Environmental Metals in Australian Historic Lichens, Fungi and Wildfire Ash

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This thesis is presented for the degree of Doctor of Philosophy.

Cover photos:

Lichens were studied in this research.

Grey-white ash samples were collected from Forcett wildfire site.

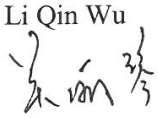
DECLARATION

I certify that the work in this thesis entitled 'Environmental Metals in Australian Historic Lichens, Fungi and Wildfire Ash' has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree at any other university or institution other than Macquarie University.

I also certify that the thesis is an original piece of research and it has been written by me. Any help and assistance that I have received in my research work and the preparation of the thesis itself has been appropriately acknowledged.

In addition, I certify that all information sources and literature used are indicated in the thesis.

Li Qin Wu



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ABSTRACT

Australia has a well-established record of environmental metal (e.g. Cu, Pb and Zn) contamination dating back to early mining activities in South Australia in the 1840s. Over the last two centuries, base metal mining and processing, industrial development, the use of leaded petrol in motor vehicle and urban expansion have generated large-scale emissions and depositions of metals into the environment. To date, work to reconstruct the historic and contemporary extent of human impact on environmental contamination in Australia, using biological archives and the products of wildfires, has been spatially limited.

This thesis focuses on reconstructing the historic and contemporary records of trace metal atmospheric emissions using two lichen genera and one fungus collected over a 150-year period from the Greater Sydney area and from central and southern Victoria. Recycling of industrial Pb is assessed via measurement of ash residue released from four Australian wildfires that occurred in 2012 and 2013. The Pb isotope ratios of lichens, fungi, air filters, ash, river sediments, soils and rocks are also determined and combined with published isotopic data of various potential emission sources to elucidate the relative importance of each likely emission source.

The findings in this thesis show that early metal mining activities have been responsible for elevated Cu, Pb and Zn levels observed in lichen and fungi archives dating back to the 1880s, particularly in central and southern Victoria. Elevated median Pb and Zn values were also measured in archival samples from the leaded petrol era (1932–2001) for both the Greater Sydney and central and southern Victoria regions. Peak Pb enrichments (relative to upper crustal Pb concentrations) were found in the Greater Sydney samples during this time. Lower median Pb levels were found in samples collected post 2002, following the cessation of leaded petrol consumption in 2002. The Pb concentrations measured in ash residues were low, with the exception ash samples from the Duffys Forest on the northern outskirts of Sydney, where median Pb values were an order of magnitude above the local background soil and rock samples.

The Pb isotope ratios of lichen and fungi samples in the Greater Sydney area and from central and southern Victoria show a marked fall from the period of 1850–1931 to the period of 1932–1984, following the introduction of leaded petrol in 1932. The Pb isotopic compositions of wildfire ash demonstrate that, in addition to lithogenic Pb, anthropogenic inputs from former leaded petrol deposition are identifiable. Despite the removal of Pb from petrol, the contemporary lichen and fungi samples and wildfire ash deposits investigated in this study

demonstrate that emissions from metal sources are persistent in the environment. Thus, while the data indicates that contemporary impacts from environmental emissions are reduced, the evidence shows that the consequences of the legacy of contamination persist. The issue of environmental metal contamination remains a significant and ongoing challenge for scientists addressing accurately the sources and deleterious consequences of toxic metal emissions on both environmental systems and human health.

TABLE OF CONTENTS

Notes regarding thesis format and author contributions to publications

Chapters within this thesis have been written as manuscripts suitable for publication in relevant scientific journals, together with supporting text to link the thesis. The first chapter consists of a broad introduction to the scientific background, the aims of the study and details of the study locations. These objectives are addressed in the four studies that comprise Chapters 2 to 5. A summary of how each paper fits into the overall thesis is presented at the commencement of each of these chapters. Chapter 6 presents the discussion and implication section of the thesis, which examines the overall findings and places them in context with the international literature. Chapter 7 details the thesis conclusions.

CHAPTER TWO: Australian atmospheric lead deposition reconstructed using lead concentrations and isotopic compositions of archival lichen and fungi

Wu, L. (75%), Taylor, M.P. (18%), Handley, H.K. (5%), Wu, M. (2%), 2016. Australian atmospheric lead deposition reconstructed using lead concentrations and isotopic compositions of archival lichen and fungi. *Environmental Pollution* 208, 678-687.

The concept of this paper was developed by myself and Prof. Taylor. I visited the various herbaria where I selected the relevant lichen and fungi specimens and also carried out all the fieldwork and laboratory analyses. Prof. Taylor, Dr. Handley and Dr. Wu discussed the results and edited and reviewed the paper prior to publication.

CHAPTER THREE: Insights into past atmospheric lead emissions using lead concentrations and isotopic compositions in historic lichens and fungi (1852–2008) from central and southern Victoria, Australia

Wu, L. (75%), Taylor, M.P. (15%), Handley, H.K. (8%), Gulson, B.L. (2%), 2016. Insights into past atmospheric lead deposition from lead concentrations and isotopic compositions of historic lichens and fungi (1852-2008) from central and southern Victoria, Australia. *Atmospheric Environment* 139, 46-55.

This paper was developed by myself and Prof. Taylor. I visited the relevant herbaria and selected suitable lichen and fungi samples. I conducted all the laboratory analyses. Fieldwork for this study was jointly carried out by myself, Prof. Taylor and Dr. Handley. Prof. Taylor, Dr. Handley and Emeritus Prof. Gulson assisted with data interpretation and reviewed and edited the text.

CHAPTER FOUR: Accumulation of atmospheric trace metals in historic lichens and fungi in eastern and southeastern Australia

Wu, L. (80%), Taylor, M.P. (12%), Handley, H.K. (8%). Accumulation of atmospheric trace metals in historic lichens and fungi in eastern and southeastern Australia. To be submitted to *Science of the Total Environment*.

I developed the concept for this paper, visited the appropriate herbaria and selected suitable herbarium specimens for the study and carried out all the laboratory analyses. The text was edited and reviewed by Prof. Taylor and Dr. Handley.

CHAPTER FIVE: Recycling of industrial lead contamination during Australian wildfires

Wu, L. (70%), Taylor, M.P. (25%), Handley, H.K. (5%). Recycling of industrial lead contamination during Australian wildfires. Submitted to *Environmental Science & Technology*.

The concept for this paper came from Prof. Taylor and it was developed further by Prof. Taylor and myself. Prof. Taylor and I worked together to complete the field work for the study. I carried out the laboratory analyses. The text was edited and reviewed by Prof. Taylor and Dr. Handley.

Acronyms and Abbreviations

ABS	Australian Bureau of Statistics
Ag	silver
Al	aluminum
As	arsenic
CA	Cluster Analysis
CBD	Central Business District
Cd	cadmium
Cu	copper
EFs	Enrichment Factors
EPA	Environment Protection Authority
Fe	iron
Hg	mercury
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
kt	kilotons
mg/kg	milligram per kilogram
MEL	Melbourne
Mn	manganese
Mt	megaton
NEPM	National Environment Protection Council
Ni	nickel
NMI	National Measurement Institute
NPI	National Pollutant Inventory
NSW	New South Wales
NT	Northern Territory
Pb	lead
PCA	Principal Component Analysis
QLD	Queensland
SA	South Australia
TAS	Tasmania
Th	thorium
Ti	titanium
TSP	Total Suspended Particulates
µg/g	microgram per gram (units of metal in lichen and fungi measurement)
$\mu g/m^3$	microgram per cubic metre (units of lead in air measurement)
U	uranium
USA	United States of America
VIC	Victoria
WA	West Australia
Zn	zinc

CHAPTER 1: INTRODUCTION

1.1 Metal Pollution

Toxic metals such as cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn) are widely distributed as environmental pollutants in ecosystems. Accumulation of toxic metals (e.g. Cd, Hg, Pb) over large areas and for long periods of time can pose a serious threat to the environment and human health (Nriagu, 1996; Martinez-Cortizas et al., 1997; Kampa and Castanas, 2008; Needleman, 2008; Dai et al., 2012). The environmental impacts resulting from various human activities have triggered significant changes in the total circulation of atmospheric metal emissions. Lead is one of the most widespread pollutants and is known to have potentially harmful effects on human health, especially that of infants, children and pregnant women (Needleman et al., 1990; Gulson et al., 1997; Canfield et al., 2003; Lanphear et al., 2005; NTP, 2012). Therefore, to ensure the protection of environmental and human health, it is imperative that the impacts of toxic metals on ecosystems be quantified and where necessary addressed with mitigation strategies to limit further preventable toxic exposures.

1.1.1 An Overview of Atmospheric Metal Emissions

Over the last four decades, global atmospheric inventories of toxic metals have provided critical information relating to the trajectories of atmospheric cycling of toxic elements on a regional and local scale (Ferry et al., 1973; Andersen et al., 1978; Nriagu and Pacyna, 1988; Bollhöfer and Rosman, 2002; Nickel et al., 2014; de Paula et al., 2015). Many studies have identified a mixture of lithogenic and anthropogenic sources of atmospheric toxic element emissions (Pacyna, 1984; Nriagu, 1989; Bollhöfer and Rosman, 2000, 2001; McConnell et al., 2014). The principal lithogenic sources of atmospheric metal emissions are wind-blown soils, volcanoes and fumaroles, sea spray, wildfires and biogenic origins (e.g. Nriagu, 1989). In addition to lithogenic sources, anthropogenic inputs, including non-ferrous metal production, combustion of leaded petrol and general industrial activities (e.g. coal combustion, waste incineration, smelters and thermal power stations) are identifiable in many regions (Nriagu, 1979; Zoller, 1984; Boutron et al., 1994; Rosman et al., 1994; Bollhöfer and Rosman, 2000, 2001; Von Storch et al., 2003; Komárek et al., 2008; Lahd Geagea et al., 2008; Kelly et al., 2009; Ndungu et al., 2016).

1.1.1.1 Mining and Metal Processing

Mining and metal production has been ongoing for about 7000 years, starting in China (Lee et al., 2008) and having a marked effect on environmental quality from Roman times onwards (Rosman and Chisholm, 1996). The impact of Roman mining and smelting was such that its

fingerprint has been identified in Arctic ice cores (Hong et al., 1994, 1996; Rosman et al., 1997). In recent times, environmental metal contamination originating from mining and metal production has received increasing attention at a global scale (Nriagu, 1994; Dudka and Adriano, 1997; Pacyna and Pacyna, 2001; Liu et al., 2005; Ettler et al., 2006; Csavina et al., 2012; Resongles et al., 2014). It has been estimated that the global Cu production increased from ~3 kilotons (kt) in 1750 to 15.7 megatons (Mt) in 2008 (Mudd, 2009) and that in excess of 3.5 Mt of Pb and more than 11 Mt of Zn was produced globally in 2008 (Mudd, 2009). Shortly after European settlement of Australia in 1788, mining and metal production began in earnest in South Australia in the 1840s (Drew, 2011). One of the world's largest Pb-Zn-Ag (silver) ore bodies was discovered at Broken Hill in western New South Wales (NSW) during the early 1880s (Solomon, 1988). Mining and metal production at Broken Hill have resulted in substantial environmental and human problems both within and beyond the mining community (Thompson, 1893; Gulson et al., 1994a; Gulson et al., 1994b; Lyle et al., 2001; Boreland et al., 2002; Lesjak et al., 2013; Taylor et al., 2014; Dong et al., 2015; Kristensen et al., 2015; Kristensen and Taylor, 2016). Mining activities at another major Pb-Zn-Ag-Cu deposit, Mount Isa, located in north-western Queensland, has also triggered environmental and health issues similar to those identified at Broken Hill (Parry, 2000; Mackay et al., 2007; Taylor et al., 2009; Munksgaard et al., 2010; Taylor et al., 2010; Mackay et al., 2013). In addition to ores mined at Broken Hill and Mount Isa, other base metal mines in Australia include Olympic Dam (South Australia), McArthur River (Northern Territory), Cannington Mine (Queensland) and Rosebery (Tasmania).

1.1.1.2 Leaded Petrol

Industrial activities include consumption of leaded petrol. Leaded petrol has been an important anthropogenic source of global atmospheric Pb burden since the 1920s (Nriagu, 1990). During the second half of the last century, emissions from leaded petrol accounted for 75% of global atmospheric Pb (Dunlap et al., 2008). Leaded petrol was introduced to the Australian market in 1932 and phased-out in 2002 (Cook and Gale, 2005). In the 70-year period of Australian leaded petrol consumption, Kristensen (2015) calculated that over 240,000 tonnes of Pb were released into the atmosphere (Figure 1.1). Lead emissions from leaded petrol peaked in the early 1970s to the 1980s and declined thereafter following the introduction of unleaded petrol in 1985 and the concomitant reduction in allowable Pb petrol concentrations. Consequently, Pb concentrations in the atmosphere have gradually declined in all major Australian cities (Kristensen, 2015). Thus combustion of leaded petrol in automotive vehicles has been identified as a dominant source of atmospheric Pb pollution in Australia (Gulson et al., 1983; Chiaradia et al., 1997b; Cohen, 1999; Bollhöfer and Rosman, 2000;

Cohen et al., 2002; Cohen et al., 2011; Kristensen et al., 2016; Taylor et al., 2016).

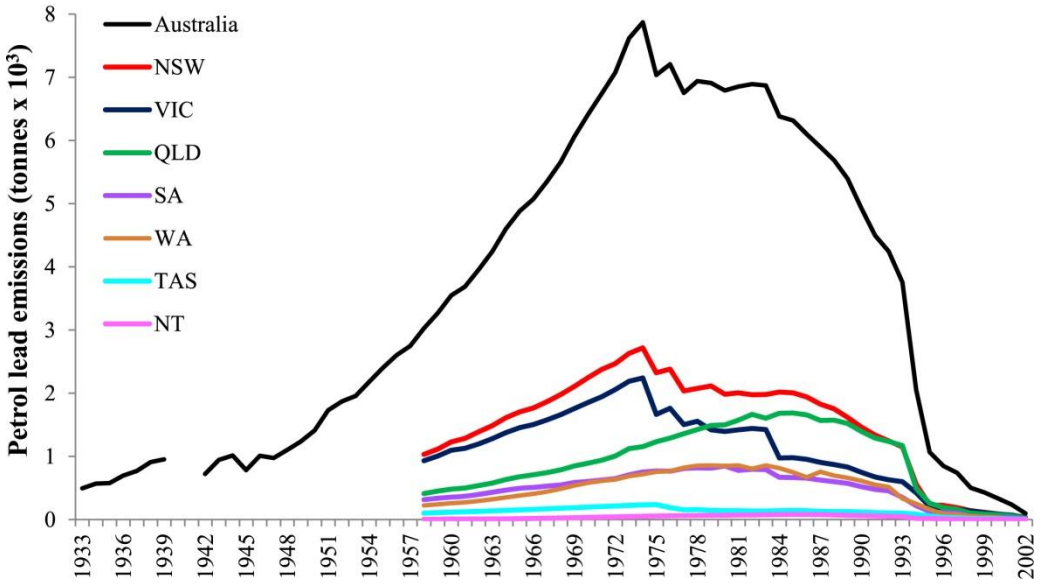

Figure 1.1: Lead emissions from leaded petrol combustion in Australia from 1933 and then within each state or territory after 1958 (Kristensen, 2015).

1.1.1.3 Industrial Emissions

Industrial activities have caused a major environmental issue in the world since the industrial revolution. Investigations of aerosols, slag, dust, fly ash, fumes and ingots originating from steel works, smelters, metal fabrication workshops, industrial incinerators and metallurgical processes, have demonstrated that these industrial activities have had a significant influence on atmospheric metal contamination (e.g. Candelone et al., 1995; Brännvall et al., 1999; Komárek et al., 2008). Coal combustion, the primary fuel source worldwide, is considered to have been a dominant contributor of toxic metal contamination during the early industrialisation era (Carlson and Adriano, 1993; Mukai et al., 1993; Wang et al., 2000; McConnell and Edwards, 2008; Díaz-Somoano et al., 2009). In Australia, similar polluting industrial activities, such as non-ferrous ore smelters, coal-fired power stations, refineries and industrial waste incinerators have contributed atmospheric metal contamination to urban and industrialised areas (Gulson et al., 1983; Chiaradia et al., 1997a; Gulson et al., 2004; Cohen et al., 2012). Utilisation of Australian coal in combustion processes has resulted in the release of metal pollutants such as Hg and Pb to the atmosphere (Nelson, 2007; Marx et al., 2010). Combustion of black and brown coal accounts for 32% of Australian total energy consumption, while 61% of electricity is predominantly produced from coal combustion in 2013–2014 (Ball et al., 2015). Emission of Pb from electricity generation from over 250 Australian power stations in 2013–2014 was 12 tonnes (NPI, 2015). Furthermore, the calculated Pb emission from coal-fired power stations in 2013/2014 was approximately 7.2 tonnes. By contrast, the estimate of Hg emission from coal burning was 1.5 tonnes (NPI,

2015). Although increasing attention has been paid to the study of environmental metal pollution sourced from industrial activities in Australia, the number of studies with respect to toxic metal contamination is minimal when compared to those originating from countries in the northern hemisphere (e.g. Kelly et al., 1996; Monna et al., 1997; Renberg et al., 2000; Cheng, 2003; Järup, 2003; Ettler et al., 2004; Carignan et al., 2005; Rabinowitz, 2005; Cloquet et al., 2006b; Harmens et al., 2010; Schreck et al., 2012).

1.1.2 Air pollution monitoring

The quantification of atmospheric toxic metal emissions and investigation of their sources have been traditionally carried out via high-volume aerosol measurements (Monna et al., 1997; Bollhöfer and Rosman, 2000; Bilos et al., 2001; Bollhöfer and Rosman, 2001; Valavanidis et al., 2006; Csavina et al., 2011). In 1998, the National Environment Protection Measure (NEPM) was set by the National Environment Protection Council to monitor harmful contaminants including As, Cd, and Pb emitted from anthropogenic sources such as mining and industrial activities in Australia (NEPM, 1998). Previous studies reported that the presence of toxic metals (e.g. Pb) from human activities, especially those associated with petrol Pb, can be detectable in air filters collected from major cities of Australia (O'Connor et al., 1990; Cohen et al., 1994; Simpson and Xu, 1994; Chiaradia et al., 1997b; Chan et al., 1999; Gulson et al., 2007; Cohen et al., 2011; Kristensen et al., 2016). In the United States, the available Pb-in-air data in urban areas dates back to the 1950s (Mielke and Zahran, 2012). By contrast, the availability of historic aerosol data in Australia is limited to the period between 1981 and 2001(Australian State of the Environment Committee, 2001). The lack of long-term aerosol data highlights the need for using non-traditional, complementary methods to evaluate temporal and spatial shifts in atmospheric metal emissions in Australia. Herbarium lichen and fungi archives are considered to be eminently suitable to provide a potential environmental approach.

1.1.3 Environmental Archives

Environmental archives, including peat bogs, lake and marine sediments, ice cores, snow, tree rings, corals and herbarium collections (lichen; Figure 1.2) can be used as proxies to record the chronology and degree of atmospheric metal pollution, and also to identify the sources of the pollutants on a regional and global scale (Shen and Boyle, 1987; Weiss et al., 1999; Shotyk et al., 2005; Mihaljevič et al., 2011; Agnan et al., 2014). The advantages of using bio-organisms rather than air filters and deposition collectors have been documented in several studies (Garty, 2001; Giordano et al., 2013; Schram et al., 2015). These advantages include: ease of sampling; widespread distribution in the field (from urban/suburban areas to remote areas); and no requirement for expensive technical instrumentation (Sloof, 1993). The

diversity and relative abundance of historic, archived lichen specimens make them well-accepted proxies for air quality as they provide a measurement of integrated exposure to atmospheric contaminants over time (Szczepaniak and Biziuk, 2003; Zschau et al., 2003; Purvis et al., 2007).

