dn 4%	up 3%
household income median weekly income of households	$748	$790	-5%	up 21%	up 37%
workforce participation % of adults 15+ in labour force	46%	54%	-8%	same	up 6%
unemployment % of unemployed in workforce	22%	8%	+14%	dn 2%	dn 5%
employed employed adults as % of population	22%	41%	-19%	up 2%	up 4%
pre-school % of infants under 5 in education	17%	25%	-8%	same	-
teenage education % of 15–19 year-olds in education	55%	66%	-11%	up 12%	up 3%
children at school % of 5–14 year olds in education	81%	88%	-8%	dn 1%	dn 4%
Year 12 completion % of adults (15+) who have completed 12 years school	14%	24%	-10%	up 5%	up 2%
average schooling average years schooling for adults (aged 15+)	9.8 yrs	10.0 yrs	0.3 yrs	+0.4 yrs	+0.2 yrs
tertiary qualifications % of adults 15+ with a post-school qualification	40%	45%	-5%	up 3%	up 8%
degree % of adults 15+ with a degree or higher qualification	3%	8%	-4%	up 1%	same
postgrad % of adults 15+ with a postgraduate qualification	1%	2%	-1%	up 1%	same
disability* % of adults with a severe, long-term disability	5.5%	7.5%	-2.0%	up 0.2%	-
median income* median weekly income of adults (15+)	$355	$421	-16%	up 31%	up 8%

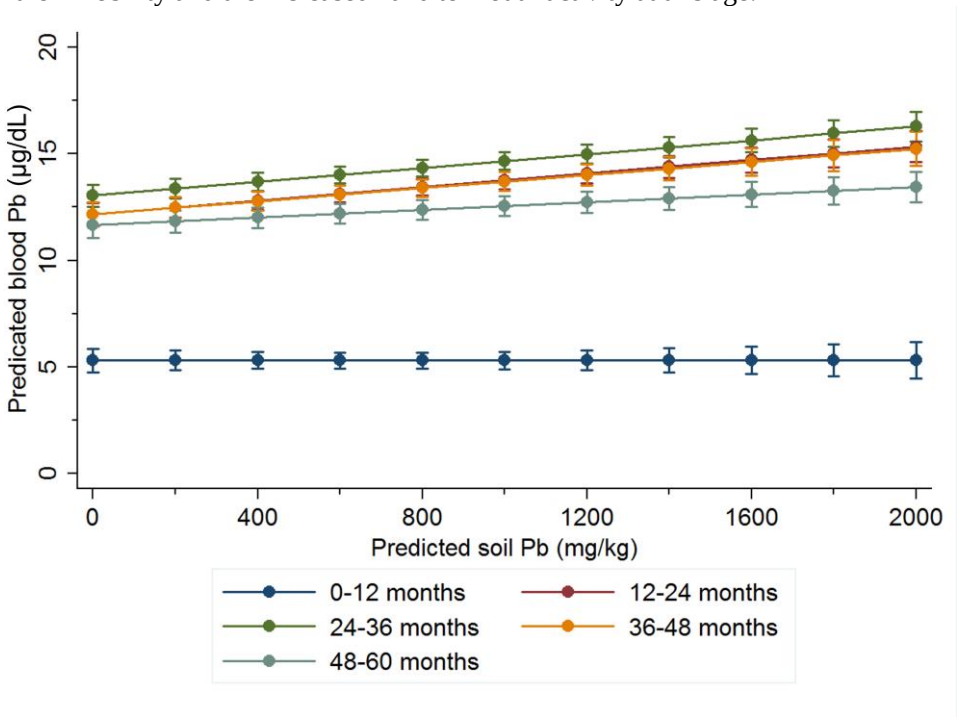
* Personal income and disability data compare Aboriginal rates with those of the whole population in Broken Hill, due to the way the ABS reports income and disability data.

Community Portrait of Broken Hill page 4

Supplementary Figure S4. Relationship between mean soil Pb and petri-dish dust Pb flux (μg/m^2/30 days) (R^2=0.11, n=94, p<0.05).



Supplementary Figure S5. Predicted PbB based on soil Pb (mg/kg) by age groups. Gradients of soil Pb versus PbB showing that that children aged 12-48 months are the most vulnerable to exposure, which is likely a function of their mobility and the increased hand to mouth activity at this age.



Supplementary Figure S6. Contaminated ceiling dust leaking into living spaces in older Broken Hill homes.

Supplementary References

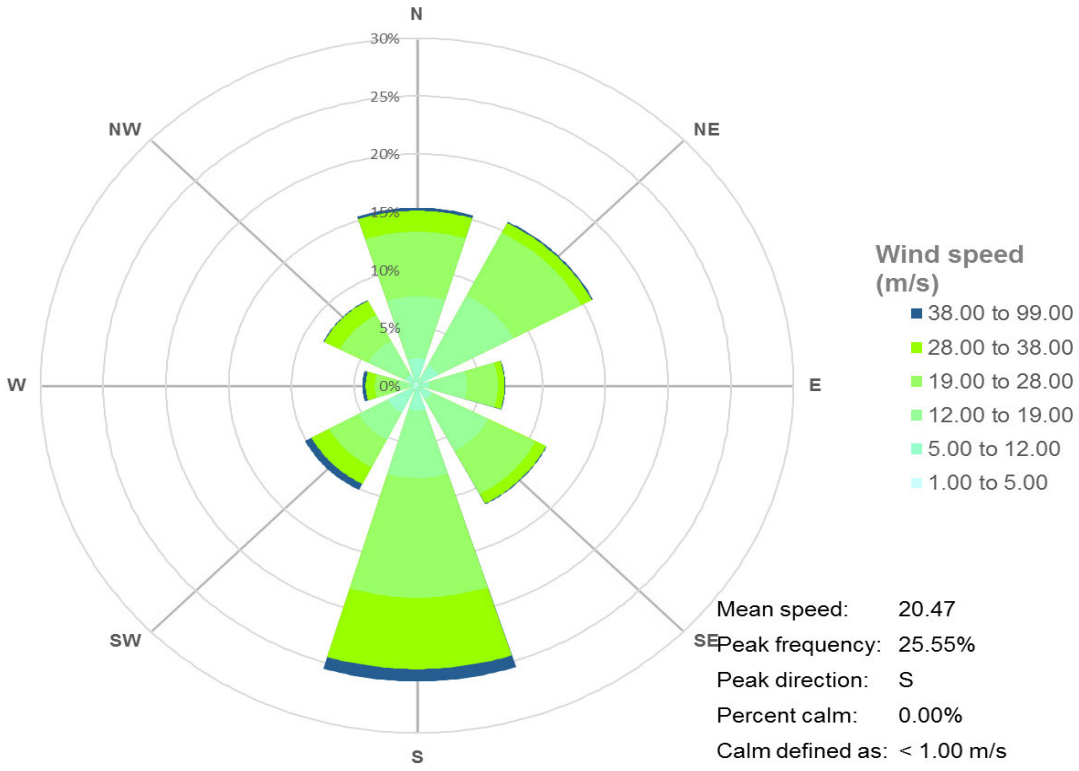
New South Wales (NSW) Government, 2017. Community Portrait Broken Hill LGA-A portrait of the Aboriginal community of Broken Hill, compared with NSW, from the 2011 and earlier Censuses. http://www.aboriginalaffairs.nsw.gov.au/pdfs/profiles/local-government-areas/Broken-Hill.pdf (accessed 11.07.17).

Appendix H

Supplementary Table S1. Reported estimates of atmospheric Pb emissions of Perilya Broken Hill Limited (NPI, 2017).

Years	Atmospheric Pb emissions (tonnes)
1999	0.07
2000	0.65
2001	0.79
2002	0.72
2003	0.79
2004	4.3
2005	4.2
2006	0.25
2007	0.51
2008	0.99
2009	0.68
2010	0.69
2011	11
2012	28
2013	27
2014	31
2015	29
2016	29
Total	169.64

Supplementary Figure S2. Rose of Broken Hill wind direction vs. wind speed in km/h (9 am, 01 Jun 2012 to 30 Jun 2016). The range of prevailing wind direction is from SSE to SSW.



Supplementary Table S3. Characteristics of variables of interest by wind directions.

	In prevailing direction	In non-prevailing direction
Aboriginal (observations & %)	479 (19.6%)	679 (28.2%)
non-Aboriginal (observations & %)	1962 (80.4%)	1732 (71.8%)
Distance (mean value)	3.87 km	3.46 km
SES (mean value)	919.38	875.98
<1 year of age (observations & %)	615 (25.2%)	556 (23.1%)
≥1 year of age (observations & %)	1826 (74.8%)	1855 (76.9%)

Notes: The SES data can not represent the real socio-economic status of Aboriginal homes but that of the corresponding census tract where Aboriginal children live.

Supplementary References

National Pollutant Inventory (NPI), 2017. Search by form. http://www.npi.gov.au/npidata/action/load/advance-search (accessed 08.08.17).