1.1.3.1 Lichens as proxies for air quality

Lichens are acknowledged as excellent proxies for air quality because they are ubiquitous, slow growing and can trap and accumulate mineral nutrients from the atmosphere (Garty, 2001). They are symbiotic organisms composed of mycobionts (fungi) and photobionts (green algae or cyanobacteria) (Brodo et al., 2001). From as early as the mid-19th century in Europe, lichens have been widely used to investigate not only atmospheric metal contamination but also sources of contamination (De Bary, 1866). Carignan et al. (2002) showed that significantly high Pb levels measured in epiphytic lichens from north-eastern North America between 1994-1996, were attributed to industrial emissions from the USA and Canada. In many European countries, anthropogenic sources such as combustion of leaded petrol and industrial activities have been the principal sources of a high proportion of Pb in epiphytic lichens (Doucet and Carignan, 2001; Cloquet et al., 2006a; Purvis et al., 2007; Lahd Geagea et al., 2008; Agnan et al., 2013; Minganti et al., 2014; Cloquet et al., 2015). Herbarium lichens which have a broad geographic distribution and a prolonged accumulation history, are useful as proxies for recording long-term atmospheric Pb deposition (See Figure 1.2). In North America, recent studies of historic collections of the lace lichen (*Ramalina menziesii*) conducted by Flegal et al. (2010) revealed that peak lichen Pb concentrations of

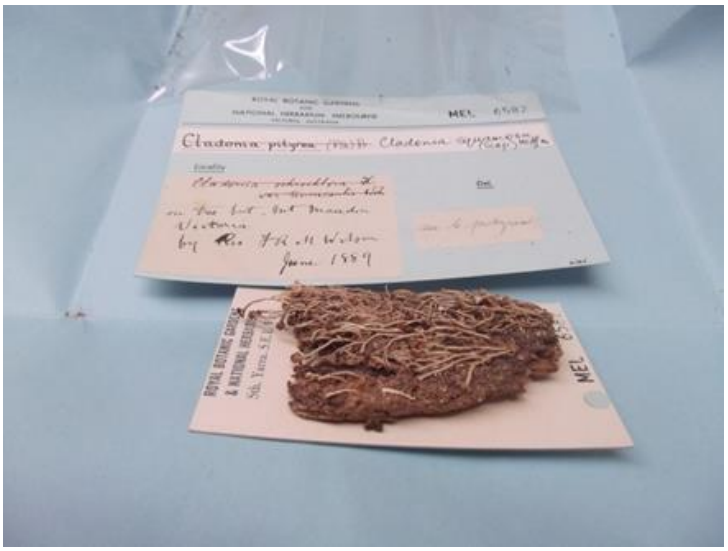

Figure 1.2: An old lichen specimen (*Cladonia squamosal*) collected from Mount Macedon in Victoria in 1889. The sample was provided by the National Herbarium of Victoria (Melbourne) for the purpose of this study.

880 µg/g occurred in 1976, a finding which is consistent with the maximum annual leaded petrol emissions recorded in California, USA at that time (Mielke et al., 2010). Although there is a wide distribution of lichen species across the Australian continent (Archer, 1992; Walker, 1996), there have been very few lichen studies carried out that determine the impact of toxic metals on the atmosphere and evaluate the sources of atmospheric metal emissions in Australia (Vitarana, 2013). Vitarana (2013) analysed *Usnea inermis* lichens from Collie, south-western Australia for arsenic (As), Cd, chromium (Cr), Cu, Pb, manganese (Mn), Hg, nickel (Ni) and Zn, and identified coal mines and an aluminium refinery as the source of high As and Mn concentrations measured in the lichens.

1.1.3.2 Fungi as proxies of atmospheric metal pollution

Fungi play an essential biogeochemical role in the recycling of organic and inorganic nutrients and many are an important food source for animals and humans (Newbound et al., 2010). The chemical composition of fruiting bodies of macrofungi (mushrooms) was first determined during the early 1900s in Germany (Zellner, 1907). There are a number of macrofungal species capable of absorbing and accumulating trace elements in their fruiting bodies (Mleczek et al., 2013) even when growing in soils with low metal concentrations. Consequently, mushrooms have been frequently used as proxies to evaluate heavy metal pollution (Svoboda et al., 2000; Carvalho et al., 2005; Svoboda et al., 2006; Petkovšek and Pokorny, 2013; Schlecht and Säumel, 2015). For example, significant Pb concentrations were measured (20-40 mg/kg) in wild mushrooms collected from a heavily polluted area of an historic Pb mining and smelting locality in the Czech Republic. The Pb isotopic compositions of the mushrooms revealed that the elevated Pb levels were due to atmospheric pollution (Komárek et al., 2007).

1.1.4 Remobilisation of metals during wildfires

Wildfires have been recognised as a major natural source of environmental contamination by the associated release of large quantities of toxic contaminants from the terrestrial biosphere to the atmosphere (Nriagu, 1989; Artaxo et al., 2000; Wotawa and Trainer, 2000). Previous studies indicated that toxic metals such as As, Cu, Zn, Hg and Pb were derived from pyrogenic emissions (Kashparov et al., 2000; Yamasoe et al., 2000; Andreae and Merlet, 2001; Biswas et al., 2007; Odigie and Flegal, 2011). It is generally accepted that anthropogenic climate change is consistent with an increase in wildfire frequency throughout the world (Parry et al., 2007). Data from historic Canadian wildfires have demonstrated that there has been an increasing area of land burned over the last three decades (Gillett et al., 2004). While toxic metal emissions from wildfires are known, the metal toxicity aspect is less well explained but there are recent studies on the impacts of wildfires on toxic metal emissions

throughout Europe and the USA (Wiedinmyer and Friedli, 2007; Finley et al., 2009; Witt et al., 2009; Pereira and Úbeda, 2010; Odigie and Flegal, 2014; Campos et al., 2015; Campos et al., 2016). In contrast, there have been very few studies into the environmental impacts of wildfires on the remobilisation of industrial Pb in Australia (Kristensen et al., 2014).

Figure 1.3: A forested area burnt in the wildfire that occurred in Forcett, south-eastern Tasmania, in January 2013.

1.1.5 Lead isotopes as indicators of pollution sources

It is widely accepted that Pb present in the environment is a complex mix of Pb originating from both lithogenic and anthropogenic sources that vary in time and space. There are four Pb stable isotopes in the environment: ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%), and ^{204}Pb (1%) (Bollhöfer and Martin, 2003). Three of the four isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) are produced by radioactive decay and form the stable end members of the decay chains of uranium (U) and thorium (Th). ^{206}Pb is the end-member of the ^{238}U decay chain; ^{207}Pb is produced from ^{235}U and ^{208}Pb is the stable end-member of the ^{232}Th decay chain. ^{204}Pb is a primordial isotope and is not formed from radiogenic decay (Figure 1.4). In general, the Pb isotopic compositions are commonly expressed as ratios of ^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb. Each ore body exhibits different Pb isotopic composition according to its geological age. For example, Broken Hill, formed about 1700-1800 million years ago, has ^{206}Pb/^{204}Pb ratios of 16.0~16.1, whereas the ^{206}Pb/^{204}Pb ratios of geologically-younger (400-500 million years) deposits in eastern Australia and western Tasmania are higher, approximately 18.0 (Gulson, 2008). In Australia, Broken Hill Pb is used for most industrial manufacturing, and was the dominant source of tetraethyl Pb in petrol production (Kristensen, 2015). This means that analyses of Pb isotopic compositions have significant potential to be used to distinguish different ore bodies. In addition to identifying various ore bodies, Pb isotopic compositions are applied to identify

non-ore body sources in environmental samples and human tissues such as: air aerosols (Chiaradia et al., 1997b; Bollhöfer and Rosman, 2000; Gulson et al., 2007; Kristensen et al., 2016); soil and dust (Gulson et al., 1995; Taylor et al., 2014; Kristensen et al., 2015); blood (Gulson et al., 2006); lake and marine sediment (Chiaradia et al., 1997a; Larsen et al., 2012; Townsend and Seen, 2012); ash residues (Kristensen et al., 2014) and peat bogs (Marx et al., 2010). However, to the best of the author's knowledge Pb isotopes have not previously been determined for archival lichens and fungi in Australia.

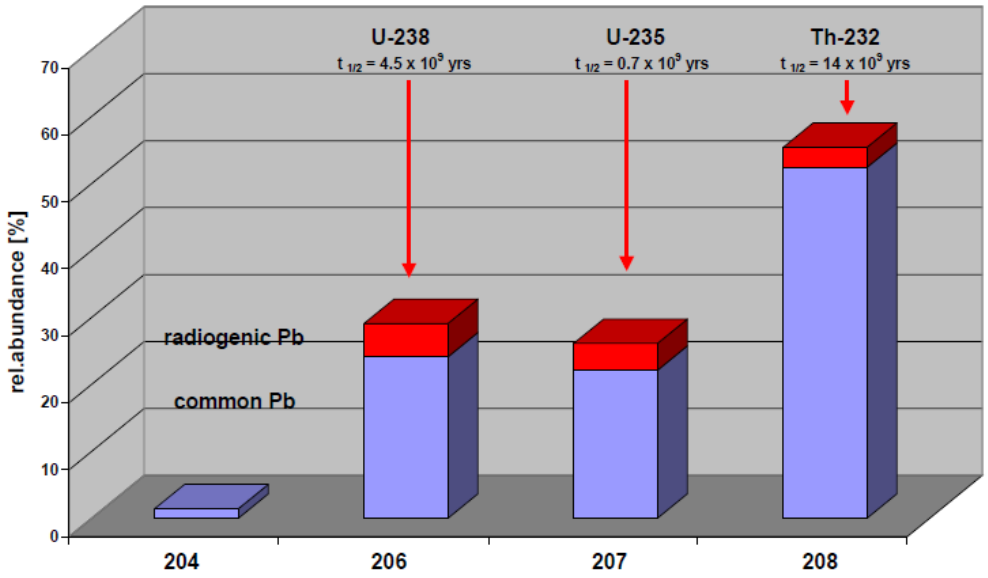

Figure 1.4: Abundance of stable Pb isotopes (Bollhöfer and Martin, 2003)

1.2 Aims

Emissions of toxic anthropogenic metals into the environment represent a serious health hazard (Tchounwou et al., 2003; Gulson, 2008). Although more stringent environmental regulations and standardised guidelines for the reduction and monitoring of toxic metals in urban and suburban areas have been promulgated and applied in Australia today (NEPM, 1998), historic and current anthropogenic inputs of toxic elements have previously been reported to persist in the environment (Kristensen et al., 2014; Kristensen et al., 2016). The lack of historic aerosol data in Australia indicates the need for utilising and developing non-traditional, complementary approaches using proxies, such as the investigation of archival specimens of living organisms and wildfire ash to obtain greater information on present and past pollution. The knowledge gained will contribute to the understanding of environmental impact, in particular the persistence of toxic contaminants and the associated risk to human health.

The overall aims of this thesis are to:

(i) Evaluate temporal and spatial patterns of environmental toxic metal contamination in Australia over the last 150 years using archival lichens and fungi collections, together with wildfire ash, as environmental proxies.

(ii) Determine natural and anthropogenic sources of environmental toxic metal emissions using stable Pb isotopic compositions and statistical analysis.

(iii) Assess the applicability of different environmental samples as proxies in the determination of atmospheric toxic metal pollution levels and source identification in Australia.

Through fulfilling these aims, it is anticipated that the alternative techniques utilised in this study will complement more traditional studies, and allow for a better understanding of the pervasive effects of environmental toxic metal emissions from lithogenic and anthropogenic sources.

1.3 Aspects and Investigations

This study has focused on two lichen genera and one fungus genus using herbarium specimens collected over a period of more than a century; ash production from four recent wildfires; and environmental samples from air filters, soil, rock and river sediments from four Australian states: New South Wales (NSW), Victoria (VIC), South Australia (SA) and Tasmania (TAS) (Figure 1.5).

1.3.1 Study Sites

1.3.1.1 The Greater Sydney Area, New South Wales

Sydney, the largest city in Australia, is an industrialised metropolis with a population close to five million people (ABS, 2014). The major anthropogenic sources of metal contaminants are the use of leaded petrol in motor vehicles, industrial emissions (e.g. smelters, waste incineration), coal combustion and the use of Pb paint in Sydney region (Gulson et al., 1983; Gulson et al., 1995; Chiaradia et al., 1997b; Cohen et al., 2002; Birch and Scollen, 2003; Davis and Gulson, 2005; Cohen et al., 2012; Laidlaw et al., 2014). Thus, the Greater Sydney area is an appropriate location in which to study the effects of industrial pollutants on urban environments. The Permian and Triassic sedimentary strata of the Greater Sydney area are primarily composed of sandstones, shales and siltstones of the Shoalhaven Series, the Illawarra and Newcastle Series, the Narrabeen Series, the Hawkesbury Group and the Wianamatta Group (Mayne et al., 1974). Two sites within the Greater Sydney area were chosen for wildfire ash studies sites. The first of these, Woy Woy is a coastal town located approximately 79 km north of the Sydney Central Business District (CBD) with soil derived from Hawkesbury Sandstone(Haworth, 2003). The second, Duffys Forest, is a relatively

pristine region of *Eucalyptus* woodland and forest on soils derived from Wianamatta Shales which cap Hawkesbury Sandstones (Haworth, 2003), located on the west of Ku-ring-gai Chase National Park and approximately 28 km north of the Sydney CBD.

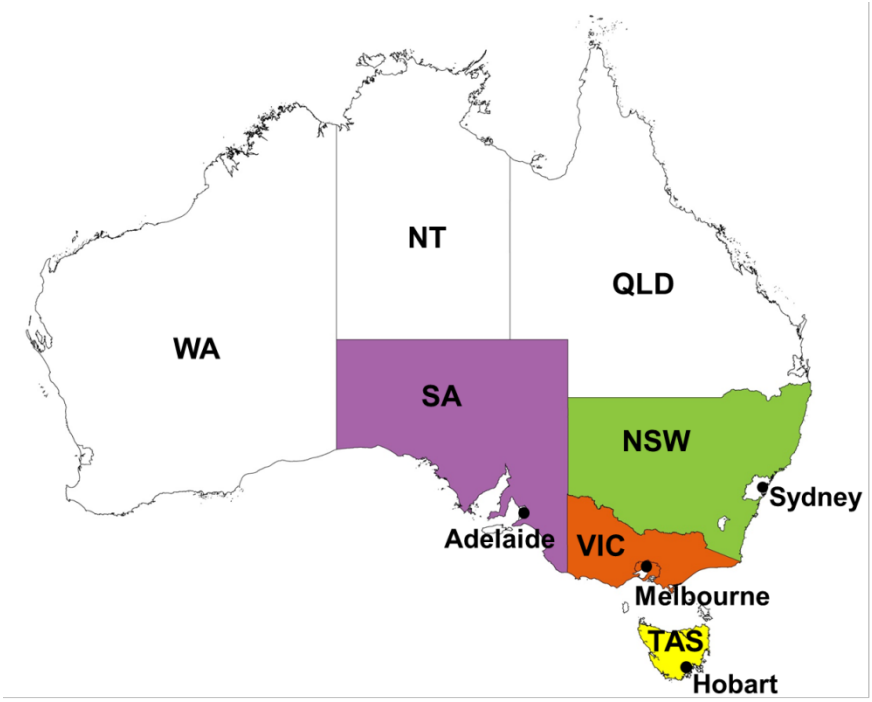

Figure 1.5: Map of Australia showing states where lichen and ash samples have been collected and analysed for this thesis: New South Wales (n = 103), Victoria (n = 107), South Australia (n = 13) and Tasmania (n = 36).

1.3.1.2 Central and Southern Victoria

Melbourne, located on the southern coastline of Victoria, is the second largest city of Australia with a population of 4.4 million people (ABS, 2014). The history of base metal mining history in Victoria dates back to the 1850s (Phillips and Hughes, 1996). The goldfields of central Victoria have left a legacy of high levels of heavy metals, including As, Cr and Pb, in the surrounding environment (Noble et al., 2010). In addition, Melbourne city derives large quantities of metal emissions from roadside dust, local manufacturing industries, vehicle exhausts and other combustion sources (Chan et al., 2008) and consequently is an ideal site for evaluating the impacts of mining and industrial activities on environmental metal contamination. Silurian–Devonian marine sediments and Tertiary Older Volcanic basalts dominates the Dandenong Ranges river sediments, whereas Silurian–Devonian marine sediments and Devonian volcanic bedrocks form the Yarra Ranges (Tweed et al., 2006).

1.3.1.3 Cherryville, South Australia

Cherryville is a rural area in the Adelaide Hills, in the Mountain Lofty Ranges of South Australia, approximately 16 km east of Adelaide. The Cherryville area is predominantly

underlain by Upper Proterozoic, Cambrian and Ordovician rocks (Drexel et al., 1993). The Cherryville site was chosen as a wildfire occurred in this region in May 2013.

1.3.1.4 Forcett, Tasmania

Forcett is a small town in south-eastern Tasmania, approximately 30 km southeast of Hobart, predominantly underlain by mainly Palaeozoic and Permian basaltic rocks (Burrett and Martin, 1989; Wang et al., 1996). Forcett was an opportunistic ash-sampling site as the Forcett wildfire event occurred in January 2013.

1.3.2 Study Materials

The historic lichen genera *Cladonia* (n = 87) and *Usnea* (n = 52) and the fungus genus *Trametes* (n = 42) were collected between 1852 and 2010 from the Greater Sydney area (n = 84) and central and southern Victoria (n = 107). These lichens and fungi are widely distributed across the Australian continent (Archer, 1992; Walker, 1996; Stevens, 2004) and therefore can be analysed to demonstrate environmental contamination over large areas and for long periods of time. Archival samples were obtained in 2013 from various Australian herbaria. Ash released from four wildfire sites were sampled during 2012–2013. Soil profile samples, unweathered rocks and river surface sediments were collected from natural parks and reserves adjacent to each sampling site. In addition to the environmental elemental and isotopic data produced in this thesis, results are supported with additional Pb isotope data available in the literature. Air filters (Total Suspended Particulates, TSP) were collected from archived samples for Sydney CBD and Rozelle covering the years 1978 to 2004 from the New South Wales Office of Environment and Heritage, Lidcombe, Sydney. Lichen, fungus, air filter and ash samples were used to establish temporal and spatial metal concentrations and Pb isotopic compositions in order to understand the correlations between trace elements and to identify the sources. Soil profiles together with rock and river sediment samples were used to establish background Pb concentrations and isotopic compositions.

1.3.3 Analyses

Metal concentrations and Pb isotopic compositions of the lichen specimens (two genera) and fungus specimens (one genus) were compared using the non-parametric Kruskal-Wallis H test in Chapters 3-5. In Chapter 4, elemental classification of different lichen and fungi genera was determined with Cluster Analysis (CA) and Principal component analysis (PCA). The changing occurrence of lithogenic and anthropogenic sources of environmental metal emissions can be identified using a combination of elemental statistical analyses and Pb isotopic compositions. Enrichment Factors (EFs) were used to evaluate the intensity of metal contamination in historic lichen and fungi collections. Specific details of the study materials,

methods and data analyses used for each study of this thesis are provided within each chapter.

1.4 Structure of the Thesis

In this thesis four studies are presented on the applicability and usefulness of different environmental media as suitable proxies for recording historic and contemporary environmental toxic metal pollution in Australian urban and remote areas. Chapter 1 introduces background information on toxic metal contamination in ecosystems and describes previous studies with respect to using concentration patterns and sources of environmental toxic metals using herbarium archives and ash production. Chapter 2 characterises the historic variations of atmospheric Pb and fingerprints potential sources of Pb in Australia's largest and most populated city, Sydney, using archival lichens and fungi. Chapter 3 uses herbarium archived samples from central and southern Victoria to assess Pb concentration and isotopic compositions of past and recent atmospheric Pb deposition in this region. Chapter 4 determines geographic and temporal trends in Pb and other toxic metal concentrations to elucidate the impact of past and current atmospheric metal pollution in both urban and relatively pristine environments in the Greater Sydney area and central and southern Victoria. In addition to lithogenic sources and anthropogenic inputs, wildfire is considered to be another source of environmental toxic metal emission. Chapter 5 investigates the remobilisation of Pb in ash residues produced from Australian wildfires and identifies the sources of the Pb. Chapter 6 discusses the overall thesis results, central findings and implications of this thesis. Thesis conclusions are provided in chapter 7.

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CHAPTER 2

Paper One

Australian atmospheric lead deposition reconstructed using lead concentrations and isotopic compositions of archival lichen and fungi

Wu, L., Taylor, M.P., Handley, H.K., Wu, M. (2016)

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This paper fills a gap in our knowledge on long-term emissions of lead into the atmosphere, emissions primarily originating from the consumption of leaded petrol in major Australian cities. In Australia, in the 70 years from 1932 to 2001, more than 240,000 tonnes of lead derived from petrol has been released into the atmosphere. However, annual air lead emission data is only available for Australian capital cities between 1981 and 2001. This study presents lead concentrations and lead isotopic compositions in archival lichens and fungi collected over the past 120 years in Sydney, Australia's largest city. The data are used to evaluate past and current atmospheric lead pollution and to determine the probable sources of lead.