Appendix I

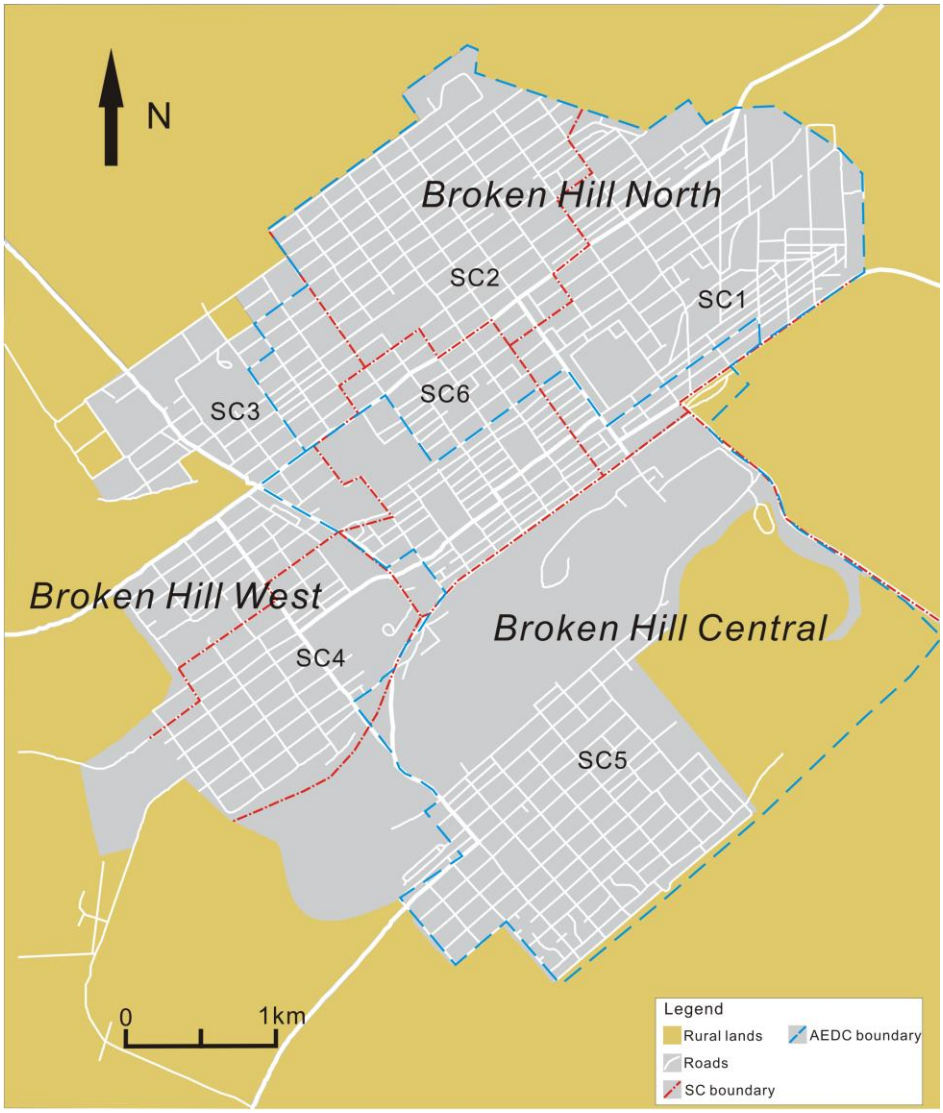
Supplementary Table S1. Arsenic, Cd and Pb concentration of 34 surface soils analyzed by ICP-MS across Broken Hill.

School catchment	Sample name	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
SC1	NBH1_0-2	29	17	2890
	NBH5_0-2	16	12	1060
	NBH4_0-2	4.4	1.4	150
SC2	NBH3_0-2	6.1	1.9	530
	LOLE5_0-2	6	1.4	300
	LOLE6_0-2	4	1.03	395
	HS6_0-2	2.3	0.94	170
SC3	NBH2_0-2	3.8	0.61	140
	BHW3_0-2	5	0.74	170
	LOLW4_0-2	2	0.27	46
SC4	WBH1_0-2	7.1	2	330
	WBH2_0-2	100	9.2	1340
	LOLW3_0-2	8	1	200
SC5	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
	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
SC6	NBH6_0-2	9.9	3.9	1300
	NBH8_0-2	14	3.9	1170

Supplementary Table S2. Lead concentration of 23 surface soils analyzed by portable XRF across Broken Hill.

School catchment	Sample name	Pb (mg/kg)
SC1	Soil_11	102
	Soil_12	45
	Soil_13	1017
	Soil_16	1243
	Soil_17	557
SC2	Soil_3	61
	Soil_4	77
	Soil_14	50
	Soil_15	143
SC3	Soil_9	116
	Soil_10	58
SC4	Soil_7	175
	Soil_8	279
SC5	Soil_18	6925
	Soil_19	1691
	Soil_20	617
	Soil_21	680
	Soil_22	1692
	Soil_23	2272
SC6	Soil_1	1093
	Soil_2	248
	Soil_5	1248
	Soil_6	429

Supplementary Figure S3. 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 S4. Summary of children developmentally vulnerable in different areas based on national and Broken Hill local community levels.

Community	Number of children surveyed	Proportion of children developmentally vulnerable (%)							
		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

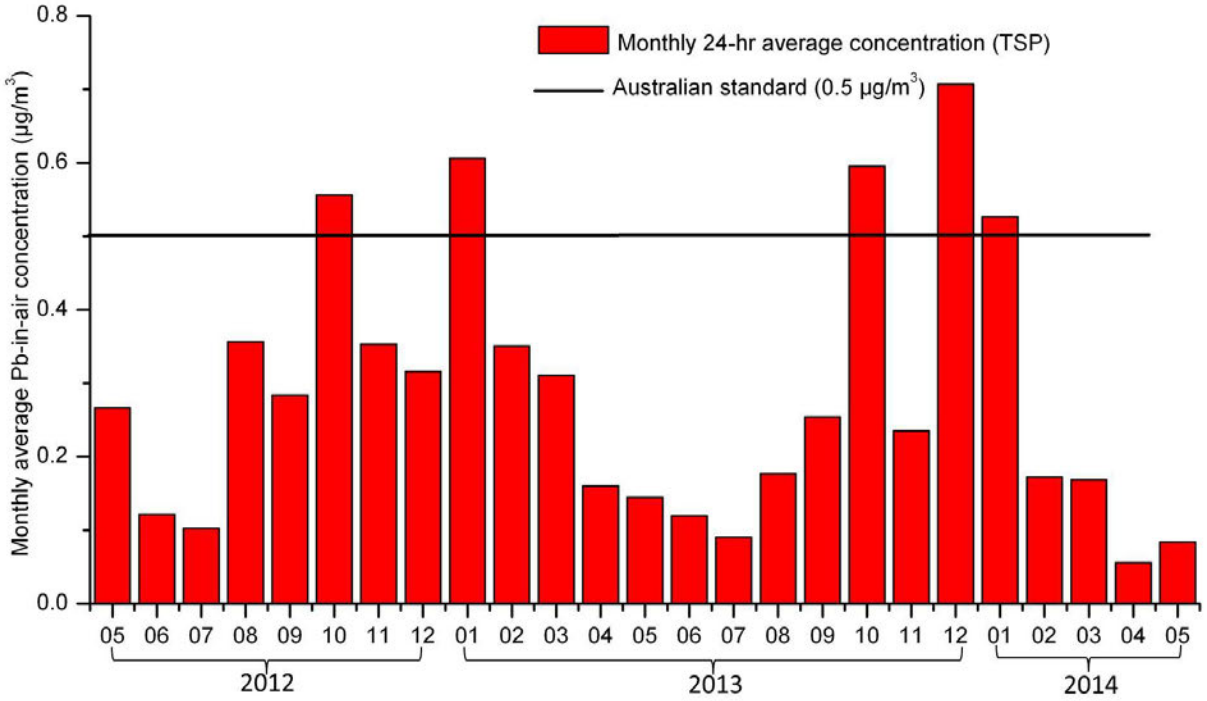
Note: the Australian Early Development Census (AEDC) data and Broken Hill local community SEIFA data are from Australian Early Development Census (AEDC), 2014a. The Australian national SEIFA average is from Australian Bureau of Statistics (ABS), 2013. AEDC results are typically reported as proportions 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).

Supplementary Table S5. Summary of Broken Hill schools.

School codes	Primary school	Secondary school
A1	✔	
A2	✔	
A3	✔	
A4	✔	
A5	✔	
A6	✔	
A7	✔	
A8	✔	
A9		✔
A10		✔

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.