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Australian atmospheric lead deposition reconstructed using lead concentrations and isotopic compositions of archival lichen and fungi

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ABSTRACT

Lead concentrations and their isotopic compositions were measured in lichen genera *Cladonia* and *Usnea* and fungi genus *Trametes* from the Greater Sydney region (New South Wales, Australia) that had been collected and archived over the past 120 years. The median lead concentrations were elevated in lichens and fungi prior to the introduction of leaded petrol (*Cladonia* 12.5 mg/kg; *Usnea* 15.6 mg/kg; *Trametes* 1.85 mg/kg) corresponding to early industrial development. During the period of leaded petrol use in Australian automobiles from 1932 to 2002, total median lead concentrations rose: *Cladonia* 18.8 mg/kg; *Usnea* 21.5 mg/kg; *Trametes* 4.3 mg/kg. Following the cessation of leaded petrol use, median total lead concentrations decreased sharply in the 2000s: *Cladonia* 4.8 mg/kg; *Usnea* 1.7 mg/kg. The lichen and fungi isotopic compositions reveal a significant decrease in $^{206}Pb/^{207}Pb$ ratios from the end of 19th century to the 1970s. The following decades were characterised by lower allowable levels of lead additive in fuel and the introduction of unleaded petrol in 1985. The environmental response to these regulatory changes was that lichen and fungi $^{206}Pb/^{207}Pb$ ratios increased, particularly from 1995 onwards. Although the lead isotope ratios of lichens continued to increase in the 2000s they do not return to pre-leaded petrol values. This demonstrates that historic leaded petrol emissions, *inter alia* other sources, remain a persistent source of anthropogenic contamination in the Greater Sydney region.

1. Introduction

Over the past one hundred years, industrial activity has resulted in millions of tonnes of lead being released to the atmosphere and biosphere (Marx et al., 2010). Leaded petrol was first introduced in North America in the 1920s (Nriagu, 1990), where it is estimated that over 5 million tonnes of lead additives were used between 1927 and 1994 (Mielke et al., 2010). Following the introduction of unleaded petrol in mid-1975 and the phase-out of leaded petrol in 1995, atmospheric lead levels in North America have fallen significantly (Bridbord and Hanson, 2009). In Australia, mining and metal production became a major source of atmospheric lead pollution by the 1890s (Mudd, 2007), which has been recorded in aged-dated Antarctic ice cores (Vallelonga et al., 2002). Following the introduction of leaded petrol in Australia in 1932, and an increase in car ownership and use, atmospheric lead emissions rose during the 20th century (Cook and Gale, 2005). Peak atmospheric lead concentrations occurred in the 1970s and early 1980s (Kristensen, 2015). Following the introduction of lead-free petrol in 1985, atmospheric lead emissions decreased in all Australian major cities and concentrations fell below 0.5 $\mu g/m^3$ after the end of leaded petrol sales in Australia in 2002 (Kristensen, 2015). Using a combination of sales data, lead additive concentrations in fuel and vehicles emissions, Kristensen (2015) calculated that more than 240,000 tonnes of lead were emitted to the atmosphere during the 70-year period of Australian leaded petrol consumption. Consequently, it was anticipated that these marked changes to environmental emissions would be recorded in Australian lichens that extract moisture and associated contaminants from the ambient environment.

Lichens are useful natural biomonitors of air quality because of their ability to accumulate mineral nutrients from the atmosphere

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(Garty, 2001). European scientists identified the value of lichens as biomonitors as early as the mid-19th century (De Bary, 1866; Schwendener, 1867). Subsequently, lichens have been used frequently as bioindicators of temporal shifts in atmospheric metal composition across North America and Europe (Ferry et al., 1973; Adamo et al., 2003; Nicolardi et al., 2012; Vannini et al., 2014). Lead isotope analysis of epiphytic lichens in North America has shown that lead in lichen samples is derived from multiple anthropogenic sources, including zinc and lead smelters, industrial emissions, leaded petrol and natural lead (Carignan et al., 2002; Simonetti et al., 2003). Flegal et al. (2010) examined lace lichen (*Ramalina menziesii*) and measured maximum lichen lead concentrations of 880 μg/g in lichens from 1976, which is coincident with the peak of leaded petrol emissions in California, USA. European studies of atmospheric lead dispersion using epiphytic lichens as a proxy have also shown that historic leaded petrol and various industrial activities were major sources of atmospheric lead pollution (Cloquet et al., 2006).

Fungi play a fundamental biogeochemical role in the recycling of organic and inorganic nutrients and are an important food source for animals and humans (Newbound et al., 2010). A large number of fungi species are capable of absorbing and accumulating trace metals in their fruiting bodies (Mleczek et al., 2013). Extensive research has shown that mushroom lead concentrations are markedly different between polluted (near lead smelters, mining areas, highways etc.) and unpolluted areas (Kuthan, 1979; Kalač and Stašková, 1991; Sova et al., 1991; Svoboda et al., 2000; Carvalho et al., 2005; Svoboda et al., 2006; Petkovšek and Pokorny, 2013; Schlecht and Säumel, 2015). A recent lead isotopic composition study of mushrooms collected in the Czech Republic has showed that different lead isotope ratios are measured in mushroom fruiting bodies (Komárek et al., 2007).

There are limited published trace metal concentration data for Australian lichens (Vitarana, 2013), fungi (Zeng et al., 2012), and mosses (Godbeer et al., 1981; Archibold and Crisp, 1983; Swaine et al., 1983; Huang and Gulson, 2002), which have been used to assess atmospheric lead depositions or the source apportionment of lead. This is surprising given the abundance of lichen and fungi genera present in Australia and that many have been stored at various herbaria (Archer, 1992; Walker, 1996; Stevens, 2004). Therefore, the aims of this study were to: (i) Measure lead concentrations and lead isotopic compositions in lichens and fungi collected from 1885 to 2010 in the Greater Sydney region to document the impact of anthropogenic emissions on the samples. (ii) Determine the lead isotopic compositions of available Sydney air filter samples from 1978 to 2004 to verify that lichen and fungi samples are a suitable proxy for atmospheric assessment.

2. Materials and methods

2.1. Lichen and fungi samples

Forty-six *Cladonia* and 28 *Usnea* lichen and 10 *Trametes* fungi samples spanning the period 1885 to 2010 were collected between March to December 2013 from herbaria in Canberra (Australian National Herbarium), Sydney (National Herbarium of New South Wales, Macquarie University Downing Herbarium) and Melbourne (National Herbarium of Victoria and University of Melbourne Herbarium). Lichen and fungi samples were originally collected within a 100 km radius of Sydney Central Business District (CBD). The samples have been grouped into five broad geographical sample zones, corresponding to their position relative to Sydney CBD. These are: Blue Mountains, North Sydney, West/Northwest/Southwest Sydney, South Sydney and, Central/East-Central Sydney (Fig. 1).

The genus *Cladonia* is one of most common lichens and grows on a variety of substrates including bark, soil, peat, wood or rock (Brodo et al., 2001). Sydney *Cladonia* lichens were originally collected and archived in several Australian herbaria between the years 1885–2009 (Table 1). The annual growth rate of *Cladonia* is in the range of 3.4–5.8 mm $year^{-1}$ (Scotter, 1963; Pegau, 1968; Helle et al., 1983). The outermost 20 mm of the archived lichens were sampled to capture the growth phase contemporaneous to the date that the lichens were originally sampled in the field.

The fruticose lichen genus *Usnea*, which appear as beard-like growths, predominantly on tree branches and shrubs (Brodo et al., 2001) were also sampled for the study, covering a 109-year period (1901–2010) (Table 2). Li et al. (2014) reported that the growth rate of *Usnea aurantiacoatra* is 4.3–5.5 mm $year^{-1}$. The same sampling procedure used for the archived *Cladonia* lichens was applied to the *Usnea* lichens. Similar to *Cladonia*, there was a marked dearth of *Usnea* lichens collected and stored by herbaria for the period 1914–1972, with only 3 *Usnea* lichen samples available from this period.

Growth rates within a single lichen thallus are dependent on the lichen species, habitat structure and climatic conditions of exposure (Abdulmanova and Ektova, 2015). To determine the age and growth rate of individual lichen thalli and thallus parts, various dating techniques have been utilized (Innes, 1988). Most lichen growth rate estimates are based on direct periodic measurements. The ^{14}C dating technique has been used to estimate lichen age and growth rate (Clark et al., 2000; Li et al., 2014). Consequently, based on the published average annual growth rate data of *Cladonia* and *Usnea* lichens (Scotter, 1963; Pegau, 1968; Helle et al., 1983; Li et al., 2014), we conclude that sampling the outermost 20 mm for analysis represents a short time period, approximately 5 years.

Given the significant data gap in the archived lichen samples, *Trametes* fungi were obtained for the years between 1926 and 1988 (Table 3). As fungi forms a component of the lichen organism, their use is suitable as a substitute for lichen. Algae or cyanobacteria and fungi exist in a symbiotic relationship within lichen, to produce a composite organism (Brodo et al., 2001). *Trametes* fungi is wood-decaying genus that uptake trace metals from deposition of particles predominantly from the atmosphere (Gabriel et al., 1997). Fungi fruiting bodies consist of caps and stipes. Caps of each *Trametes* fungi were sampled in this study as previous data showed that lead concentrations in the caps were higher than in the stems (Lepšová and Král, 1988; Sayegh-Petkovsek et al., 2002). To the best of our knowledge, the lichen and fungi samples used in this study have not been treated with lead-containing biocides. Following the retrieval of lichen and fungi samples from herbaria, the samples were stored in a clean room at the National Measurement Institute (NMI), North Ryde, Sydney (ICPMS).

2.2. Air filter, soil and rock samples

Total suspended particulates collected on air filter samples ($n = 193$) from 1978 to 2004 were obtained in 2014 from the New South Wales Office of Environment and Heritage, Lidcombe. Air samples were collected in Sydney CBD using a high volume air sampler (HVAS) following Australian Standard AS 2724.3-1984, which was located 4 m above ground on a street awning (Chiaradia et al., 1997). Soil and rock (Hawkesbury sandstone) samples (comprising 4 surface soils, 4 subsurface soils and 10 rock samples) were collected from the Sydney region to characterize the *in situ* lead concentration and isotopic composition of local (natural) lead sources (Table 4). National parks and reserves were targeted for sampling (Fig. 1), as they are likely to be less disturbed than urban locations. Soils were collected using established procedures (Taylor et al., 2010) from depths of 0–2 cm (surface) and 30–40 cm

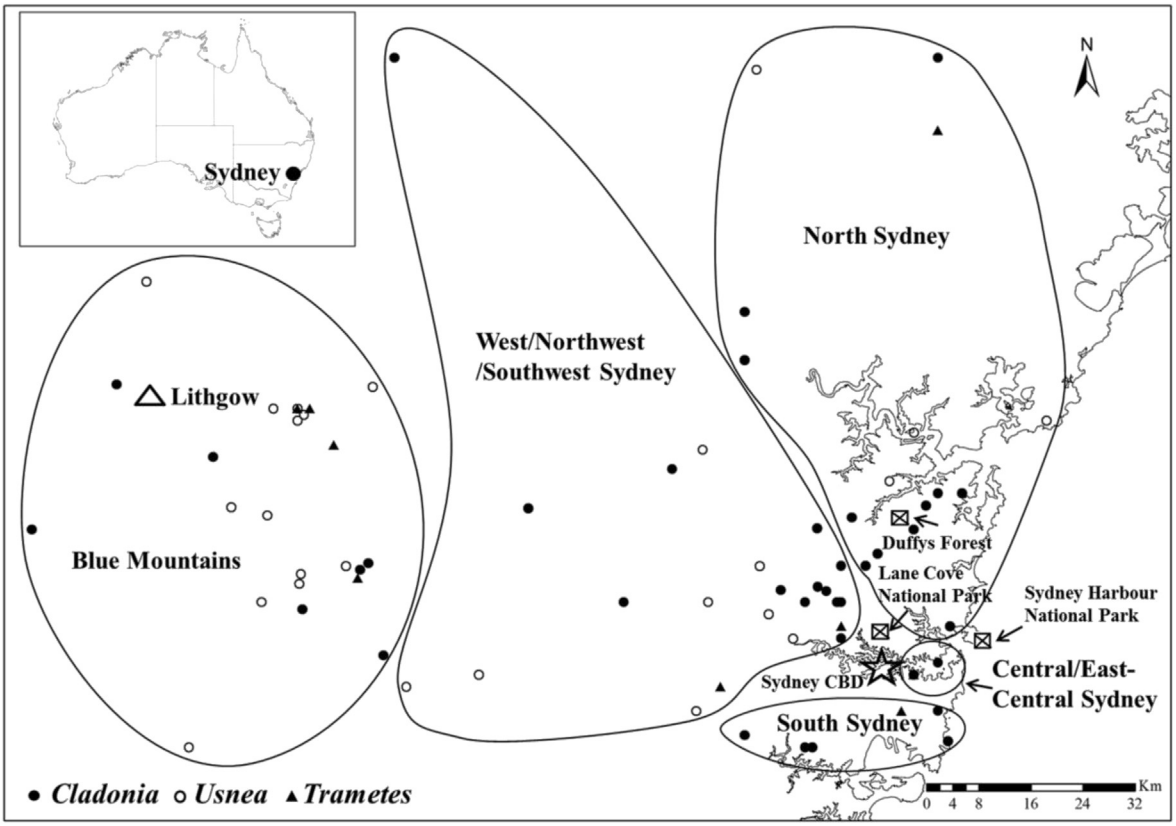

Fig. 1. Map of *Cladonia* lichen (n = 46), *Usnea* lichen (n = 28) and *Trametes* fungi (n = 10) sample collection sites within the Greater Sydney area, Australia. The sites correspond to five broad geographic zones (detailed in the text). The black star represents Sydney CBD; the black squares with a cross represent the Sydney Harbour National Park, Lane Cove National Park and Duffys Forest samples.

(subsurface). Rock samples were also collected from adjacent locations. Soil and rock samples were placed in sealed plastic bags and taken to the NMI for analysis of lead concentration and lead isotopic composition.

2.3. Sample preparation and geochemical analysis

Lichen and fungi cap samples were separated from any attached substrate material (tree bark and soil) with a plastic knife. *Cladonia* lichen samples were rinsed with Milli-Q water in order to remove attached soil particles and air-dried on clean polythene sheets at room temperature following published methods (Boamponsem et al., 2010; Giordano et al., 2013). Between 10 and 400 mg of lichen sample and 30–400 mg of fungi were digested with concentrated, ultrapure HNO_3 (NMI Methods, 2014a). After substrate removal, low sample weights were obtained for two lichen samples (10 mg) and one fungi sample (30 mg), which may have affected the quality of data for these samples due to the low abundance of ^{204}Pb (approximately 1%). A portion of the air filter paper was sub-sampled (one-sixteenth) using clean scissors. Approximately 0.5 g of soil and rock and the sub-portion of air filter papers were digested in HNO_3 and HCl (NMI Methods, 2014b). Procedural blanks, the matrix spike and sample duplicates were prepared and analysed concurrently with samples. Blanks returned <0.1 mg/kg for lichen samples, <0.3 μg/filter for air filter samples and <0.5 mg/kg for soil and rock samples. Total lead concentration was measured using a single-collector, Perkin Elmer Elan DRC II, Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the National Measurement Institute, North Ryde, Sydney. Analysis of the Standard Reference Material IEAE 336 (lichen), AGAL-10 (river sediment) and the material quality control sample AGAL-12 (biosoil) were used to assess the quality of analytical procedures and data. Recovery rates (mean ± RSD) of lead were 102 ± 4.3%, 91 ± 2.3%, 97 ± 3.3% for IEAE 336 (n = 8), AGAL-10 (n = 8) and AGAL-12 (n = 8), respectively. Accuracy and reproducibility were determined through repeated analysis of the lichen, sediment and biosoil standards. Lead concentration replicate results were within ±4% of the reference and quality control materials. Lead isotopic compositions were determined with concurrent measurements of National Institute of Standards and Technology (NIST) SRM 981 (common lead), bracketing between samples in order to correct for isotopic fractionation. In order to assess the reproducibility of the lead isotopic measurements, one lichen sample (LC2009) and one air filter sample (S03-01) were measured repeatedly (n = 8), returning a Relative Standard Deviation (RSD) of 0.63%, 0.37% and 0.35% for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ for the lichen; and 1.22%, 0.71% and 0.26% for the air filter. The median and mean total lead concentration, mean lead isotope ratios, standard deviation and recovery rates were calculated using SPSS software, version 13.0.

3. Results and discussion

3.1. Lead concentration and lead isotope data

Lead concentrations and isotopic compositions in *Cladonia* and *Usnea* lichens and *Trametes* fungi covering the period 1885 to 2010 are summarised in Tables 1–3, respectively. *Cladonia* lichen lead concentrations range between 2.6 and 570 mg/kg and from 1.0 to 181 mg/kg in *Usnea* lichens. The lead concentration in *Trametes* fungi varies from 0.5 to 16.6 mg/kg. The median lead concentration

Table 1
Lead concentrations and lead isotopic compositions of *Cladonia* lichens collected between 1885 and 2009.

No.	Year	Species	Location	Pb (mg/kg)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
1	1885	*Cladonia furcata*	Ross Cave, Mt Victoria	7.0	18.18	1.167	2.456
2	1894	*Cladonia cervicornis*	Eastern Creek, Near Blacktown	5.0	17.99	1.152	2.442
3	1897	*Cladonia fimbriata*	Lithgow	32.3	17.99	1.150	2.437
4	1898	*Cladonia floerkeana*	Penshurst	6.8	17.57	1.134	2.414
5	1899	*Cladonia floerkeana*	Sydney	9.6	17.56	1.129	2.405
6	1900	*Cladonia floerkeana*	Randwick	26.7	17.39	1.121	2.398
7	1902	*Cladonia floerkeana*	Hurstville	9.5	17.50	1.133	2.429
8	1903	*Cladonia fimbriata*	Oatley	14.2	17.44	1.122	2.402
9	1906	*Cladonia pertricosa*	Gladesville	8.2	17.41	1.122	2.396
10	1907	*Cladonia humilis*	Gladesville, Sydney	12.5	17.77	1.139	2.426
11	1908	*Cladonia fimbriata*	Wahroonga, near Sydney	20.0	17.66	1.135	2.416
12	1909	*Cladonia furcata*	Near Manly, Sydney	17.4	17.69	1.139	2.419
13	1910	*Cladonia fimbriata*	Penshurst	79.3	17.83	1.146	2.429
14	1911	*Cladonia sulcata*	Gladesville	6.1	17.79	1.146	2.432
15	1914	*Cladonia pertricosa*	Balmoral, Sydney	19.2	17.60	1.128	2.410
16	1971	*Cladonia P.Browne*	Terrey Hills	20.6	16.94	1.091	2.369
17	1974	*Cladonia* sp	Bradleys Head, Sydney	18.5	16.93	1.087	2.369
18	1977	*Cladonia ramulosa*	Jamieson Valley, Blue Mtns	3.6	17.50	1.122	2.396
19	1978	*Cladonia cervicornis*	Old Great Northern Rd, Sydney	25.7	17.25	1.111	2.385
20	1980	*Cladonia kuringaiensis*	Grosvenor Track	54.7	16.98	1.103	2.372
21	1981	*Cladonia floerkeana*	Near McCarrs Creek	10.3	17.23	1.109	2.384
22	1982	*Cladonia furcata*	Epping, near Devlins Creek	73.4	17.36	1.115	2.384
23	1983	*Cladonia praetermissa*	Towler Bay, 30 km N of Sydney	42.0	17.02	1.095	2.371
24	1984	*Cladonia sulcata*	Mona Vale Rd, 18 km N of Sydney	16.0	16.90	1.090	2.363
25	1985Feb	*Cladonia kuringaiensis*	Galston Gorge near Sydney	24.9	16.92	1.081	2.363
26	1985Mar	*Cladonia floerkeana*	Yeomans Bay	17.3	16.65	1.091	2.374
27	1985July	*Cladonia pertricosa*	Erskine Creek, Blue Mtns	15.4	16.78	1.083	2.361
28	1986	*Cladonia fruticulosa*	Tobys Glen, Blue Mtns	18.4	17.27	1.112	2.399
29	1987Mar	*Cladonia floerkeana*	Jenolan Caves, Blue Mtns	2.7	17.29	1.114	2.392
30	1987Sep	*Cladonia sulcata*	Hazelbrook, Blue Mtns	4.4	17.07	1.095	2.375
31	1988	*Cladonia floerkeana*	Terrey Hills	5.2	16.91	1.089	2.368
32	1989	*Cladonia cervicornis*	Hazelbrook, Blue Mtns	6.9	17.06	1.100	2.378
33	1990	*Cladonia ochrochlora*	Bradleys Head	41.4	16.72	1.084	2.364
34	1991	*Cladonia praetermissa*	Macquarie University, Sydney	106	16.68	1.083	2.362
35	1992	*Cladonia ochrochlora*	Lane Cove National Park	29.9	17.01	1.100	2.377
36	1993	*Cladonia praetermissa*	Macquarie University, Sydney	37.5	17.09	1.100	2.380
37	1995	*Cladonia cerricornis*	Dyarrabin Nature Reserve, Maroota	12.3	16.92	1.092	2.371
38	1996	*Cladonia furcata*	Smith Park, East Hills	29.9	16.91	1.090	2.363
39	1997	*Cladonia praetermissa*	Terrys Creek	43.3	16.80	1.093	2.369
40	1998	*Cladonia floerkeana*	West Pennant Hills, Palm Gully	19.1	16.95	1.087	2.356
41	1999	*Cladonia floerkeana*	Pennant Hills Park, Cheltenham	3.3	17.09	1.103	2.380
42	2000	*Cladonia furcata*	Lyrebird Gully track, Mt Kuring-gai	4.8	17.25	1.110	2.383
43	2001	*Cladonia praetermissa*	Near Maroubra Beach	570	16.11	1.044	2.319
44	2002	*Cladonia corniculata*	Rickards Road, SW of Richmond	4.0	17.06	1.096	2.369
45	2003	*Cladonia celata*	Oatley West	22.4	17.57	1.126	2.415
46	2009*	*Cladonia chlorophaea*	East of Pitt Town	2.6	17.33	1.112	2.393

Sample marked with (*) was processed eight times.

in *Cladonia* lichens (Table 1), prior to the start of the use of leaded petrol in 1932, is 12.5 mg/kg, rising to 18.8 mg/kg by the end of 20th century (1999), and decreasing to a median lead concentration of 4.8 mg/kg in the 2000s. *Usnea* lichens have similar median temporal lead concentrations (Table 2): 15.6 mg/kg prior to the introduction of leaded petrol in 1932, 21.5 mg/kg between 1939 and 1999, then decreasing to 1.7 mg/kg between 2000 and 2010. It is noteworthy that sample lead concentrations were elevated prior to the introduction of leaded petrol, which is likely due to lead emissions from early industrial activity close to some of the sample locations (Fig. 2). Similarly elevated lead levels were recorded in Scottish mosses between 1838 and 1926 before leaded petrol use (Farmer et al., 2002). The sources of the elevated lead concentrations were ascribed to emissions from anthropogenic activities including coal combustion and lead smelting (Farmer et al., 2002). Notwithstanding the small, post-2000 sample numbers in this study, lead concentrations are lower in these samples than those from the pre-leaded petrol and the leaded petrol eras (Fig. 2). The large reduction in median lead concentrations for modern lichen samples indicates that industrial lead emissions are currently far lower than they were prior to, and during, the period of leaded petrol use.