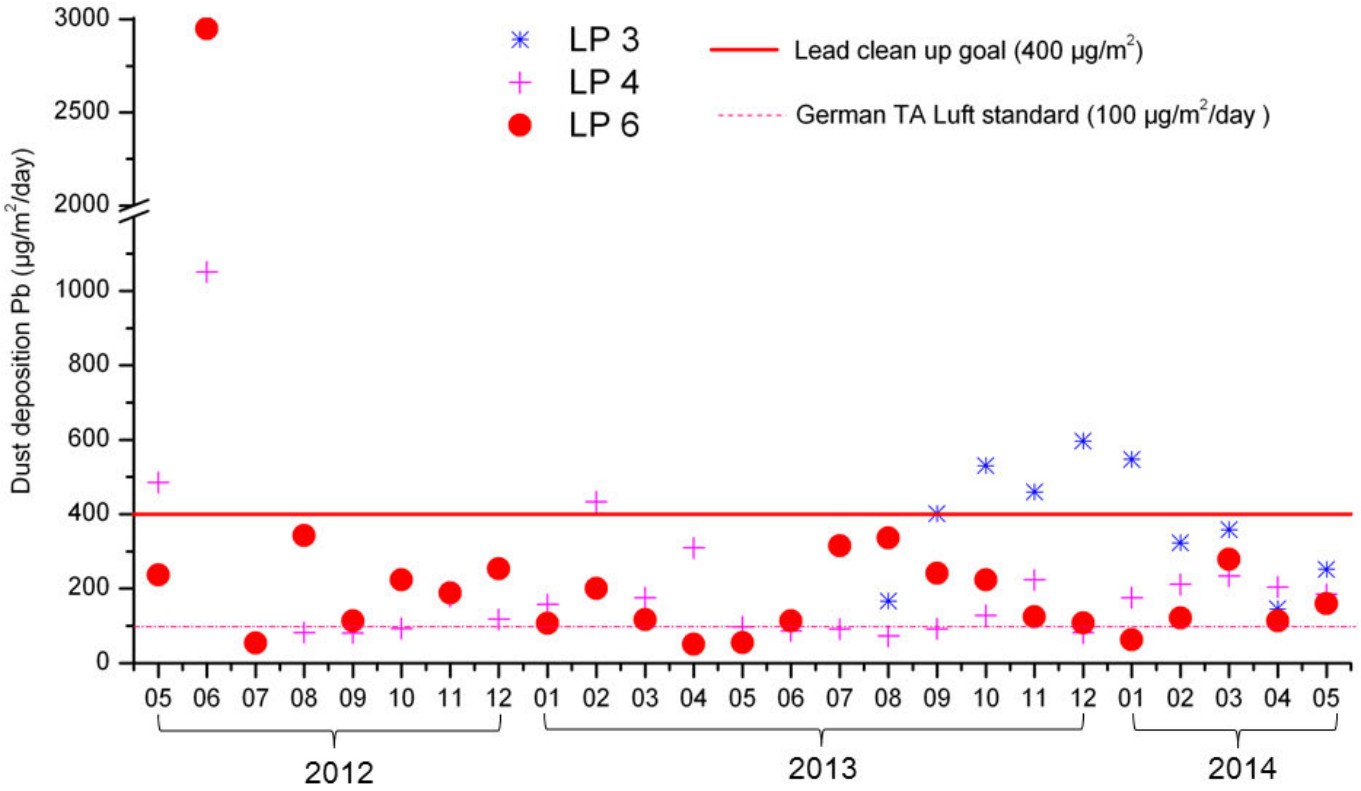
Supplementary Figure S6. Monthly 24-h average of lead-in-air concentration based on TSP (µg/m^3) recorded at LP12 station between May 2012 and May 2014. Measurement of TSP and Pb in TSP is undertaken every 6th day for 24-h.



Supplementary Table S7. Monthly 24-h average lead-in-air concentration based on TSP (µg/m^3) and dust gauge deposited Pb (g/m^2/month) recorded between May 2012 and May 2014 (Perilya Limited, 2015). ND: no data.

Date	Monthly Average lead-in-air Concentration (µg/m^3)	Total deposited Pb (g/m^2/month)			Total deposited Pb (µg/m^2/day) (original data calculated over 30 days)		
	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	*ND*	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 Figure S8. Monthly average lead dust loading (µg/m^2/day) recorded at dust gauge stations (i.e., LP3, LP4 and LP6) between May 2012 and May 2014.



Supplementary Table S9. Arsenic, Cd and Pb concentrations in dust wipes for school A9 and four properties in Broken Hill.

Property	Location	As (µg/m^2)	Cd (µg/m^2)	Pb (µg/m^2)
School A9 (2012 samples)	BH_DW1_1907 (PE STOREROOM)	510.9	211.7	52919.7
	BH_DW2_1907 (WINDOWSILL)	83.8	46.3	6283.5
	BH_DW3_W_SILL	475.7	62.7	23495.7
	BH_DW4_W_SILL	410.8	57.7	20612.8
	BH_DW5_W_SILL	552.6	71.3	27775.8
School A9 (2013 samples)	PE_STOREROOM WALL	86.96	30.43	10434.78
	PE_STOREROOM AIR VENT	161.33	74.76	21248.97
	PE_STOREROOM SHELF	686.87	404.04	86060.61
	WINDOW SILL 1 FAR (NR PE STORE)	52.29	16.09	13837.49
	WINDOW SILL 2-4TH (NR PE STORE)	41.03	12.07	3298.47
	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
House 1	SURFACE 1- ELECTRICAL BOX	48.67	8.00	2466.67
	SURFACE 2- PLAY EQUIPMENT	6.11	1.11	355.56
	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
House 2	WATER TANK	7.67	1.67	444.44
	KITCHEN_SILL	*BDL*	*BDL*	125.32
	PIANO	2.22	1.07	131.63
House 3	SURFACE 1_GLASS TABLE	17.78	4.00	822.22
	SURFACE 2_KITCHEN SILL	15.00	3.50	600.00
	SURFACE 3_WINDOW SILL_SOUTH SIDE	73.98	11.05	2551.02
House 4	SURFACE 1 WATER TANK	122.22	63.33	17888.89
	SURFACE 2 LOUNGE DOOR	12.29	7.84	2268.43
	SURFACE 3 WINDOW SILL LOUNGE	1.65	1.50	278.97
	SURFACE 4 TOP OF KITCHEN CUPBOARD	0.91	0.84	160.06

	SURFACE 5 WALL ABOVE COT	*BDL*	*BDL*	52.83

Note: *BDL* – below detection limit.

Supplementary Table S10. 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 (in review). 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.

Supplementary Table S11. Arsenic, Cd and Pb concentrations in soil for the school A9 and four domestic residences in Broken Hill.

Property	Sample name	As (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
School A9	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
	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
House 1	SOIL_1 BACK GARDEN	3.2	0.5	100
	SOIL_2 VEGGIE PATCH	1.1	*BDL*	15
	SOIL_3 FRONT GARDEN	3.6	0.71	280
House 2	SOIL_1 FRONT	5.1	1.5	420
	SOIL_2 SIDE	16	5.1	1130
	SOIL_3 BACK	4.5	1.2	250
House 3	SOIL_1 VEGGE PATCH	1.8	*BDL*	14
	SOIL_2 FRONT	2.7	0.5	140
	SOIL_3 BACK	3	0.94	300
House 4	SOIL_1 VEGGIE PATCH	11	7.2	2260
	SOIL_2 BACK YARD	3	98	360
	SOIL_3 FRONT YARD	15	8.4	2160

Note: *BDL* – below detection limit.

Supplementary Table S12. Australian Early Development Census (AEDC) results standardized by socio-economic index of the Broken Hill central children vulnerability.

Community	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
Broken Hill Central	2.4	2.4	2.4	1.7	2.9	1.7	2.6
Broken Hill North	1.8	1.1	0.6	1.4	1.8	1.3	1.5
Broken Hill West	1.5	0.9	1.1	1.5	1.4	1.2	1.5
Broken Hill average	1.9	1.5	1.4	1.5	2.0	1.4	1.9

Supplementary Table S13. Summary of the National Assessment Program – Literacy and Numeracy (NAPLAN) data from Broken Hill schools.

Year 3															
A1	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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	366	334	424	364	333	396	352
2013	360	419	361	323	416	356	337	411	352	342	428	363	331	397	348
A2	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A3	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A4	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A5	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A6	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A7	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A8	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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

Year 5

A1	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A2	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A3	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
2008	500	484	463	485	486	467	482	484	466	491	496	472	505	476	455
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

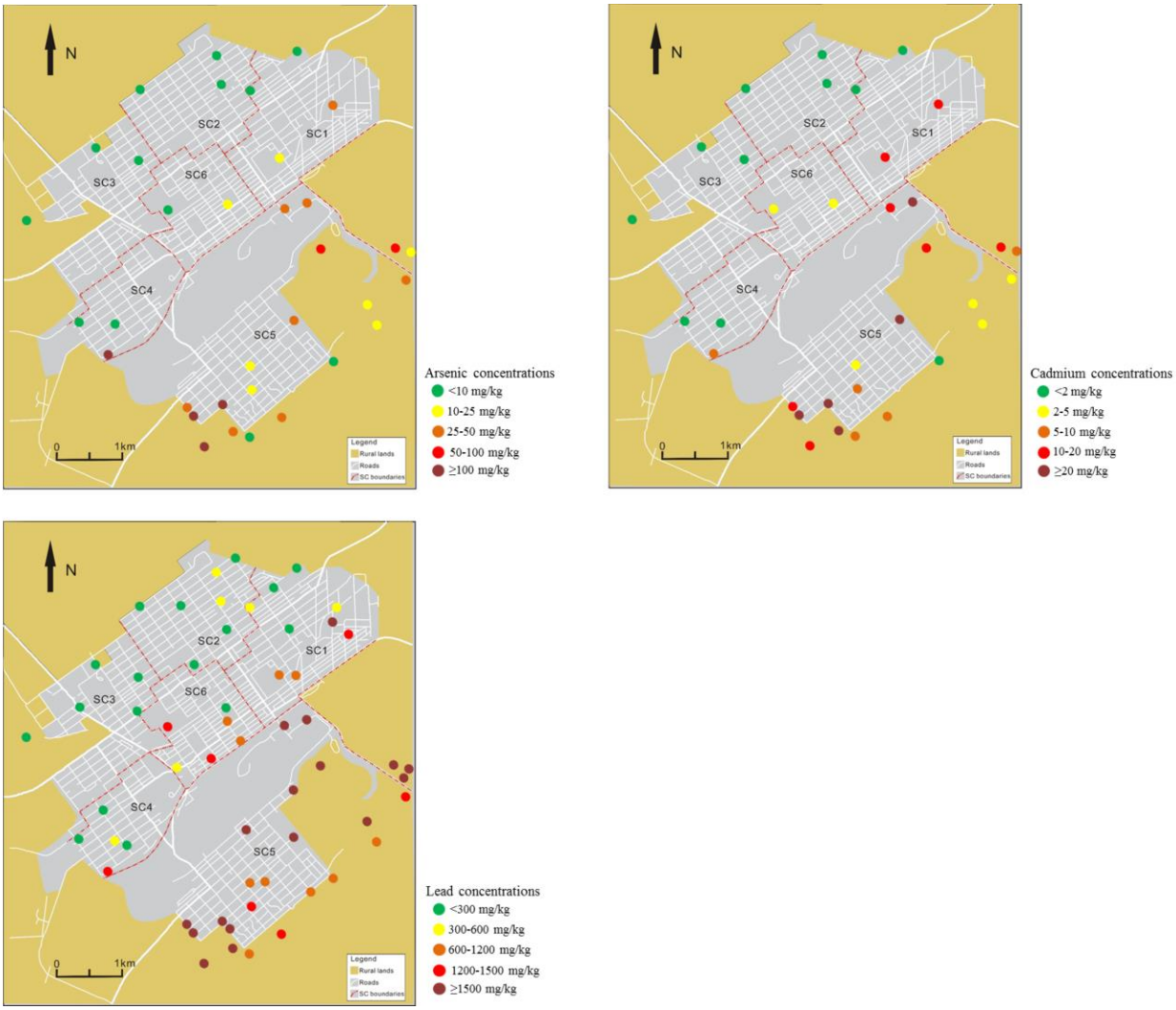
A4	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
2008	462	484	460	477	486	464	471	484	463	473	496	467	472	476	451
2009	498	494	468	447	485	462	478	487	466	470	500	469	474	487	463
2010	445	487	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
A5	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A6	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
A7	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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	491
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
A8	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
Year 7															
A9	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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	495	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
A10	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
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
2013	502	541	504	464	517	476	518	549	512	482	535	492	521	542	505
Year 9															
A9	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
2008	559	578	555	539	569	540	549	577	554	546	569	542	558	582	555
2009	554	580	557	534	569	537	575	576	552	554	574	548	561	589	562