The lowest median lead concentrations of the *Cladonia* and *Usnea* lichens and *Trametes* fungi are from the bush-dominated region of the Blue Mountains (Blue Mtns) (Fig. 1) with 7.0 mg/kg, 8.1 mg/kg and 1.5 mg/kg, respectively. The highest median lead content in *Cladonia* lichens corresponds to the more populated, South Sydney area (median = 24.6 mg/kg) (Fig. 1). The highest median concentration in *Usnea* lichen samples (43.2 mg/kg) comes from the heavily urbanized North Sydney region (Fig. 1), thus showing that lichen lead concentrations can discriminate between undeveloped and more developed areas.

A comparison of the lead isotope ratios of lichens and fungi collected for the same year is summarised in Table 5. Variable lead isotope ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) were measured in *Trametes* fungi and *Cladonia* and *Usnea* lichens collected in different geographical zones but in the same year (1951, 1982). However, similar lead isotope ratios ($^{206}Pb/^{207}Pb$) were obtained from lichen and fungi samples from the same geographical sites (Table 5).

Temporal changes in $^{206}Pb/^{207}Pb$ ratios of the lichens and fungi

Table 2
Lead concentrations and lead isotopic compositions of archived *Usnea* lichens collected between 1901 and 2010.

No.	Year	Species	Location	Pb (mg/kg)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
1	1901	*Usnea scabrida*	Hurstville	15.0	17.05	1.112	2.396
2	1902	*Usnea*	Pine Ridge, Liverpool	5.5	16.75	1.085	2.367
3	1903	*Usnea baileyi*	Toongabbie	9.6	17.50	1.129	2.417
4	1906	*Usnea*	Junction of the Nepean and Warragamba Rivers	9.3	17.29	1.112	2.394
5	1907	*Usnea*	Nepean and Warragamba Rivers	30.0	17.41	1.112	2.387
6	1908	*Usnea*	Parramatta	16.2	17.30	1.121	2.397
7	1910	*Usnea*	Ermington	87.6	17.65	1.138	2.424
8	1917	*Usnea*	Castle Hill	19.8	17.63	1.139	2.415
9	1939	*Usnea*	Hazelbrook, S side of railway line, Blue Mtns	9.3	17.02	1.081	2.354
10	1951	*Usnea angulata*	Kowmung River to Kiaramba Ridge, Blue Mtns	6.8	16.83	1.092	2.362
11	1965	*Usnea*	23 miles S of Milbrodale	47.9	16.57	1.076	2.354
12	1972	*Usnea*	Mount Irvine	28.1	16.99	1.096	2.361
13	1977	*Usnea*	Jamieson Valley, below Katoomba Falls	27.6	17.23	1.108	2.380
14	1978	*Usnea*	Mount Bouddi, Bouddi National Park	44.5	17.13	1.107	2.377
15	1984Nov	*Usnea*	25 km NNE of Katoomba	30.7	16.78	1.083	2.359
16	1984Nov	*Usnea*	Zig-Zag Road, Mount Wilson	181	16.55	1.072	2.346
17	1988	*Usnea*	Mount Wilson, Blue Mtns	8.1	16.88	1.080	2.349
18	1989	*Usnea*	Ku Ring Gai Chase National Park, Sydney	18.1	16.83	1.082	2.362
19	1990	*Usnea*	Brooklyn, Long Island Nature Reserve	41.9	16.87	1.084	2.359
20	1991	*Usnea inermis*	12 km E of Cullen Bullen	5.7	16.83	1.092	2.368
21	1996	*Usnea*	Wentworth Falls	17.9	16.80	1.085	2.361
22	1997	*Usnea* sp	North Rocks, Lomatia Creek	21.5	16.76	1.084	2.364
23	1999	*Usnea*	Little Switzerland Drive, Wentworth Falls	3.6	17.18	1.104	2.375
24	2000	*Usnea*	Centennial Glen, Blackheath	1.4	17.24	1.118	2.381
25	2001	*Usnea*	Blue Mountains National Park	2.5	17.36	1.115	2.384
26	2002	*Usnea undulata*	Grand Canyon track, Blackheath	2.6	16.98	1.105	2.374
27	2009	*Usnea*	Blue Mountains National Park	1.7	17.07	1.102	2.368
28	2010	*Usnea*	Mitchell Park, part of Cattai National Park	1.0	17.45	1.130	2.405

along with the average annual air filter samples are shown in Fig. 3. The data show predominantly higher lead isotope ratios for the lichen-fungi samples in the 1880s/early 1900s. This can probably be attributed to a mix of geogenic inputs and large-scale regional industrial development and associated inputs to the atmosphere (including coal burning). The data are consistent with the relatively high lead concentrations measured in lichens at this time (Fig. 2). The decrease in lead isotope ratios in lichen and fungi samples in subsequent decades (Fig. 3) corresponds with the introduction of leaded petrol in 1932 and a reducing influence of other industrial emissions. The large range of $^{206}Pb/^{207}Pb$ ratios for lichens (*Cladonia*: 1.122–1.081; *Usnea*: 1.108–1.072) and air filters (1.148–1.074) measured during the period of the 1970–1980s is attributed to the supply of tetraethyl lead petrol additives from different sources (Gulson et al., 1983). Specifically, from 1995 onwards, isotopic compositions exhibit more radiogenic values for both lichens and air filters (Fig. 3). This is paralleled by lower median lead concentrations in lichen samples (*Cladonia* 4.8 mg/kg; *Usnea* 1.7 mg/kg) and shows the reduced impact of leaded petrol emissions on Sydney's atmosphere. However, lead isotope ratios for contemporary lichen and air filter samples have not reached background rock and deep soil values (Figs. 3 and 4), indicating that historic leaded petrol and other anthropogenic sources persist in the environment.

3.2. Source apportionment

3.2.1. Geogenic sources of lead in lichens

Unweathered rock samples (n = 10) and deep soils (30–40 cm depth, n = 4) from national parks and reserves in Sydney (Fig. 1), representing natural local lead sources, have $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope ratios of 1.176–1.123 and 2.500–2.413, respectively (Table 4). The variation in lead isotope ratios is considered to be due to inherent lithologic variation between the different sampling locations. The measured $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of Sydney subsoils (30–40 cm) vary from 1.123 to 1.146 and 2.430 to 2.459. These values are bracketed by the composition of unweathered Sydney rock samples indicating that deeper soils reflect natural lead sources. Lichen and fungi samples collected prior to the introduction of leaded petrol (*Cladonia* mean $^{206}Pb/^{207}Pb$: 1.138; mean $^{208}Pb/^{207}Pb$: 2.421, n = 14; *Usnea* mean $^{206}Pb/^{207}Pb$: 1.119; mean $^{208}Pb/^{207}Pb$: 2.400, n = 7; *Trametes* $^{206}Pb/^{207}Pb$: 1.112–1.132; $^{208}Pb/^{207}Pb$: 2.387–2.411) parallel Sydney rock and subsoil lead isotope values (Fig. 4). These data imply that geogenic inputs are one of several potential sources of atmospheric lead during the pre-

Table 3
Lead concentrations and lead isotopic compositions of archived *Trametes* fungi collected between 1924 and 1988.

No.	Year	Species	Location	Pb (mg/kg)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
1	1924	*Trametes versicolor*	Fairfield, Canley Vale	1.9	17.25	1.132	2.411
2	1926	*Trametes*	Mount Wilson	1.8	17.04	1.112	2.387
3	1939	*Trametes versicolor*	Hazelbrook and Bullaburra Glen, Blue Mtns	3.2	16.84	1.081	2.359
4	1951	*Trametes lactinea*	Royal Botanic Gardens, Sydney	6.5	16.52	1.075	2.357
5	1953	*Trametes lactinea*	North Ryde, Sydney	16.6	16.49	1.067	2.344
6	1955	*Trametes lactinea*	Royal Botanic Gardens, Sydney	1.1	16.45	1.071	2.350
7	1956	*Trametes ochracea*	Beaconsfield, Alexandria	0.9	16.36	1.072	2.357
8	1982	*Trametes versicolor*	Mount Tomah, Blue Mtns	1.2	16.84	1.086	2.355
9	1983	*Trametes hirsuta*	Opposite “Cedar Vale”, 10.4 km NNW of Yarramalong Public School	4.4	16.96	1.095	2.371
10	1988	*Trametes versicolor*	Mount Wilson, 17 NE of Mount Victoria	0.5	16.76	1.086	2.361

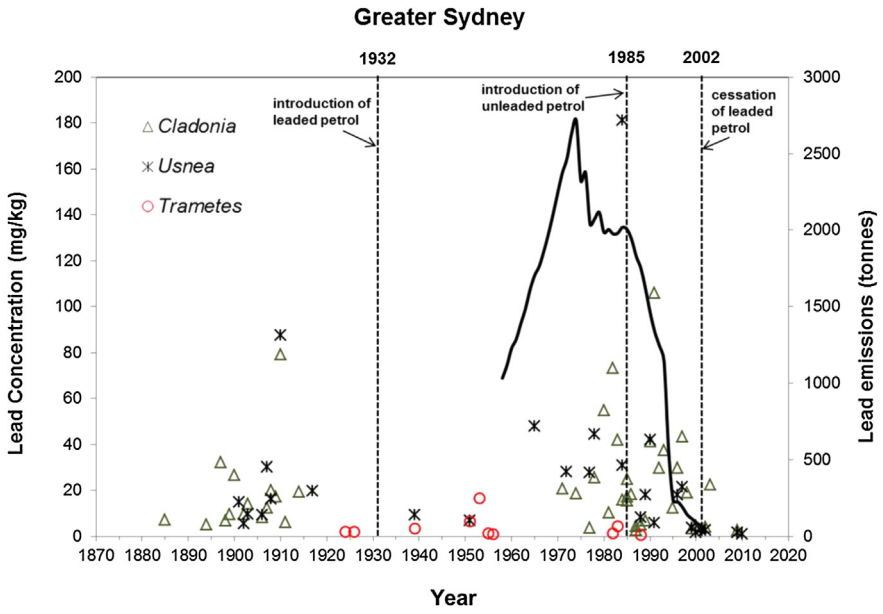

Fig. 2. Lead concentrations in *Cladonia* lichens (1885–2009) and *Usnea* lichens (1901–2010) and *Trametes* fungi (1924–1988) from the Greater Sydney region over time. An outlier value of 570 mg/kg from 2001 (Table 1) is not shown. Petrol lead emissions (tonnes/year) in New South Wales from 1958 to 2002 are also shown (Kristensen, 2015).

Table 4
Lead concentrations and lead isotope ratios of rocks and surface and subsurface soils from the Greater Sydney area.

Sample no.	Location	Pb (mg/kg)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
SYD_Rock_1	Sydney Harbour National Park	15.0	18.04	1.159	2.478
SYD_Rock_2	Sydney Harbour National Park	5.5	17.96	1.160	2.434
SYD_Rock_3	Sydney Harbour National Park	9.6	17.84	1.142	2.447
SYD_Rock_4	Sydney Harbour National Park	19.8	17.42	1.124	2.413
SYD_Rock_5	Sydney Harbour National Park	9.3	18.02	1.158	2.464
SYD_Rock_6	Lane Cove National Park	9.3	17.72	1.127	2.434
SYD_Rock_7	Lane Cove National Park	30.0	18.13	1.165	2.476
SYD_Rock_8	Lane Cove National Park	16.2	18.44	1.176	2.500
SYD_Rock_9	Lane Cove National Park	87.6	18.04	1.156	2.467
SYD_Rock_10	Duffys Forest	3.5	17.73	1.134	2.426
SYD_Soil_1_0-2	Sydney Harbour National Park	17.9	17.27	1.114	2.402
SYD_Soil_2_0-2	Sydney Harbour National Park	49.2	17.09	1.108	2.388
SYD_Soil_3_0-2	Lane Cove National Park	13.3	17.03	1.098	2.394
SYD_Soil_4_0-2	Duffys Forest	7.6	17.30	1.121	2.432
SYD_Soil_1_30-40	Sydney Harbour National Park	6.8	17.86	1.144	2.459
SYD_Soil_2_30-40	Sydney Harbour National Park	28.1	17.77	1.146	2.445
SYD_Soil_3_30-40	Lane Cove National Park	7.4	17.63	1.123	2.441
SYD_Soil_4_30-40	Duffys Forest	6.7	17.71	1.135	2.430

Table 5
Comparison of lead isotope ratios from *Cladonia* and *Usnea* lichens and *Trametes* fungi collected during the same year.

Year	Species	Location	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
1939	*Trametes versicolor*	Hazelbrook and Bullaburra Glen, Blue Mtns	16.84	1.081	2.359
	Usnea	Hazelbrook, south side of railway line, Blue Mtns	17.02	1.081	2.354
1951	*Trametes elegans*	Royal Botanic Garden, Sydney	16.78	1.083	2.358
	Usnea angulata	Kowmung River to Kiaramba Ridge, Blue Mtns	16.83	1.092	2.362
1982	*Trametes versicolor*	Mount Wilson, Blue Mtns	16.95	1.099	2.366
	Cladonia furcata	Epping, near Devlins Creek	17.36	1.115	2.384
1983	*Trametes hirsuta*	Opposite “Cedar Vale”, 10.4 km NNW of Yarramalong Public School	16.96	1.095	2.371
	Cladonia praetermissa	Towler Bay, 30 km north of Sydney	17.02	1.095	2.371
1988	*Trametes versicolor*	Mount Wilson, 17 km northeast of Mount Victoria	16.76	1.086	2.361
	Usnea	Mount Wilson	16.88	1.080	2.349

leaded petrol era.

3.2.2. Leaded petrol contributions to lichen lead concentrations

The lead isotopic composition of petrol sold in Sydney during the 1978–1981 period is characterised by $^{206}Pb/^{207}Pb$ ratios of 1.081–1.193 and $^{208}Pb/^{207}Pb$ ratios of 2.353–2.440 (Gulson et al., 1983). Gulson et al. (1983) demonstrated that the wide variation in petrol isotope data was the result of the lead in petrol being

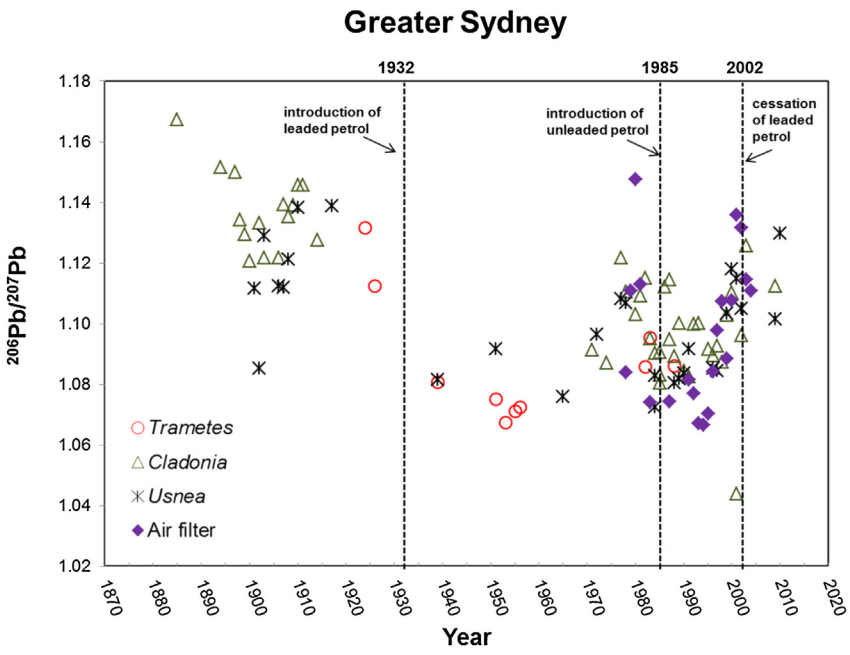

Fig. 3. Lead isotopic compositions ($^{206}Pb/^{207}Pb$) in *Cladonia* lichens (1885–2009), *Usnea* lichens (1901–2010), *Trametes* fungi (1924–1988) and air filters (1978–2004) from the Greater Sydney region over time.

sourced from Broken Hill/Mount Isa, Mississippi Valley and 'Woodlawn-type' ore deposits. In the 1990s the petrol ratio shifted to $^{206}Pb/^{207}Pb$ of 1.059–1.127 and $^{208}Pb/^{207}Pb$ of 2.333–2.383 (B.L. Gulson, personal communication, Supplementary Table S1).

Cladonia mean $^{206}Pb/^{207}Pb$ isotope values of 1.103 (1970s) and 1.098 (1980s) and $^{208}Pb/^{207}Pb$ values of 2.380 and 2.376, lie within the lower 1978–1981 petrol lead isotope envelope (Supplementary Table S1). Similarly, *Usnea* lichen mean $^{206}Pb/^{207}Pb$ ratios of 1.104 (1970s) and 1.079 (1980s) and mean $^{208}Pb/^{207}Pb$ ratios of 2.372 and 2.354 fall predominantly within the lower leaded petrol values during that period (Supplementary Table S1). Likewise, *Trametes* fungi (1980s) average $^{206}Pb/^{207}Pb$ of 1.089 and $^{208}Pb/^{207}Pb$ of 2.362 are also within the lower range of the petrol envelope (Supplementary Table S1). The suggestion that lead taken up by lichens in the 1970s–1980s is derived from leaded petrol emissions concurs with concurs with Gulson et al. (1983), who calculated that approximately 90% of the lead in Sydney air in the 1980s was derived from lead petrol additives. The measured $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in air filters analysed in this study from 1978 to 1999 were within the range of the petrol lead reported in Sydney from the end of the 1970s–1990s (Supplementary Table S1). This confirms the assumption that air filter lead corresponds with petrol lead sources in this region.

The mean lead isotope ratios for both *Cladonia* and *Usnea* lichens collected in the 1990s are close to, or overlap with Sydney leaded petrol ratios (Supplementary Table S1), indicating that leaded

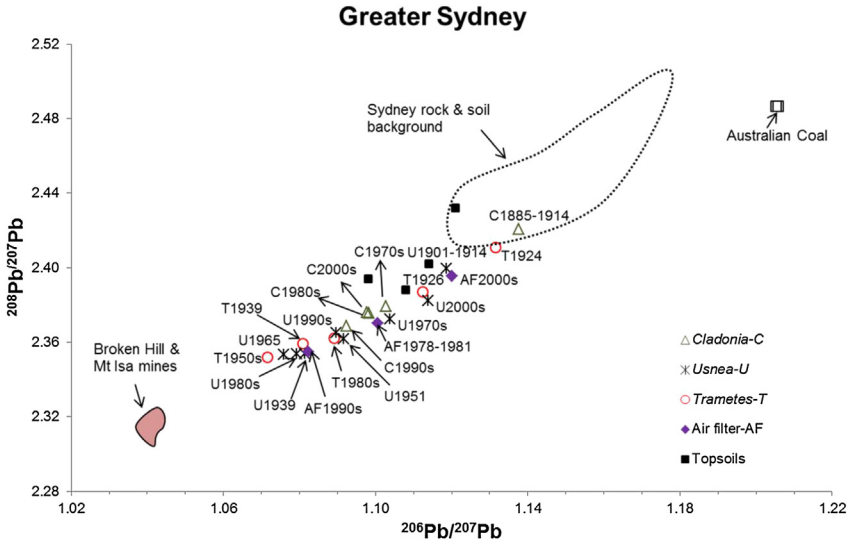

Fig. 4. Lead isotopic compositions of *Cladonia* lichens (from 1885 to 2009), *Usnea* lichens (from 1901 to 2010) and *Trametes* fungi (1924–1988) collected from Sydney. Data for Sydney lichen and fungi, topsoils and rocks are given in Tables 1–4. Air filters, Australian ores and Australian coal data sources are presented in Supplementary Table S1. Samples in the figure represent average values for the stated time period, e.g. C1980s – *Cladonia* for the decade of the 1980s.

petrol was still a major contributor to atmospheric depositions despite the introduction of lead-free petrol in 1985. The isotopic composition of Sydney aerosols in 1994 were $^{206}Pb/^{207}Pb$: 1.067 ± 0.001 and $^{208}Pb/^{207}Pb$: 2.342 ± 0.001 (Bollhöfer and Rosman, 2000), which is bracketed by leaded petrol values from the 1990s ($^{206}Pb/^{207}Pb$: 1.059–1.127 and $^{208}Pb/^{207}Pb$: 2.333–2.383, Supplementary Table S1).

Mean lead isotope ratios determined in *Cladonia* and *Usnea* lichens collected from the Greater Sydney region in the 2000s (*Cladonia*: $^{206}Pb/^{207}Pb$: 1.098, $^{208}Pb/^{207}Pb$: 2.376 and *Usnea*: $^{206}Pb/^{207}Pb$: 1.114, $^{208}Pb/^{207}Pb$: 2.382) overlap with leaded petrol isotope values (Supplementary Table S1). This indicates that although Australian leaded petrol was removed from sale in 2002, it remains a persistent environmental contaminant (Flegal et al., 2010). Our lichen results mirror Gulson et al. (2007) and Cohen et al.'s (2012) assertion that air particulate analysis from leaded petrol emissions prior to 2001 continued to contribute to atmospheric particulate lead in the Sydney Basin during the period 1998 to 2009. Marine surface sediment analysis shows that leaded petrol has contributed up to 68% of lead sources in sediment samples collected in Sydney harbour (Larsen et al., 2012). This is not surprising since vehicle movements have been associated with the resuspension of legacy lead depositions (Laidlaw et al., 2012; Kristensen, 2015) and remobilisation also occurs during wild fires (Odigie and Flegal, 2011; Kristensen et al., 2014).

3.2.3. Additional environmental sources of lichen and fungi lead concentrations

3.2.3.1. Coal combustion. Lead emissions from coal combustion have been shown to be another significant contributor of atmospheric lead pollution in Europe, United States and Asia (Mukai et al., 1993; Graney et al., 1995; Farmer et al., 1999; Vile et al., 2000; Novák et al., 2003). There is limited published lead isotope data for Australian coals ($^{206}Pb/^{207}Pb = 1.21$ and $^{208}Pb/^{207}Pb = 2.50$, (Díaz-Somoano et al., 2009) in spite of the fact that approximately 77% of Australian electricity production is generated from coal combustion (Wells and Donaldson, 2005). Relatively high lead isotopic ratios in Australian coal corroborates the suggestion by Marx et al. (2010) that more radiogenic signatures are present in fly ash samples from Australian coal-fired power stations. Approximately 25 MT yr^{-1} of coal is burnt from eight coal-fired power stations in New South Wales (Cohen et al., 2012) making it an important potential source. Fig. 4 shows that the lead isotope ratios of Australian coals have higher $^{206}Pb/^{207}Pb$ ratios than the Sydney rock and soil samples but overlap with the $^{208}Pb/^{207}Pb$ ratios of rocks and soils. Given the elevated lead concentrations in lichen and fungi prior to the introduction of leaded petrol (Fig. 2), it is highly likely that coal combustion was a major contributory source. However, the partial overlap of the isotopes make it difficult to separate the contribution from coal versus that from natural rocks and soils.

3.2.3.2. Soil-derived sources. Lead concentrations and isotope ratios in topsoils collected during 2013–2014 are summarised in Table 4 and plotted in Fig. 4. Lead concentrations in Sydney topsoils (0–2 cm) collected from national parks and reserves are 17.9 mg/kg, 13.3 mg/kg, 49.2 mg/kg and 7.6 mg/kg, respectively. These are higher than background soil (30–40 cm) lead concentrations (6.8 mg/kg, 7.4 mg/kg, 28.1 mg/kg and 6.7 mg/kg, respectively (Table 4). Birch et al. (2011) reported that surface soil lead values ranged from 3 to 9653 mg/kg from the Sydney estuary catchment. Rouillon et al. (2013) reported that Lithgow city topsoils (the northwestern edge of our lichen sample locations, see Fig. 1) were enriched with lead compared to background soils by a factor of 7.6. Sydney topsoil $^{206}Pb/^{207}Pb$ ratios range from 1.098 to 1.121 and $^{208}Pb/^{207}Pb$ from 2.388 to 2.432 (Table 4). These surface soil values are attributed to atmospheric lead depositions, which are similar to *Cladonia*, *Usnea* and air filter mean lead isotopic values of samples collected in the 2000s (Fig. 4).

3.2.3.3. Industrial sources. Local industrial utilities such as gas works (e.g. Canada Bay), lead smelters (e.g. Rhodes, Cabarita Point) and incinerators (e.g. Balmain) would have contributed to atmospheric lead in the Greater Sydney region (Birch, 2007; Hatheway, 2010; Birch et al., 2015). For example, British Australian Lead Manufactures/Dulux Paints operated from the 1920s until 1995 on the shoreline of Hen and Chicken Bay within Sydney Harbour and manufactured mainly white lead products (Townsend, 2011). Unfortunately, a paucity of available data prevents emissions from these sources from being quantified due to a lack of lead isotope data.

3.2.3.4. Other possible sources. In addition to the aforementioned predominant anthropogenic lead sources in the Greater Sydney area, a number of specific, point sources could have also contributed to lead found in lichen samples. For example, a single *Cladonia* lichen sample collected adjacent to Anzac Rifle Range in 2001 had low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of 1.044 and 2.319, respectively, which is consistent with the Australian lead used in the propellant for the cartridges (Gulson et al., 2002a, 2002b). Other sources of unmeasured lead would include wood burning, runoff, road dust and lead paint (Chiaradia et al., 1997; Cohen, 1999; Cohen et al., 2002; Birch and Scollen, 2003; Davis and Gulson, 2005; Gulson et al., 2007; Cohen et al., 2012; Laidlaw et al., 2014). Notwithstanding the fact that these sources cannot be evaluated due to lack of available data, the lichen and fungi results presented herein reveal marked shifts in both lead concentration and isotope composition consistent with the timing of industrial activity (including coal combustion), geogenic inputs and leaded petrol emissions.

4. Conclusions

Analysis of archival lichen and fungi samples reveal that industrial lead emissions, dominated by those from leaded petrol, remain a persistent source of anthropogenic contamination in the Greater Sydney region. The findings from this study are consistent with temporal studies of archival mosses from United Kingdom and lichens from USA, revealing the utility of Australian lichen and fungi for reconstructing atmospheric pollution records. In light of the near universal paradigm that there is no safe level of lead exposure, it is clear that maximum regulatory effort is required to eliminate existing emissions, mitigate resuspension and exposure from legacy sources that still permeate Sydney basin, which contains Australia's most populated city.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.10.046.

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CHAPTER 3

Paper Two

Insights into past atmospheric lead emissions using lead concentrations and isotopic compositions in historic lichens and fungi (1852–2008) from central and southern Victoria, Australia

Wu, L., Taylor, M.P., Handley, H.K., Gulson, B.L. (2016)

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This study further assesses the validity of using lichen and fungi as environmental proxies for monitoring atmospheric lead contamination in a different region of Australia. Lead concentrations and isotopic compositions of archival lichens and fungi from central and southern Victoria were determined to investigate the temporal evolution of atmospheric Pb contamination from known industrial emissions over the last 150 years. The results demonstrate that emissions from anthropogenic lead sources, including leaded petrol, are persistent and do not 'go away' despite the cessation of the use of lead additives in petrol in 2002. The lead concentrations and isotopic compositions mirror patterns recorded in other recent southern hemisphere studies, including studies from Antarctica.

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Insights into past atmospheric lead emissions using lead concentrations and isotopic compositions in historic lichens and fungi (1852–2008) from central and southern Victoria, Australia

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HIGHLIGHTS

- Historic lichen and fungi from southern Australia are useful atmospheric proxies.
- A 150-year record of lichen and fungi samples match shifts in industrial emissions.
- Lead isotope compositions reveal lead petrol was a dominant source of contamination.
- Former leaded petrol emissions remain a persistent environmental contaminant.

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ABSTRACT

Lead concentrations and lead isotopic compositions were determined in historic central and southern Victoria, Australia lichen (*Cladonia* and *Usnea*) and fungi (*Trametes*) samples collected between 1852 and 2008 to evaluate long-term atmospheric lead contamination sources. The data are grouped into four time intervals of 1850–1931, 1932–1984, 1985–2001 and 2002–2008 corresponding to the history of leaded petrol use in Australia. Elevated lichen and fungi lead concentrations and relatively high isotopic compositions from the period 1850–1931 are attributed to lithogenic sources, gold mining activities and early industrialisation. Significant increases in lichen and fungi lead concentrations and concomitant lower lead isotopic compositions correspond to the marked increase in lead emissions from leaded petrol use after 1932. Following the end of leaded petrol use in 2002 lead isotopic composition values 'recover' toward more lithogenic values. However, the lead isotopic composition data indicate that the environmental impact from leaded petrol emissions persists in contemporary samples dated to 2002–2008. Overall, the data reveal that herbarium lichens and fungi from central and southern Victoria can be used as proxies for environmental lead emissions over the past 150 years.

1. Introduction

Lichens absorb most of their nutrients and minerals from the atmosphere and consequently are potential useful biomonitors of atmospheric contamination (Brodo et al., 2001). Lichens have been used as a proxy for atmospheric contamination in Europe since the 19th century (De Bary, 1866). Previous studies of historic lichens and mosses focused on assessing temporal changes of atmospheric lead contamination and identifying their potential sources and dispersion throughout Europe, Asia and the USA (Satake and Virtanen, 1995; Herpin et al., 1997; Weiss et al., 1999; Garty, 2001; Farmer et al., 2002; Klaminder et al., 2005; Steinnes et al., 2005; Komárek et al., 2007; Cao et al., 2008; Flegal et al., 2010; Agnan et al., 2014). Previous lichen studies have shown that large variations in lead concentrations were observed between polluted sites (e.g. adjacent to motorways, smelting and mining areas) and unpolluted sites (e.g. forest areas) (Cuny et al., 2001; Spiro et al., 2004; Pawlik-Skowronska et al., 2008; Søndergaard et al., 2010).

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Similar findings have been reported for fungi in Europe (Kalač and Stašková, 1991; Svoboda et al., 2000, 2006; Petkovšek and Pokorny, 2013).

Lead has four natural isotopes in the environment: ^{204}Pb (1%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{208}Pb (52%) (Bollhöfer and Martin, 2003). The ^{206}Pb, ^{207}Pb and ^{208}Pb are produced by radioactive decay and form the stable end-members of the decay chains of ^{238}U, ^{235}U and ^{232}Th with a half-life of 4.5, 0.7, and 14 billion years, respectively (Kunert et al., 1999). ^{204}Pb is a primordial isotope and is not formed from radiogenic decay. In general, the Pb isotopic compositions are commonly expressed as ratios of ^{206}Pb/^{204}Pb, ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb. The usefulness of isotope ratio measurement for identifying various ore body and tracing geogenic and anthropogenic inputs of lead contamination into the environment, has been demonstrated multiple times in the literature (e.g. Chow and Patterson, 1962; Shirahata et al., 1980; Flegal et al., 1989; Rosman and Chisholm, 1996; Erel et al., 1997; Gulson, 2008; Komárek et al., 2008; Cheng and Hu, 2010).

In Australia, sources of atmospheric lead have included lithogenic lead, mining and smelting activities, various industrial activities (e.g. waste incinerators, lead smelters), coal combustion and vehicle exhausts from the use of leaded petrol (Gulson, 2008). Leaded petrol was used in Australia for over 70 years (1932–2002) and resulted in the release of more than 240,000 tonnes of lead into the atmosphere (Kristensen, 2015). Leaded petrol was introduced in Australia in 1932, with the maximum consumption of leaded petrol and associated emissions occurring in the 1970s and the 1980s, respectively (Kristensen, 2015). The phasing out of leaded petrol for automobile use in Australia started in 1985 and was finally prohibited for sale in 2002. A recent evaluation of historic lichens and fungi collected from the Greater Sydney area, Australia's largest and most populated urban region, showed that temporal shifts from former leaded petrol emissions along with other sources were recorded in herbarium samples (Wu et al., 2016). However, the wider application of this technique to the Australian continent is unknown. Therefore, this study: (i) evaluates lead concentrations and isotopic compositions in archival lichen and fungi samples from central and southern Victoria for their potential as an environmental proxy; (ii) analyses the resulting environmental data against known possible sources of atmospheric lead contamination, including, petrol lead emissions, industrial emissions (e.g. coal combustion), sources from neighbouring Victorian goldfields, soils and river sediments.

2. Materials and methods

2.1. Study area and sampling materials

Two lichen genera (*Cladonia* and *Usnea*) and one fungi genus (*Trametes*) were obtained from collections at the Australian National Herbarium (Canberra), the National Herbarium of New South Wales and Macquarie University Downing Herbarium (Sydney) and the National Herbarium of Victoria and the University of Melbourne Herbarium (Melbourne). The archived samples span dates from 1852 to 2008 and were all collected within a 150 km radius of Melbourne Central Business District (CBD) (Fig. 1). The sample period covers nearly the full European history of the Melbourne city, which was established in 1847 (Lewis, 1995). Sample location details are provided in Fig. 1 and Supplementary Tables S1–S3.

Cladonia lichen is known to grow on bark, soil, peat, wood or rock substrates, and accumulate chemicals mainly from the surrounding atmosphere and possibly from the soil, while the *Usnea* lichen grows on tree bark and shrubs and absorbs nutrients from the atmosphere (Brodo et al., 2001). Archived *Trametes* fungi were also collected to supplement the data set (cf. Wu et al., 2016). *Trametes* fungi are a wood-rotting genus which mainly uptake trace metals from the atmosphere (Gabriel et al., 1997). To the best of our knowledge, lead-related preservation treatments had not been applied to the samples.

2.2. Sampling procedure

The procedure for sampling the lichen and fungi archives from the herbaria are described in Wu et al. (2016). Soil from two sites and riverbed sediment samples were collected from the same geographic area from which the lichens and fungi samples were collected in order to characterize the *in situ* lead concentration and isotopic composition of background lead (Supplementary Table S4). Soil samples were collected using established procedures (Taylor et al., 2010) from depths of 0–2 cm to provide information on the effects of atmospheric depositions and from a depth of 40–50 cm to provide supplementary information on uncontaminated lithogenic values. Four surface sediments (0–2 cm) were collected from the centre of dry creek beds flowing through Yarra Ranges National Park and Dandenong Ranges National Park (Fig. 1, Supplementary Table S4). Lichen and fungi as well as soil and sediment samples were placed in sealed plastic bags prior to analysis at the National Measurement Institute (NMI), Sydney.

2.3. Sample preparation and analysis

Cladonia lichen samples were separated from attached substrate (soil) using a clean plastic knife. Sixty-five dried lichen samples (approximately 10–200 mg) and 32 fungi samples (between 50 and 500 mg) were digested with ultrapure 16 M HNO_3 (NMI, 2014a). Approximately 0.5 g of the soil and sediment samples were digested in 16 M HNO_3 and 10 M HCl (NMI, 2014b). Lead concentrations and isotopic compositions were determined using a Perkin Elmer Elan DRC II, Inductively Coupled Plasma Mass Spectrometer (ICP-MS). After substrate removal, low sample weights were obtained for three lichen samples (~10 mg), which may have affected the quality of lead isotope data for these samples, especially for the low abundance ^{204}Pb isotope. Sample lead isotopic compositions were bracketed with the measurement of National Institute of Standards and Technology (NIST) certified reference material SRM 981 (common lead) to correct for mass fractionation. For the lead concentration analysis, Standard Reference Material IEAE 336 (lichen, n = 8), AGAL-10 (river sediment, n = 8) and the material quality control sample AGAL-12 (biosoil, n = 8), returned lead recovery rates (mean ± RSD) of 98 ± 2.6%, 99 ± 2.3%, 101 ± 3.4%, respectively. Overall analytical precision (±1 RSD) for these three reference materials was within ±6% of the certified values for lead concentration determination. Total blank contamination was generally less than 0.01 mg/kg. Replicate analysis (n = 8) of one lichen (*Cladonia* 1995, Supplementary Table S1) gave relative standard deviations (RSD) for lead concentration of ±3%, and, ±0.9%, ±0.6% and ±0.4% for ^{206}Pb/^{204}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios, respectively.

2.4. Statistical analyses

Medians and box plots were undertaken using SPSS 21.0 and Microsoft Excel in order to assess the relationship between the lead concentrations and isotopic compositions of the three genera and the four time periods of known shifts in lead emissions to the atmosphere. Sample statistical differences were analysed using the Kruskal-Wallis test.

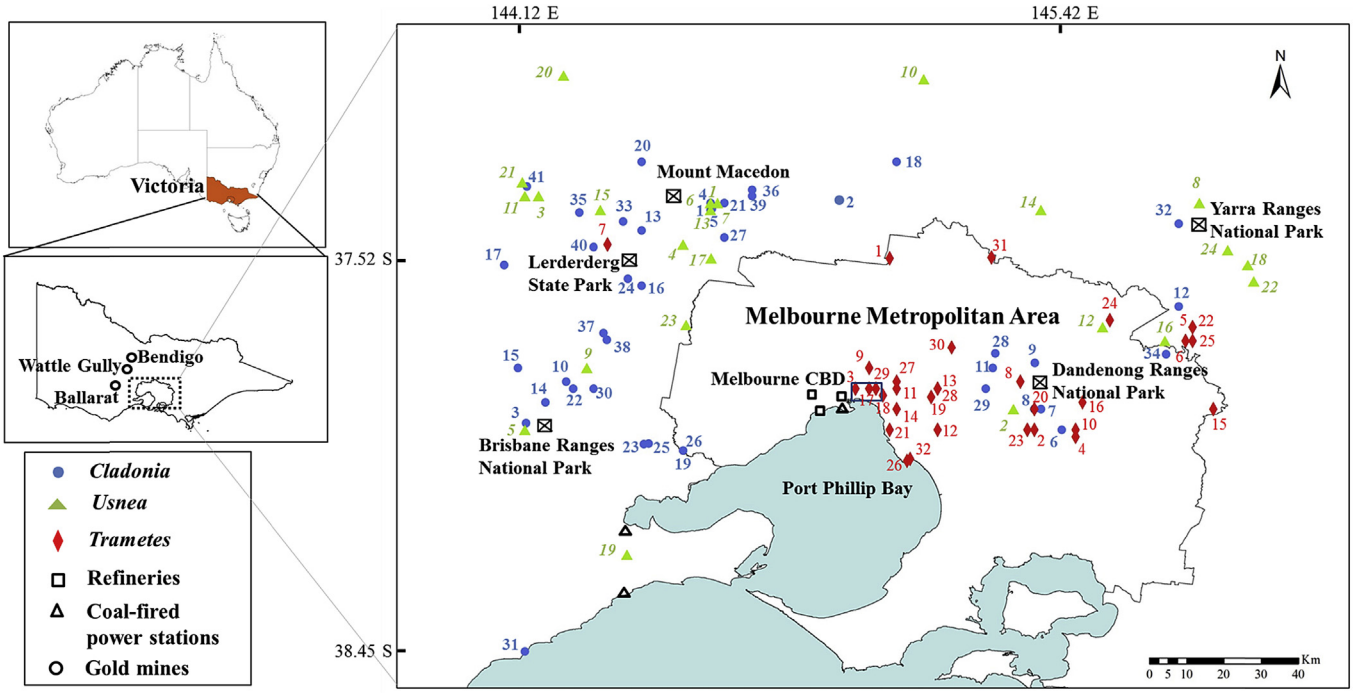

Fig. 1. Map of the sampling sites of *Cladonia* lichen, *Usnea* lichen and *Trametes* fungi in central and southern Victoria, Australia. The blue rectangle represents Melbourne Central Business District (CBD); the black squares with a cross represent National Parks: Mount Macedon, Lerderderg, Brisbane Ranges, Yarra Ranges and Dandenong Ranges. The inset of Australia shows the location of the state of Victoria. The locations of three gold mines referred to in the text are shown on the inset of Victoria. Sample IDs of *Cladonia* lichens are presented in blue; sample IDs of *Usnea* lichens in green and in *italics;* sample IDs of *Trametes* fungi in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Lead concentrations in lichens and fungi

Lead concentrations are listed in Supplementary Tables S1–S3 for *Cladonia* and *Usnea* lichens and *Trametes* fungi. The median lead concentrations in *Cladonia, Usnea* and *Trametes* were 3.6 mg/kg (range 0.2–439 mg/kg), 13 mg/kg (range 0.4–86 mg/kg) and 3.4 mg/kg (range 0.2–24 mg/kg), respectively. Lead concentrations between the three genera were statistically different ($p < 0.05$).