2010	541	574	543	533	568	527	560	579	549	544	579	542	549	585	550
2011	550	580	549	519	566	517	555	581	549	543	572	534	551	583	548
2012	553	575	541	515	554	510	552	577	545	542	573	538	555	584	549
2013	561	580	551	497	554	507	565	583	552	542	573	531	555	584	544
A10	D1	AUS average	Similar average	D2	AUS average	Similar average	D3	AUS average	Similar average	D4	AUS average	Similar average	D5	AUS average	Similar average
2008	557	578	559	512	569	545	559	577	558	546	569	548	550	582	559
2009	550	580	561	513	569	543	554	576	556	545	574	553	552	589	567
2010	549	574	546	464	568	532	544	579	552	534	579	547	544	585	553
2011	551	580	553	514	566	523	560	581	553	549	572	539	556	583	552
2012	541	575	543	487	554	513	546	577	547	540	573	541	547	584	551
2013	547	580	547	476	554	501	556	583	548	528	573	525	541	584	539

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 Figure S14. Soil As, Cd and Pb concentrations across Broken Hill six school catchments.



Supplementary Table S15. Summary of children developmentally vulnerable in different areas based on national, Mount Isa and Port Pirie local communities levels.

Community	Number of children surveyed	Proportion of children developmentally vulnerable (%)							
		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.

Supplementary Table S16. Australian Early Development Census (AEDC) results standardised by socio-economic index based on the Mount Isa and Port Pirie local communities levels.

	Proportion of children developmentally vulnerable (%)						
	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**
Happy Valley/Parkside	0.5	0.9	0.9	1.3	0.0	0.6	0.8
Healy	0.3	1.4	1.7	1.0	0.4	0.7	1.2
North Mount Isa	1.9	2.2	2.4	2.3	2.3	1.8	2.5
Townview and Surrounds	1.4	1.1	0.4	2.6	1.7	1.4	1.3
Mount Isa average	1.0	1.4	1.4	1.8	1.1	1.2	1.5
Port Pirie and surrounds	1.7	1.7	1.8	1.4	0.7	1.3	1.4
Broken Hill average	1.9	1.5	1.4	1.5	2.0	1.4	1.9

Note: Happy Valley/Parkside, Healy, North Mount Isa and Townview and surrounds are the communities of Mount Isa. The Broken Hill average: The mean values of the vulnerable proportions of Broken Hill central, North and West.

Supplementary References

Australian Bureau of Statistics (ABS), 2013. 2033.0.55.001 Local Government Area, Indexes, SEIFA 2011. http://www.abs.gov.au/AUSSTATS/abs@.nsf/DetailsPage/2033.0.55.0012011?OpenDocument (accessed 02.05.15).

Australian Curriculum, Assessment and Reporting Authority (ACARA), 2015. My School. http://www.myschool.edu.au/ (accessed 15.05.15).

Australian Early Development Census (AEDC), 2013. Australian Early Development Census 2012 Summary Report. https://www.aedc.gov.au/resources (accessed 10.03.15).

Australian Early Development Census (AEDC), 2014a. Far West NSW community: Percentage of children developmentally vulnerable in 2012. http://www.aedc.gov.au/data/data-explorer?id=43165 (accessed 02.05.15).