The history of Australian leaded petrol use can be divided into four main stages (Figs. 2 and 3): stage 1 pre–1932, the period characterised by the absence of leaded petrol use; stage 2 represents the commencement of leaded petrol use in 1932; stage 3, the introduction of unleaded petrol in 1985; and stage 4, the period following the cessation of leaded petrol in 2002 (Kristensen, 2015). The lead concentrations of the lichen and fungi samples are presented individually in Fig. 2 and are grouped into the four main stages of Australian leaded petrol use in Fig. 3.

3.1.1. Stage 1 – pre leaded petrol era — 1850–1931

There are five *Cladonia,* one *Usnea* and one *Trametes* samples available from the herbarium collections for the period 1850 and 1931. The highest lead concentrations were measured in the two oldest *Cladonia* lichens collected from the Mount Macedon area in 1885 (439 mg/kg) and 1886 (216 mg/kg) (Fig. 1; Supplementary Table S1). The *Usnea* lichen sample from the Mount Macedon area, dated to 1900, also has a relatively high lead concentration (36 mg/kg) (Supplementary Table S2). High lead concentrations in the archival lichens from the Mount Macedon area could possibly be associated with the gold mining activity in the region (Gerasimon and Studios, 2016), which commenced in 1851 (Phillips and Hughes, 1996). Elevated lead concentrations in soils formed on gold mining waste material site in central Victoria have been attributed previously to mining activities (Sultan, 2007). Following the gold rush, rapid urbanisation of Melbourne ensued, which coincided with an increased flux of lead into a Melbourne city lake around 1890. This was followed by a marked, rapid rise after 1940 following the introduction of leaded petrol (Smith and Hamilton, 1992).

3.1.2. Stage 2 – main period of leaded petrol consumption — 1932–1984

During the period from 1932 to 1984, median lead concentrations for the three genera were: *Cladonia* 5.0 mg/kg, *Usnea* 15 mg/kg, and *Trametes* 4.2 mg/kg, although a wide range of lead values (*Cladonia* 1.3–25 mg/kg, *Usnea* 5.0–86 mg/kg, *Trametes* 0.5–24 mg/kg) were observed (Supplementary Tables S1–S3). Median data for *Usnea* samples were calculated without three outlier values (42 mg/kg, 58 mg/kg and 86 mg/kg; Supplementary Table S2) (Fig. 2). During this period, the lead concentrations for *Usnea* lichens were significantly higher ($p < 0.05$) than those in *Cladonia* and *Trametes* (Fig. 3). The three outlier samples were collected from the Coranderrk Bushland Reserve (1980) adjacent to the Healesville-Koo Wee Rup Road, and two from the gold mining areas of Mount Macedon (1981) and Trentham (1984) (Supplementary Table S2).

Lead values were largely higher in five *Trametes* collected from the Melbourne metropolitan area: 1939 (15 mg/kg), in 1957 (24 mg/kg), in 1960 (18 mg/kg), in 1963 (23 mg/kg) and in 1967 (19 mg/kg), compared with the majority of samples from this period (Fig. 2; Supplementary Table S3). In particular, high lead concentrations were measured in two *Trametes* samples collected close to main roads of Melbourne city in 1963 and in 1967 (Supplementary Table S3). The high lead concentrations from these urban samples correspond to the rise in leaded petrol emissions and local

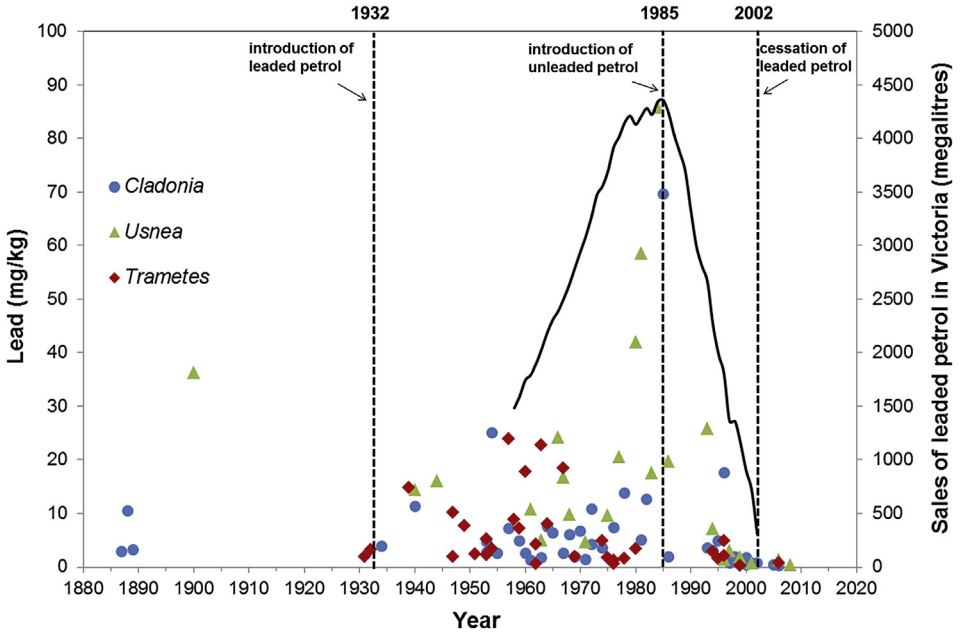

Fig. 2. Lead concentrations in *Cladonia* and *Usnea* lichens and *Trametes* fungi from central and southern Victoria over time. Two outlier values of 439 mg/kg from 1885 and 216 mg/kg from 1886 are not shown. Sales of leaded petrol (megalitres) for the state of Victoria from 1958 to 2002 are shown (solid black line; Kristensen, 2015). Also shown on the figure are four stages of leaded petrol use/not use in Australia referred to the text.

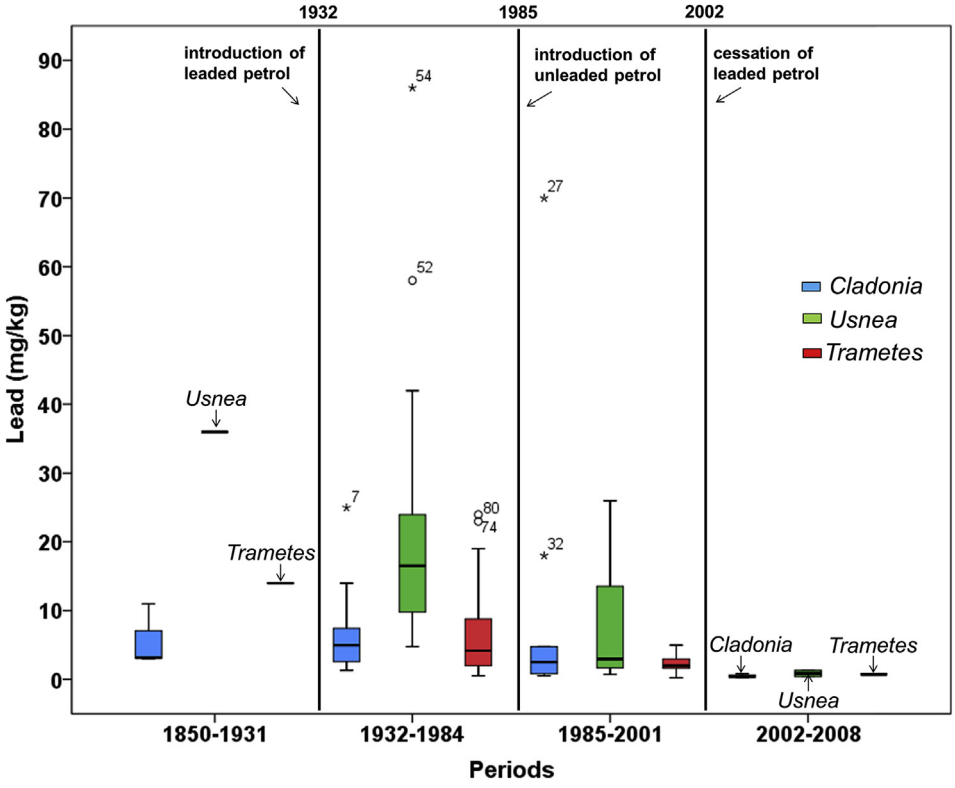

Fig. 3. Box-whisker plots for lead concentrations (mg/kg) in *Cladonia, Usnea* and *Trametes* samples for four time periods. Two outlier values of 439 mg/kg from 1885 and 216 mg/kg from 1886 are not shown. The boxes define median values and 25th and 75th percentiles of the data while the whiskers represent the 10th and 90th percentiles of the data. Also shown on the figure are four stages of leaded petrol use/not use in Australia referred to the text.

industrial activity (cf. Smith and Hamilton, 1992).

3.1.3. *Stage 3 – the introduction of unleaded petrol —1985–2001*

In the period of 1985–2001, lead concentrations for *Cladonia, Usnea* and *Trametes* samples were not significantly different ($p > 0.05$; Fig. 3). There is a marked fall in the median lead concentration for *Usnea* samples from 15 mg/kg during the period of 1932–1984 to 3.0 mg/kg between 1985 and 2001 (Supplementary

Table S2). In contrast, a small reduction of the median lead concentration for *Cladonia* lichens from 5.0 mg/kg to 2.5 mg/kg and for *Trametes* fungi from 4.2 mg/kg to 2.0 mg/kg (Supplementary Tables S1 and S3). The 1985 *Cladonia* lichen sampled adjacent to a major Melbourne city highway (Maroondah highway) returned a high lead concentration of 70 mg/kg (Supplementary Table S1; sample 27 in Fig. 3). The results presented here are consistent with recent studies of Australian leaded petrol use that reported high leaded petrol consumption during the 1980s in the state of Victoria (Fig. 2) (Kristensen, 2015).

3.1.4. Stage 4 – the period following cessation of leaded petrol consumption — 2002–present

From 2002 to 2008, lead concentrations in lichens and fungi were generally low (<1.3 mg/kg) (Supplementary Tables S1–S3), which correspond to the introduction of unleaded petrol in 1985 and the cessation of leaded petrol use in 2002. During the 1990s Melbourne atmospheric lead averaged 0.03 μg/m^3 (Bollhöfer and Rosman, 2002). The effect of the cessation of leaded petrol use is evidenced by low mean lead concentrations from $PM_{2.5}$ sampling within the Melbourne metropolitan area of 0.004 μg/m^3 in 2003 (Hawas et al., 2003) and 0.0095 μg/m^3 from 2005 to 2006 (Torre et al., 2007).

3.2. Lead isotopic compositions in lichens and fungi

Lichen and fungi lead isotopic compositions are presented in Supplementary Tables S1–S3 and Figs. 4 and 5.

3.2.1. Stage 1 – pre leaded petrol era — 1850–1931

The $^{206}Pb/^{207}Pb$ ratios in lichen and fungi samples between 1850 and 1931 were higher than those from the other three time periods (Fig. 4). Variable lead isotopic compositions, ranging from 1.143 to 1.180, for the oldest herbarium samples are likely to have been influenced by lithogenic sources, metal production and industrial activities (including coal combustion) associated with urbanisation in Melbourne and central Victoria at this time (Lewis, 1995). The Victorian slate belt gold provinces produced ~2400 tonnes of gold from 1851 to 2005 (Mudd, 2007). The *Cladonia* lichens from the Mount Macedon area dated to the period 1885 and 1889 have $^{206}Pb/^{207}Pb$ ratios of 1.151–1.178, which compare with the isotopic compositions (1.150–1.153) of the regional Bendigo and Ballarat ores (Supplementary Tables S1 and S5).

3.2.2. Stage 2 – main period of leaded petrol consumption — 1932–1984

The period 1932–1984 is characterised by the introduction and increase of leaded petrol use (Kristensen, 2015). Median $^{206}Pb/^{207}Pb$ ratios for the three genera were: *Cladonia* 1.095, *Usnea* 1.089, and *Trametes* 1.086 (Fig. 4; Supplementary Tables S1–S3). The lichens and fungi $^{206}Pb/^{207}Pb$ ratios from this time period were significantly lower than those collected during 1850–1931 ($p < 0.05$), which correspond to rise in emissions from leaded petrol and the input of lower isotopic lead into the atmosphere. From 1974 to 1981, the $^{206}Pb/^{207}Pb$ ratios of lichens and fungi show a marked shift compared to the data from 1932–1972 (Supplementary Tables S1–S3). This variation is likely attributable to lead in petrol being sourced predominantly from Broken Hill/Mount Isa which has low lead isotopic composition ratios (Supplementary Table S5). Given that most of *Trametes* fungi samples were collected within the Melbourne metropolitan area during the sampling period (Fig. 1; Supplementary Table S3), it is highly likely that petrol and local industrial emissions were significant sources of lead in the samples.

3.2.3. Stage 3 – the introduction of unleaded petrol —1985–2001

During the period between 1985–2001, no discernible trend is observed in the $^{206}Pb/^{207}Pb$ ratios of herbarium samples. The $^{206}Pb/^{207}Pb$ ratios for *Cladonia, Usnea* and *Trametes* samples from the period 1985–2001 were not statistically different from those

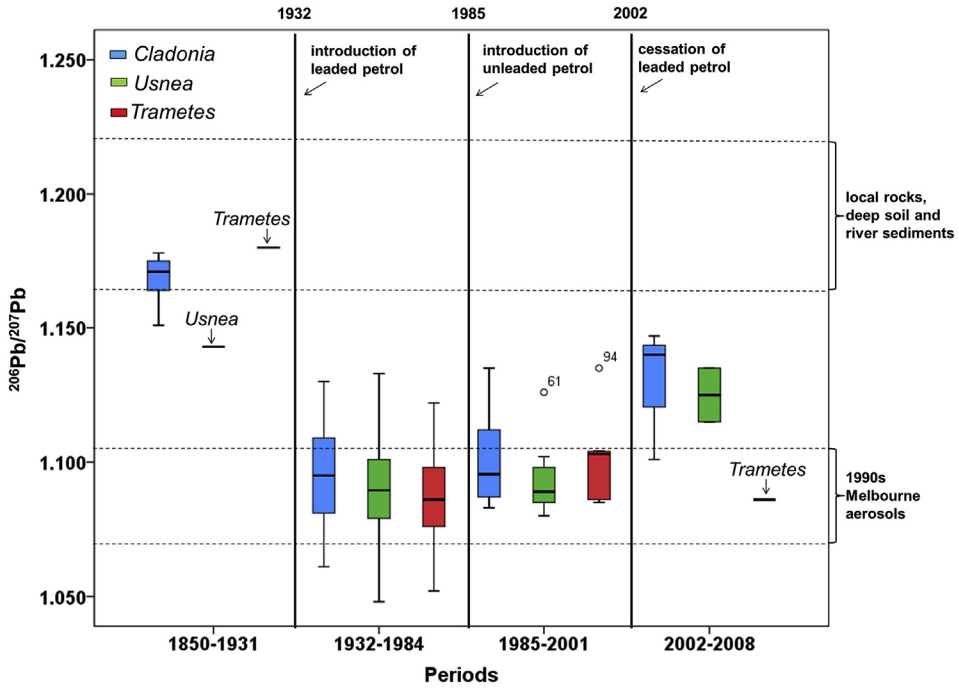

Fig. 4. Box-whisker plot comparing lead isotopic compositions ($^{206}Pb/^{207}Pb$) in *Cladonia, Usnea* and *Trametes* collected from central and southern Victoria between four time intervals. The boxes define median values and 25th and 75th percentiles of the data while the whiskers represent the 10th and 90th percentiles of the data. Four stages of leaded petrol use/not use in Australia referred to the text are shown. Also shown on the figure are isotopic compositions of background samples and the 1990s Melbourne aerosols.

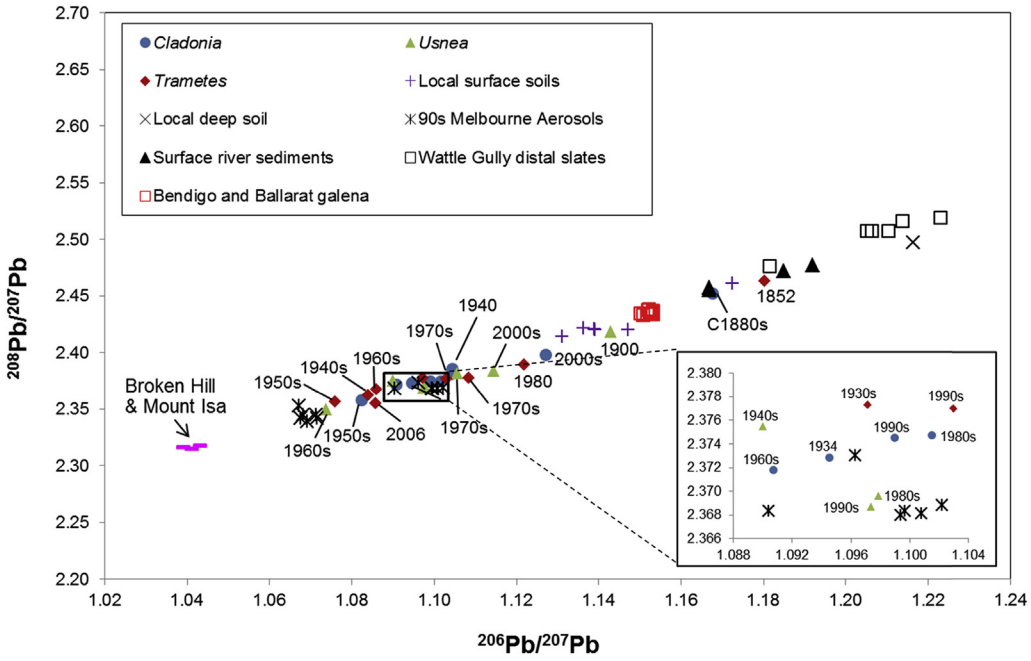

Fig. 5. Decadal average lead isotopic compositions of *Cladonia, Usnea* and *Trametes* samples collected from central and southern Victoria. Data sources for Melbourne aerosols, Australian ores and rocks from the Victorian gold mines are presented in Supplementary Table S1. Data for the local soils and river surface sediments are given in Supplementary Table S4. The insert shows that lichen and fungi samples in the 1990s have similar values to the Melbourne aerosols in 1998.

collected between 1932 and 1984 ($p > 0.05$). Fig. 5 shows that the mean lead isotopic compositions in herbarium samples (*Cladonia:* $^{206}Pb/^{207}Pb$: 1.099 ± 0.016, $^{208}Pb/^{207}Pb$: 2.375 ± 0.021; *Usnea:* $^{206}Pb/^{207}Pb$: 1.097 ± 0.017, $^{208}Pb/^{207}Pb$: 2.369 ± 0.019; *Trametes:* $^{206}Pb/^{207}Pb$: 1.103 ± 0.020, $^{208}Pb/^{207}Pb$: 2.377 ± 0.016) from the 1990s overlap with 1998 (Bollhöfer and Rosman, 2002) Melbourne aerosol values ($^{206}Pb/^{207}Pb$: 1.090–1.102; $^{208}Pb/^{207}Pb$: 2.368–2.373) (Supplementary Table S5). Bollhöfer and Rosman (2000, 2002) attributed the shift to higher lead isotopic compositions in Melbourne aerosols (*inter alia*) sampled in 1998 to either the decreased influence of leaded petrol emissions relative to industrial emissions, or, a shift in the source of alkyllead used in lead petrol. However, analysis of lead used in Sydney petrol over the same time period indicates that petrol was the likely main source (Supplementary Table S5).

3.2.4. Stage 4 — the period following cessation of leaded petrol consumption — 2002–present

Variable lead isotopic compositions were determined for the three genera during 2002–2008 (Supplementary Tables S1–S3). The number of herbarium specimens is limited to three *Cladonia* samples, two *Usnea* samples and one *Trametes* samples during this time period. Median $^{206}Pb/^{207}Pb$ ratios for the two lichen genera were: *Cladonia* 1.140 and *Usnea* 1.125 (Fig. 4; Supplementary Tables S1–S2). All herbarium sample $^{206}Pb/^{207}Pb$ ratios from this time period were significantly higher than those collected during 1985–2001 ($p < 0.05$). This increased shift can be attributed to an increased influence of lithogenic lead and the phase out of Australian leaded petrol in 2002. These results mirror those of Wu et al. (2016) from the Greater Sydney region in that there is a clear shift toward higher lead isotopic compositions that more closely match natural values in the post-2002 period. However, as identified in Sydney lichen and fungi (Wu et al., 2016), the Melbourne data indicate that the 'lingering legacy' from petrol lead emissions is limiting a return of isotopic composition values to ones that match more closely natural values from the region. Kristensen et al. (2014) concluded from the isotopic composition of lead in ash samples collected from a bushfire in Victoria in 2011 that along with lithogenic lead sources and historic leaded petrol sources were still identifiable.

Aside from petrol lead sources, coal combustion is known to contribute significantly to atmospheric lead contamination (Nriagu and Pacyna, 1988; Mukai et al., 1993; Diaz-Somoano et al., 2009). Coal is the primary source fuel for ~77% of Australia's electricity (Wells and Donaldson, 2005). Several coal-fired power stations are located in the west/southwest/northwest (upwind) of Melbourne city region (Anglesea, Geelong, Ballarat and Newport) (Fig. 1). Thus, coal combustion is also a likely contributor to atmospheric lead contamination in this region. Marx et al. (2010) determined that coal combustion contributed up to 30% of the lead in peat bog cores from the Snowy Mountains, ~600 km to the northeast of Melbourne city. Despite the paucity of isotopic composition data on Australian coal, what data exists indicate that Australian coals have high lead isotopic compositions ($^{206}Pb/^{207}Pb$ ~ 1.205 and $^{208}Pb/^{207}Pb$ ~ 2.486) (Diaz-Somoano et al., 2009) by comparison to Broken Hill/Mount Isa (Supplementary Table S5). No isotopic data exist for brown coals that are predominantly used for generating electricity in Victoria. By contrast, bituminous coal is the main fuel source used in New South Wales for energy generation. Wu et al.'s (2016) analysis of Sydney lichens and fungi indicated that coal combustion is a contributory source of atmospheric lead contamination in this region.

3.3. Comparison of herbarium samples with regional soils, rocks and river sediments

The isotopic compositions of subsurface soil collected from the Yarra Ranges National Park and distal slates from the Wattle Gully goldfield have lithogenic lead ($^{206}Pb/^{207}Pb$: 1.181–1.223; $^{208}Pb/^{207}Pb$: 2.476–2.519) (Supplementary Table S4–S5). Local surface soils (0–2 cm) collected in the Yarra Ranges National Park and Dandenong Ranges National Park have a wide range of lead

isotopic compositions ($^{206}Pb/^{207}Pb$: 1.131–1.172; $^{208}Pb/^{207}Pb$: 2.414–2.461) (Supplementary Table S4). The lead isotopic composition data in surface soils are lower than that in deep soil from the Yarra Ranges National Park (Supplementary Table S4). Moreover, lead concentrations in surface soils from the Yarra Ranges National Park are more than two times higher than those measured in subsurface soil, reflecting the effect of anthropogenic atmospheric inputs.

The lead isotopic compositions measured in river sediments collected from different national parks are: Yarra Ranges National Park: $^{206}Pb/^{207}Pb$: 1.185–1.192; $^{208}Pb/^{207}Pb$: 2.472–2.477; Dandenong Ranges National Park: $^{206}Pb/^{207}Pb$: 1.167; $^{208}Pb/^{207}Pb$: 2.455–2.457) (Supplementary Table S4). Thus, the lead isotopic compositions of river sediments overlap with the background lead derived from deep soil and slates, indicating a natural influence through crustal processes. The variation in river sediment lead isotopic compositions is likely to be derived from inherent lithologic variation in the catchment bedrock. River sediments from the Dandenong Ranges include Silurian–Devonian marine sediments and Tertiary Older Volcanic basalts, whereas Silurian–Devonian marine sediments and Devonian volcanic bedrock form the Yarra Ranges (Tweed et al., 2006).

The lead isotopic compositions for all herbarium samples lie along a mixing line between two potential end-members: one with low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios, represented by the Broken Hill and Mount Isa ores (the primary source for lead in petrol), and a more lithogenic end-member, represented by gold mining and local background samples (slates, river sediments and deep soil) (Fig. 5). The lead isotopic compositions of *Cladonia* samples from the 1880s (mean $^{206}Pb/^{207}Pb$: 1.168 ± 0.011; $^{208}Pb/^{207}Pb$: 2.452 ± 0.014), and the *Trametes* sample from 1852 ($^{206}Pb/^{207}Pb$: 1.180; $^{208}Pb/^{207}Pb$: 2.463) lie within the range of lead isotope values for the local background samples and gold ores. This indicates that lithogenic bedrock lead and sulphides associated with gold mining are likely to be dominant sources of atmospheric lead in the pre-leaded petrol era (Fig. 5). However, the atmospheric contribution of lead from local industrial activities during this time period is unknown.

3.4. Comparison of lead concentrations and isotopic compositions for the herbarium specimens between the national parks and urban/suburb areas

Lead concentrations and lead isotopic measurements of historic lichens and fungi are reported in Table 1 according to corresponding land use. During the 1939 to 2001 period, the data show that disparate geographical areas have similar lead concentrations and isotopic compositions. For example, in the urban/suburb areas, lead concentrations in *Trametes* samples from 1939 to 1996 ranged from 2 to 24 mg/kg with $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of 1.052–1.135 and from 2.327 to 2.401, respectively (Table 1). These ranges are similar ($p > 0.05$) to those measured in *Cladonia* and *Usnea* between 1955 and 2001 collected from the Brisbane Ranges National Park (Fig. 1), Lerderderg State Park and Yarra Ranges National Park samples: 0.7–20 mg/kg, $^{206}Pb/^{207}Pb$ 1.061–1.115 and $^{208}Pb/^{207}Pb$ 2.341–2.389. The similarity in the data implies that during the 1939 to 2001 period atmospheric lead sources were distributed uniformly across central and southern Victoria.

3.5. Comparison of lead isotopic compositions in environmental samples collected from the Greater Sydney area and central and southern Victoria

Greater Sydney area and central and southern Victoria have derived most of their atmospheric lead contamination from leaded petrol, coal combustion and local industrial activities since early development of urbanisation and industrialisation. Historic samples collected from the two study areas correspond to the known shifts in atmospheric lead inputs since the mid-1850s. Thus, the lead isotopic compositions of Sydney herbarium samples, leaded petrol and air filters can be compared to the isotopic data of lichens, fungi and aerosols in this study. The temporal trend in lead isotopic data from the Greater Sydney area showed a steady reduction of the $^{206}Pb/^{207}Pb$ ratios from 1.167 in 1885 to 1.072 in 1984. This was particularly evident following the introduction of leaded petrol in Australia in 1932 (Wu et al., 2016). A return toward natural values occurred after 1985, following the introduction of unleaded petrol

Table 1
Comparison of lead concentrations (mg/kg) and lead isotopic compositions ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) in the herbarium samples collected from the national parks and urban/suburban areas. Where available, the month of sampling is provided.

Zones	Year/month	Species	Locations	Pb	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Central/East/Southeast-Central Melbourne	1939	*T. versicolor*	Pole Yard, Fishermans Bend	15	1.098	2.374
(urban/suburb area)	1953/Aug	*T. velutina*	Royal Park, Melbourne	5.2	1.083	2.364
	1957	*T. velutina*	Glenferrie	24	1.076	2.353
	1960	*T. ochracea*	Caulfield	18	1.052	2.327
	1964	*T. versicolor*	Melbourne, suburb of South Yarra, Royal Botanic Gardens	8.0	1.082	2.365
	1967	*T. velutina*	Flinders ln, Suburb of Melbourne city	19	1.085	2.365
	1994	*T. versicolor*	Melbourne, Yarra Bend	3.0	1.085	2.363
	1995	*Trametes*	Wattle Park	1.6	1.086	2.361
	1996/Jul	*T. versicolor*	Melbourne, South Yarra, Royal Botanic Gardens	2.0	1.135	2.401
	1996/Jul	*T. versicolor*	Melbourne, outer suburb of Eltham, private residence	5.0	1.103	2.384
Brisbane Ranges National Park	1955	*Cladonia*	Brisbane Ranges, Reilly's Creek Gorge	2.6	1.095	2.366
(West of Melbourne CBD)	1961	*C. gracilis*	Brisbane Ranges	1.3	1.080	2.360
	1971	*Cladonia*	24 km SW of Bacchus Marsh, Brisbane Ranges	1.5	1.098	2.381
	1986	*Cladonia*	Brisbane Ranges National Park	1.9	1.083	2.362
Lerderderg State Park	1964	*C. pleurota*	Lerderderg River	7.6	1.061	2.341
(Northwest of Melbourne CBD)	1974	*Cladonia*	Near Mount Blackwood	3.6	1.115	2.389
Yarra Ranges National Park	1959	*C. fimbriata*	On the lower slopes of Mount Vinegar	4.8	1.076	2.350
(Northeast of Melbourne CBD)	1986	*Usnea*	Mount Donna Buang, 5 km NNW of Warburton	20	1.080	2.352
	1994	*U. molliuscula*	Lake Mountain Alpine Reserve	7.1	1.086	2.358
	1996	*C. fimbriata*	One Tree Hill (Mount Donna Buang)	18	1.099	2.373
	2001	*Usnea*	Cumberland Scenic Reserve	0.7	1.094	2.363

and the cessation of leaded petrol use in 2002 (Wu et al., 2016). The results presented here are consistent with these interpretations (Fig. 6). The temporal similarity in the lead isotopic compositions measured in Sydney leaded petrol, air filters and herbarium archives during 1978–1999 from the Greater Sydney area represents a pathway of lead from car-exhaust emissions to the atmosphere and trapping by lichens and fungi (Wu et al., 2016). Thus, the similarity of the Sydney data to petrol and air filters and archival samples can be used to explain the Melbourne aerosol and herbarium archive data. The lead isotopic compositions of Sydney air filters from the 1990s (Supplementary Table S5) show no significant difference ($p > 0.05$ for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) from the Melbourne aerosols from the same period (Supplementary Table S5). Similarly, no significant difference was obtained ($p > 0.05$ for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) between Sydney leaded petrol values and Melbourne aerosols collected in the 1990s (Supplementary Table S5), demonstrating that combustion of leaded petrol was the dominant source of atmospheric lead in Melbourne at this time.

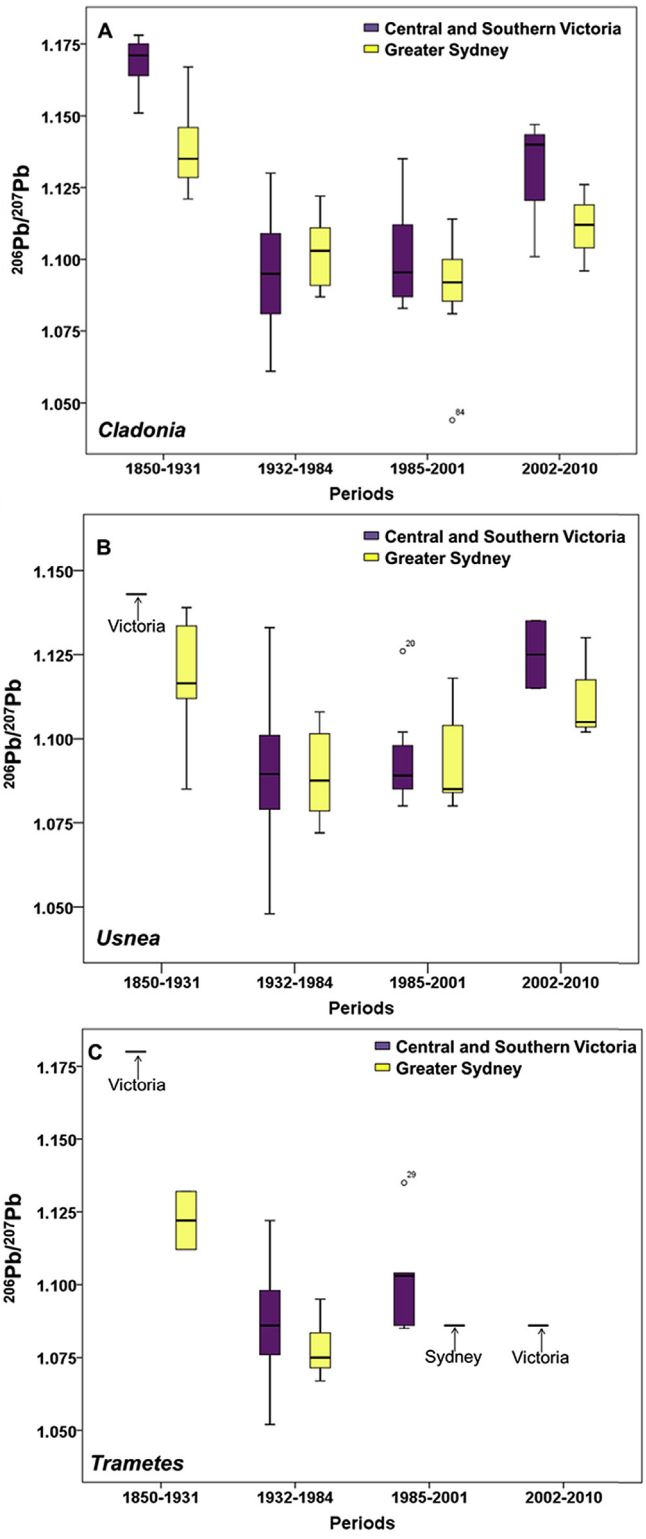

Fig. 6. Comparison of the $^{206}Pb/^{207}Pb$ ratios in *Cladonia* (A), *Usnea* (B), and *Trametes* (C) collected from central and southern Victoria and the Greater Sydney area (Wu et al., 2016) between four time intervals.

3.6. Comparison with peat bog, ice core and snow archives in Australia and Antarctica

Australian alpine peat bog lead isotopic composition analysis indicates that mining and smelting activities, leaded petrol and coal combustion were the main sources for lead contamination in the Snowy Mountains, southeastern Australia (Marx et al., 2010). Lead isotopic compositions of ice core samples from Antarctica revealed a steady reduction of the $^{206}Pb/^{207}Pb$ ratios from ~1.211 in 4500 BCE to ~1.100 in 1989, which were attributed to lead emissions from coal combustion, non-ferrous metal production and alkyl-lead additives in petrol from the countries in the southern hemisphere (Vallelonga et al., 2002). Lead isotope measurements of Antarctic snow and ice core indicate that mining and smelting from southern Australia were responsible for lead contamination during the late 19th century to present day (Van de Velde et al., 2005; McConnell et al., 2014). The Antarctic snow and ice core results also suggest that leaded petrol emissions have contributed to the decline in the lead isotopic compositions from 1948 to 1995 (Van de Velde et al., 2005; McConnell et al., 2014). The temporal similarity of the lead isotopic compositions in the archival lichen and fungi samples analysed here and the Antarctic data published elsewhere, indicates that the emitting lead sources are well mixed in the atmosphere and the anthropogenic lead emissions have measurable impact across the continents of Australia and Antarctica.

4. Conclusions

Analysis of lichens (*Cladonia* and *Usnea*) and fungi (*Trametes*) from central and southern Victoria for their lead concentrations and isotopic compositions extending over a 150-year period provide a reliable proxy record of atmospheric lead contamination. During the pre-leaded petrol era, a large proportion of lead inputs were derived from a mixture of lithogenic and anthropogenic inputs from industrial activity and gold mining following the development of Melbourne city and the Victorian gold rush. Following this period of early urban development, the data indicate that the dominant source of atmospheric lead contamination during the period 1932–1984 was leaded petrol emissions, although the contribution from industrial emissions especially coal combustion is unknown. Although unleaded petrol was introduced in 1985 throughout Australia, lead isotopic composition data in herbarium samples between 1985 and 2001 indicate that it remained a dominant, though diminishing, source of contamination. During the post-leaded petrol era after 2002, the influence of the former use of leaded petrol remains evident in lichen and fungi samples dated to 2002–2008.

On a regional and global scale, the data presented here concur with that from Antarctic ice core and snow samples, indicating

atmospheric lead mixing and widespread persistent and pervasive anthropogenic lead contamination across the southern hemisphere (Ndungu et al., 2016).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.05.022.

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CHAPTER 4

Paper Three

Accumulation of atmospheric trace metals in historic lichens and fungi in eastern and southeastern Australia

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In this paper the trace metal concentrations of Al, Fe, Ti, Cr, Cu, Ni, Zn and Pb in archival lichen and fungi samples from the Greater Sydney area and from central and southern Victoria are presented. Enrichment factors (EFs), cluster analysis (CA) and principal component analysis (PCA) techniques are used to assess correlations between element concentrations in lichen and fungi datasets. This study provides further understanding of the changing concentrations of metals and identifies their possible sources for the two regions.

Accumulation of atmospheric trace metals in historic lichens and fungi in eastern and southeastern Australia

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ABSTRACT

Archived lichens and fungi, representing a period of over 150 years, have been used to investigate the temporal evolution of atmospheric metal (Al, Fe, Ti, Cr, Cu, Ni, Zn and Pb) deposition in the Greater Sydney area (New South Wales) and central and southern Victoria. Enrichment Factors (EFs, normalised to Al), Cluster Analysis (CA) and Principal Components Analysis (PCA) have been used to evaluate the results and elucidate atmospheric metal sources. High median EFs (12–345) are obtained for Cu, Zn, and Pb reflecting a strong influence of anthropogenic metal inputs. In contrast, the EF values for Fe and Ti are low (1–5), indicative of a lithogenic source. The high median Cu, Zn and Pb EFs (>10) in the herbarium samples are attributed to a mixture of mining and metal production, industrial activities and leaded petrol emissions. Peak Pb EFs in the Sydney samples and high Pb EFs in the Victorian samples collected during the leaded petrol era (1932–2001), show a clear contribution from petrol emissions to the atmosphere at this time. The CA and PCA elicit two main groups: one group dominated by Cu, Zn, and Pb, reflecting anthropogenic sources such as mining and metal production, traffic-related sources (e.g. leaded petrol, brake lining and tire wear) and industrial activities, and the other group, which includes the lithogenic and natural elements (Al, Fe, Ti, Zn). Multi-elemental analysis of historic lichens and fungi can be used as a proxy to reconstruct historical changes in atmospheric metal deposition and evaluate potential sources of atmospheric pollutants in urban/suburban and remote environments.

Keywords: Air pollution, Metal contamination; Statistical analysis; Herbarium; Sydney; Victoria

Introduction

Atmospheric deposition of toxic metals (e.g. Cu, Zn, Hg, Pb) is well known to affect environmental and human health on a global scale (Schroeder and Munthe, 1998; Kampa and Castanas, 2008; Reimann and De Caritat, 2012; McConnell et al., 2014). Atmospheric toxic metal deposition has been attributed to both natural and anthropogenic sources (e.g. Nriagu, 1979). Fossil fuel combustion, mining and metal production, industrial activities and vehicle exhaust fumes have previously been reported to be the main anthropogenic sources of atmospheric toxic metal contamination (e.g. Nriagu and Pacyna, 1988).

There has been increasing interest in the use of living organisms (e.g. lichen, moss and herbs) as a proxy for monitoring air toxic metal contamination (Markert et al., 1997; Garty, 2001; Farmer et al., 2002; de Paula et al., 2015). Lichens can be used as biomonitors of air pollution as perennial lichens have no roots and therefore accumulate chemical nutrients mainly from the atmosphere (Brodo et al., 2001). Analysis of As, Cr, Hg, Ni, Pb, S, Sb, Se and V in *Parmelia sulcata* lichens in Portugal by Freitas et al. (1999) has identified industrial sources for these contaminants such as oil-powered plants, coal-fired power plants, vehicular traffic, local chemical industry along with some contribution from soil. Loppi (2001) demonstrated that a local geothermal power plant was a dominant source of elevated Hg and other trace metals in lichens collected in Italy. In Ghana, Sb, Mn, Cu, V, Al, Co, Hg, Cd and As measured in epiphytic lichens were attributed to metal emissions from gold mining activities, natural soil dust and agriculture-related origin (Boamponsem et al., 2010).

Fungi are known to have an important influence on the recycling of chemical nutrients in environmental systems (Newbound et al., 2010). Previous studies showed that the fruiting bodies of fungi incorporate anthropogenic contaminants such as Cd, Pb, Hg and Cu emitted from smelters, thermal power plants, high traffic areas and urban cities (Gabriel et al., 1997; Kalač and Svoboda, 2000; Petkovšek and Pokorny, 2013; Schlecht and Säumel, 2015). In spite of the wide distribution of lichen and fungi species across the Australian continent, there has been little research investigating the origins of atmospheric metal contamination in Australia using these biological samples (Zeng et al., 2012; Vitarana, 2013; Wu et al., 2016a; Wu et al., 2016b).