Australian Early Development Census (AEDC), 2014b. Mount Isa community: Percentage of children developmentally vulnerable in 2012. http://www.aedc.gov.au/data/data-explorer?id=42747 (accessed 02.05.15).

Australian Early Development Census (AEDC), 2014c. Port Pirie City and Districts community: Percentage of children developmentally vulnerable in 2012. http://www.aedc.gov.au/data/data-explorer?id=42769 (accessed 02.05.15).

Kristensen, L. J., and Taylor, M. P., Unravelling the ‘miners myth’ that environmental contamination in mining towns is naturally occurring. in review.

Perilya Limited, 2015. Monthly reports: environmental reporting. http://www.perilya.com.au/health--safety--environment/environment/reports (accessed 10.03.15).

Appendix J

Supplementary Document S1. Ethics approval letter from the Greater Western Human Research Ethics Committee.

20 January 2015

Health
Western NSW
Local Health District

Mr Chenyin Dong
PhD Candidate
Environmental Science, Environment and Geography
Macquarie University
No. 831 E7A Building
NORTH RYDE NSW 2109

Dear Mr Dong,

Greater Western Human Research Ethics Committee (HREC)
Project No. LNR/14/GWAHS/112

Evaluating the Relationship between Soil Lead Exposures, Environmental Dust Lead Deposition and Childhood Blood Lead Measures

Thank you for responding to the HREC's request for clarification and further information for the above project. The HREC sub-committee reviewed your responses at its meeting held on 20 January 2015.

The Greater Western HREC has been accredited by the NSW Ministry of Health as a lead committee to provide the single ethical and scientific review of proposals, to conduct research within the NSW public health system. Further, this committee is constituted and operates in accordance with the National Health and Medical Research Council's National Statement on Ethical Conduct in Human Research and the CPMP/ICH Note for Guidance on Good Clinical Practice.

I am pleased to advise that the HREC has granted ethical approval of this research project. The following documentation has been reviewed and approved by the HREC:

- LNR form (AU/6/C77B19) - dated 03/11/2014
- Study Protocol – undated, as submitted on 06/11/2014
- Researcher Response re purposeful soil sampling - dated 05/01/2015

Greater Western Human Research Ethics Committee
Incorporating the Western NSW & Far West Local Health Districts

PO Box 143, Level 1, 230 Howick Street, BATHURST NSW 2795
Tel: (02) 6330 5941 Fax: (02) 6332 3140

The project is approved to be conducted at the following NSW Public Health sites:

- Far West Local Health District

Please note the following conditions of approval:

1. The coordinating investigator will immediately report anything which might warrant review of ethical approval of the project in the specified format, including any unforeseen events that might affect continued ethical acceptability of the project.

2. Proposed changes to the research protocol, conduct of the research, or length of HREC approval will be provided to the HREC for review in the specified format.

3. The HREC will be notified, giving reasons, if the project is discontinued at a site before the expected date of completion.

4. The coordinating investigator will provide an annual report to the HREC and at completion of the study in the specified format.

HREC approval is valid for 4 years from the date of this letter.

This HREC approval letter constitutes ethical approval only. You are required to submit a site specific assessment application for each site at which you wish to conduct this project. You must not commence this research project at a site until separate authorisation from the Chief Executive or delegate of that site has been obtained. A copy of this letter must be forwarded to all Principal Investigators at every site for submission to the relevant Research Governance Officer as part of the site specific assessment process.

Should you have any queries about your project please do not hesitate to contact the Greater Western HREC Executive Officer on (02) 6339 5601 or via email ethics.committee@gwahs.health.nsw.gov.au .

Please quote HREC Reference No. *LNR/14/GWAHS/112* in all correspondence.

The HREC wishes you every success in your research.

Yours sincerely

Suzanne Degiorgio
Ethics & Research Governance Officer
Western NSW & Far West Local Health Districts

Supplementary Document S2. Ethics approval from Macquarie University Human Research Ethics Committee.

MACQUARIE University

CHENYIN DONG <chenyin.dong@students.mq.edu.au>

Fwd: Query about procedure for applications in which another HREC is primary

Ethics Secretariat <ethics.secretariat@mq.edu.au> Fri, Oct 16, 2015 at 4:17 PM
To: CHENYIN DONG <chenyin.dong@students.mq.edu.au>
Cc: Mark Taylor <mark.taylor@mq.edu.au>

Dear Chenyin

Thank you for sending these documents through.

Please take this email as confirmation that the project "Evaluating the relationship between soil lead exposures, environmental dust lead deposition and childhood blood lead measures" (Macquarie University Ethics ref: 5201500832) has been noted by the Macquarie University Research Office.

This project has received ethics approval from the Greater Western Area Health Service Human Research Ethics Committee.

Many thanks for providing this information for our records. No further action is required. Any amendments must be submitted to the approving HREC.

Kind regards
Fran Thorp
[Quoted text hidden]