This study determines the trace metal (Al, Fe, Ti, Cr. Cu, Ni, Zn) concentrations in historic lichens and fungi collected between 1852 and 2010 in the Greater Sydney and central and southern Victoria areas. Lead concentrations and Pb isotopic compositions have already been

determined for these samples by Wu et al. (2016a) and Wu et al. (2016b). The elevated Pb concentrations observed in the samples have been attributed to leaded petrol emissions as well as other emission sources (e.g. natural Pb, coal combustion and gold mining). However, it is apparent that few other toxic metals are utilised in such pollution studies within Australia. Therefore, the purpose of this study is two-fold: 1) to determine the concentrations of a suite of metals in historic and contemporary herbarium lichens and fungi sampled over a 150-year period from the Greater Sydney area and central and southern Victoria, and 2) to use statistical analysis of the data to elucidate the potential sources of these contaminants.

Materials and methods

Sample collection

A selection of two fruticose lichen genera (*Cladonia* n = 85; *Usnea* n = 47) and one wood-decaying fungi genus (*Trametes* n = 40) was taken from Australian herbaria in Canberra (Australian National Herbarium), Sydney (National Herbarium of New South Wales, Macquarie University Downing Herbarium), Melbourne (National Herbarium of Victoria and University of Melbourne Herbarium) and the United Kingdom (Natural History Museum). These herbarium materials were originally collected from the Greater Sydney area and central and southern Victoria (hereafter referred to as Sydney and Victoria) between 1852 and 2010.

The genus *Cladonia* can grow on a variety of substrate types: rock, soil, wood or bark and absorbs and accumulates nutrients mainly from the atmosphere and possibly from the substrate such as soil (Osyczka and Rola, 2013). *Usnea* lichens occur uniquely in a beard-like form, which typically grow on tree bark and shrubs and absorb chemicals from the surrounding atmosphere (Schram et al., 2015). *Trametes* fungi is wood-rotting genus, having no direct contact with soil; they absorb chemical nutrients mainly from the surrounding atmosphere (Čurdová et al., 2004). Detailed information about sampling locations and procedures has been published elsewhere (Wu et al., 2016a; Wu et al., 2016b). Concern about preservation treatments (e.g. biocides, leaching of ink from newspaper) contaminating herbarium samples has been raised by several authors (Herpin et al., 1997; Weiss et al., 1999; Shotbolt et al., 2007). To the best of our knowledge, the herbarium lichen and fungi samples used in this study have not been treated with biocides.

Chemical analysis

Historic lichen materials representing approximately 5 years growth, according to the published average annual growth rate of *Cladonia* and *Usnea* species (Scotter, 1963; Pegau, 1968; Helle et al., 1983; Li et al., 2014), were collected from the herbaria. *Cladonia* lichens

were isolated from their attached substratum, when necessary, and then air-dried. Only the caps of each *Trametes* fungi were sampled in this study as previous studies have shown that higher Pb concentrations were measured in the caps, compared to other tissue such as the stems (Lepšová and Král, 1988; Sayegh-Petkovsek et al., 2002). Between 10 and 500 mg of herbarium sample (n = 172) was digested in 3 mL concentrated HNO_3 (NMI, 2014) prior to elemental determination. The HNO_3 digestion procedure for lichens is identical to several published methods e.g. Purvis et al. (2007) and Gerdol et al., (2014). Concentrations of eight elements (Al, Fe, Ti, Cr, Cu, Ni, Zn and Pb) were analysed by a Perkin Elmer Elan DRC II, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the National Measurement Institute (NMI), Sydney. Mercury concentration was analysed in this study. However, it was not included in data analysis and discussion as Hg-related preservation treatments may have been applied to the samples. One lichen standard reference material (IAEA-336, n = 8) and four blanks were concurrently analysed. Blanks were < 0.5 mg/kg for Al and Fe, < 0.05 mg/kg for Ti and Cr, < 0.01 mg/kg for Cu, Ni, Zn and Pb, respectively. Detection limits for the trace elements (limits of reporting, LOR) were: 0.5 mg/kg (Al and Fe), 0.05 mg/kg (Ti and Cr) and 0.01 mg/kg (Cu, Ni, Zn, Pb). Analytical recovery was assessed by analysis of the eight standard reference material samples. Recovery rates for studied elements were 96% (Al), 98% (Fe), 88% (Cr), 94% (Cu) and 112% (Zn). There are no certified values of Ti and Ni for IAEA-336 to calculate the recovery accuracy. Relative standard deviation (RSD) of IAEA-336 metal concentrations was 1.2% (Al), 1.2% (Fe), 1.8% (Ti), 4.4% (Cr), 1.1% (Ni), 1.1% (Cu) and 0.8% (Zn), respectively. The measured elements were within ± 2% of the certified values for major and minor element determination except for Pb which had an RSD of ± 6% Pb (Wu et al., 2016a; Wu et al., 2016b). In order to assess the reproducibility of elemental concentrations, one Sydney lichen sample (*Cladonia* 2009, Appendix C, Supplementary Table S1) and one Victoria lichen sample (*Cladonia* 1995, Appendix C, Supplementary Table S4) were measured repeatedly (n = 8). The reproducibility of each element is presented in Appendix C, Supplementary Table S13.

Statistical analysis

To assess the relationships between the measured element concentrations, the results were statistically evaluated using the Ward's method of Cluster Analysis (CA) and Principal Component Analysis (PCA). These analyses were undertaken by SPSS 21.0. Ward's method of CA was chosen as it can evaluate the distances between clusters, and has proven to be a useful tool in the analysis of biological data (Loppi and De Dominicis, 1996; Conti et al., 2004; Boamponsem et al., 2010). PCA is widely used in environmental sciences to identify

sources of atmospheric metal contamination in lichen, moss and herb samples (Reimann et al., 2001; Zschau et al., 2003; de Paula et al., 2015).

Enrichment factors (EFs) are often used as a means to differentiate between lithogenic (natural) and anthropogenic atmospheric contribution in lichens (Bergamaschi et al., 2002; Rusu et al., 2006). The EF compares the ratio of the studied element to a "conservative" element (e.g. Al) to the same ratio in the average upper crust (e.g. Chester and Stoner, 1973; Sucharovà et al., 2012) and is calculated using following equation:

$$EF = \left[\frac{element}{Al}\right] Sample / \left[\frac{element}{Al}\right] Baseline$$

where 'element' refers to the elements of interest: Fe, Ti, Cr, Cu, Ni, Zn and Pb, and the baseline values are represented by the upper continental crustal values reported in Taylor and McLennan (1995).

Results

Trace metal concentrations in herbarium samples

The concentrations of eight major and minor elements (Al, Fe, Ti, Cr, Cu, Ni, Zn, Pb) in *Cladonia*, *Usnea* and *Trametes* samples from Sydney and Victoria areas, collected during 1852–2010, are given in Appendix C, Supplementary Tables S1–S6. Median trace metal

Table 1. Median metal concentrations (mg/kg) for herbarium samples collected from the Greater Sydney area and central and southern Victoria.

elements	*Cladonia*		*Usnea*		*Trametes*	
	Sydney (n = 46)	Victoria (n = 39)	Sydney (n = 25)	Victoria (n = 22)	Sydney (n = 10)	Victoria (n = 30)
Al	454	359	191	223	76	70
	(109–4104)	(61–2318)	(83–652)	(57–1058)	(20–353)	(16–758)
Fe	586	276	246	238	62	149
	(52–5791)	(61–2074)	(81–793)	(53–969)	(26–192)	(38–1284)
Ti	17	7	7	8	7	9
	(3–114)	(3–54)	(2–13)	(3–45)	(3–10)	(4–25)
Cr	0.53 (45)[a]	0.69	0.90	1.05	0.21	0.37
	(0.06–4.70)	(0.44–2.77)	(0.40–1.50)	(0.56–2.69)	(0.06–3.04)	(0.08–1.60)
Cu	3	2	2	1.4	3	6
	(1–96)	(1–25)	(1–10)	(0.6–2.7)	(2–75)	(1–39)
Ni	0.45	0.43	0.45	0.45	0.18	0.35
	(0.09–3.43)	(0.16–1.75)	(0.13–2.00)	(0.12–1.06)	(0.04–1.37)	(0.07–2.50)
Zn	18	11	15	14	19	22
	(8–266)	(4–201)	(4–69)	(4–77)	(7–68)	(5–139)
Pb	17	4	18	16	2	3
	(3–570)	(0.2–439)	(1–181)	(0.4–86)	(1–17)	(0.2–24)

[a] Number of samples with values below detection limits

concentrations for the studied archives are summarised in Table 1. There is quite a wide variation in median Al and Fe concentrations between the three genera but similar values between Sydney and Victoria within the same genera for Al (to a lesser extent for Fe). The median values of Cr, Cu, Ni and Zn for the three genera are largely comparable between Sydney and Victoria although the values for *Trametes* samples from Sydney and Victoria show the widest inter-genus variation. The Sydney *Cladonia* median concentration for Ti is higher than that of the Victoria *Cladonia* samples and the other two genera from both sampling sites. The median concentrations of Pb determined in Sydney and Victoria *Trametes* and Victoria *Cladonia* are an order of magnitude lower than the *Usnea* values in both areas and the Sydney *Cladonia* median value.

Trace metal EFs in herbarium samples

The calculation of trace metal EFs in archival lichens and fungi, relative to upper crustal abundances, are listed in Appendix C, Supplementary Tables S7–S12. Due to the degree of uncertainty in natural variations of the Earth's crustal composition, in this study conservative EFs >10 (rather than unity) are considered to reflect anthropogenic contamination of the

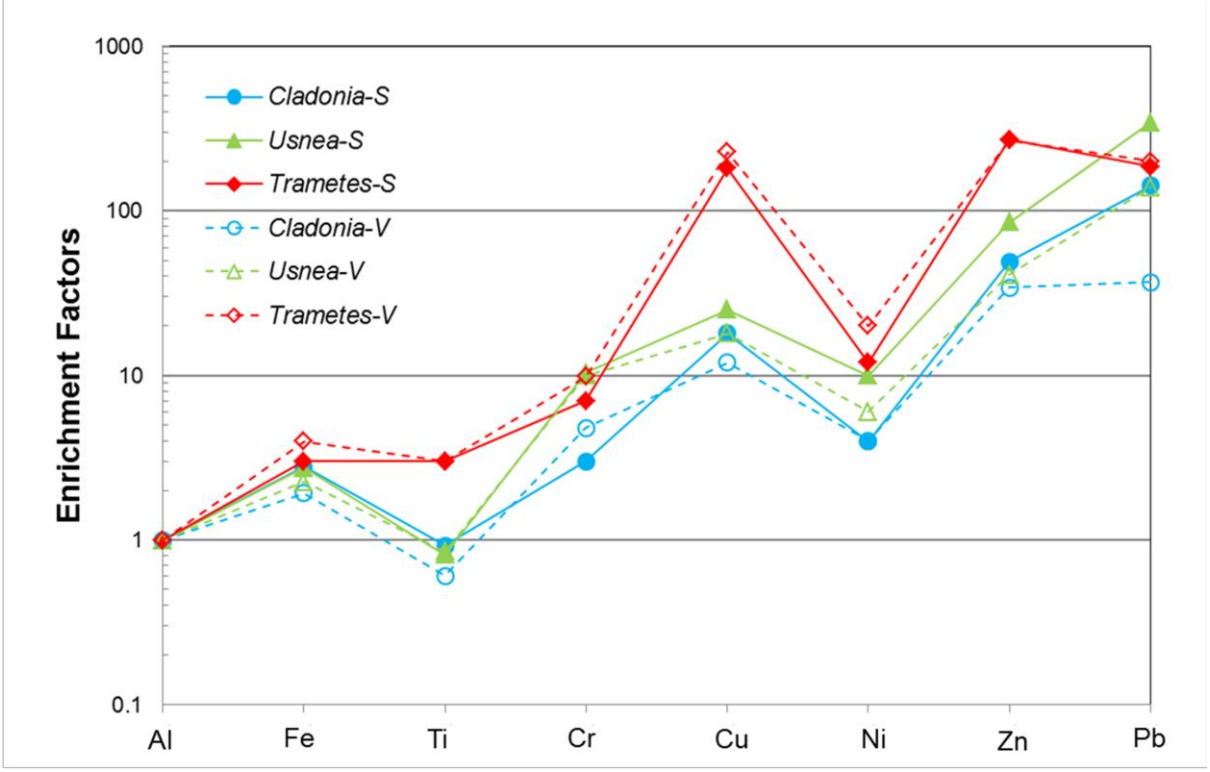

Figure 1. Median enrichment factors (EFs) of the eight elements analysed in herbarium lichens and fungi collected from the Greater Sydney area and central and southern Victoria during 1852–2010. The labels of data are shown in the legend represent median of herbarium specimens from two study sites, e.g. '*Cladonia*-S' – *Cladonia* collected from the Greater Sydney area; '*Cladonia*-V' – *Cladonia* collected from central and southern Victoria.

environment (e.g. Bilos et al., 2001). On the basis of the median EFs calculated for the two sampling areas, all samples are enriched in Cu, Zn and Pb, whereas Fe, Ti and Cr are below 10 (Figure 1). For Ni, all *Trametes* samples have EFs >10 compared with the *Cladonia* and *Usnea* values. The *Trametes* fungi samples in both Sydney and Victoria show significant enrichment in Ti, Cu and Zn but comparable enrichment in Fe, Cr, Ni and Pb compared to the *Usnea* and *Cladonia* lichen samples.

Table 2. Median enrichment factors of herbarium samples collected from the Greater Sydney area and central and southern Victoria for four interval periods.

Periods	n	Ti	Cu	Zn	Pb
Sydney - *Cladonia*					
1850-1931	15	1	17	37	72
1932-1984	9	2	19	69	218
1985-2001	19	1	19	55	161
2002-2010	3	1	11	32	46
Sydney - *Usnea*					
1850-1931	7	1	25	52	196
1932-1984	8	1	22	119	723
1985-2001	7	1	34	107	303
2002-2010	3	1	21	61	37
Sydney - *Trametes*					
1850-1931	2	3	154	384	164
1932-1984	7	2	278	244	189
1985-2001	1	3	154	207	37
2002-2010	0	-	-	-	-
Victoria - *Cladonia*					
1850-1931	3	1	21	20	922
1932-1984	23	1	11	29	44
1985-2001	10	1	18	38	30
2002-2010	3	1	12	66	5
Victoria - *Usnea*					
1850-1931	1	1	18	85	751
1932-1984	12	1	12	33	152
1985-2001	7	1	20	41	101
2002-2010	2	1	21	49	21
Victoria - *Trametes*					
1850-1931	1	2	281	149	596
1932-1984	23	2	209	238	170
1985-2001	5	5	219	648	252
2002-2010	1	4	445	376	64

Grey fill corresponds to the period of leaded-petrol use in Australia

As mentioned above, the Ti EFs calculated for the samples are close to unity, whereas Cu, Zn and Pb EF values are higher than 10 (Figure 1). Ti is considered to be a lithogenic element, while Cu, Zn and Pb are considered as toxic metals emitted from anthropogenic sources. For this reason, these four metals have been chosen to characterise atmospheric metal contamination arising from different sources (lithogenic and anthropogenic). In Australia, vehicle particle emissions are an important anthropogenic metal origin (Bollhöfer and Rosman, 2000; Cohen et al., 2002; Chan et al., 2008; Kristensen, 2015) and four time periods can be delineated according to the history of Australian leaded petrol use: 1850–1931, the

period defined by the absence of leaded petrol use; 1932–1984, the period representing the introduction and use of leaded petrol; 1985–2001, the introduction and use of unleaded petrol; 2002–2010, the period following the ban of leaded petrol sales in 2002 (Cook and Gale, 2005). To investigate the potential relationships between lichen and fungi metal enrichment and leaded petrol usage in Australia, the median EFs for Ti, Cu, Zn and Pb from the two areas have been grouped into the four main stages of Australian leaded petrol use in Table 2 and are presented in Figures 2–3. The calculated EFs for Ti do not significantly vary from unity

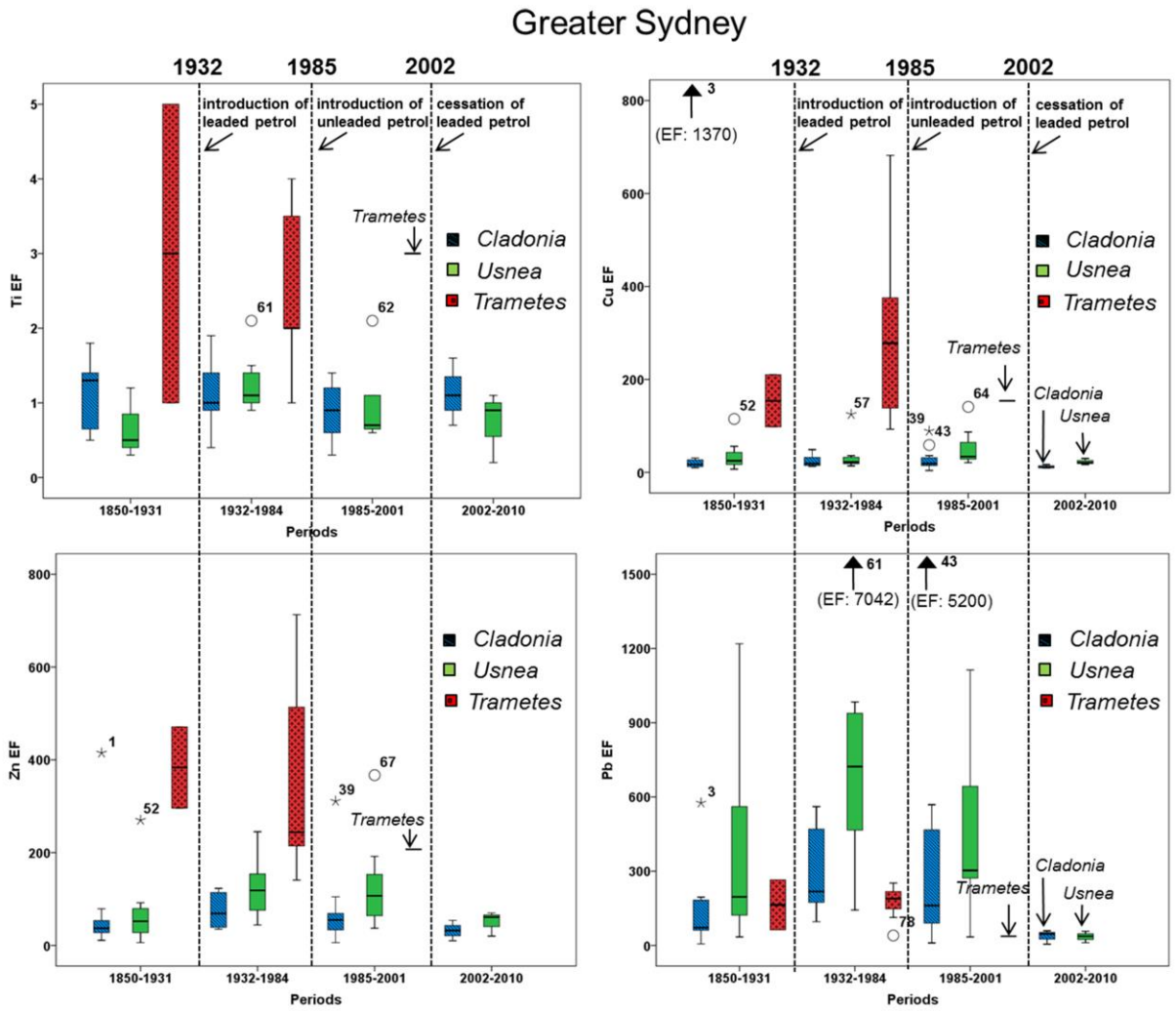

Figure 2. Box-whisker plots for Ti, Cu, Zn and Pb EFs in Sydney *Cladonia*, *Usnea* and *Trametes* samples for four time periods. The boxes define median values and 25th and 75th percentiles of the data while the whiskers represent the 10th and 90th percentiles of the data. Also shown on the figure are the four stages of leaded petrol use/not use in Australia referred to in the text.

(range 1 to 5) over the sampling period. The *Trametes* fungi samples, which display relatively higher Ti values compared to the lichens, do not show any obvious temporal patterns for Sydney and Victoria. Elevated Pb and Zn median EFs are observed in the Sydney lichen samples for the period of leaded petrol use (1932–2001) relative to the surrounding periods

when leaded-petrol was not used (Figure 2). For Victoria, the highest median Pb EFs in lichen and fungi samples are found in the period 1850–1931 and the Pb EF values generally then decrease towards the most recent time period (Figure 3). There is no temporal Cu trend and no association between Cu EF value and the period of petrol usage for any of the samples.

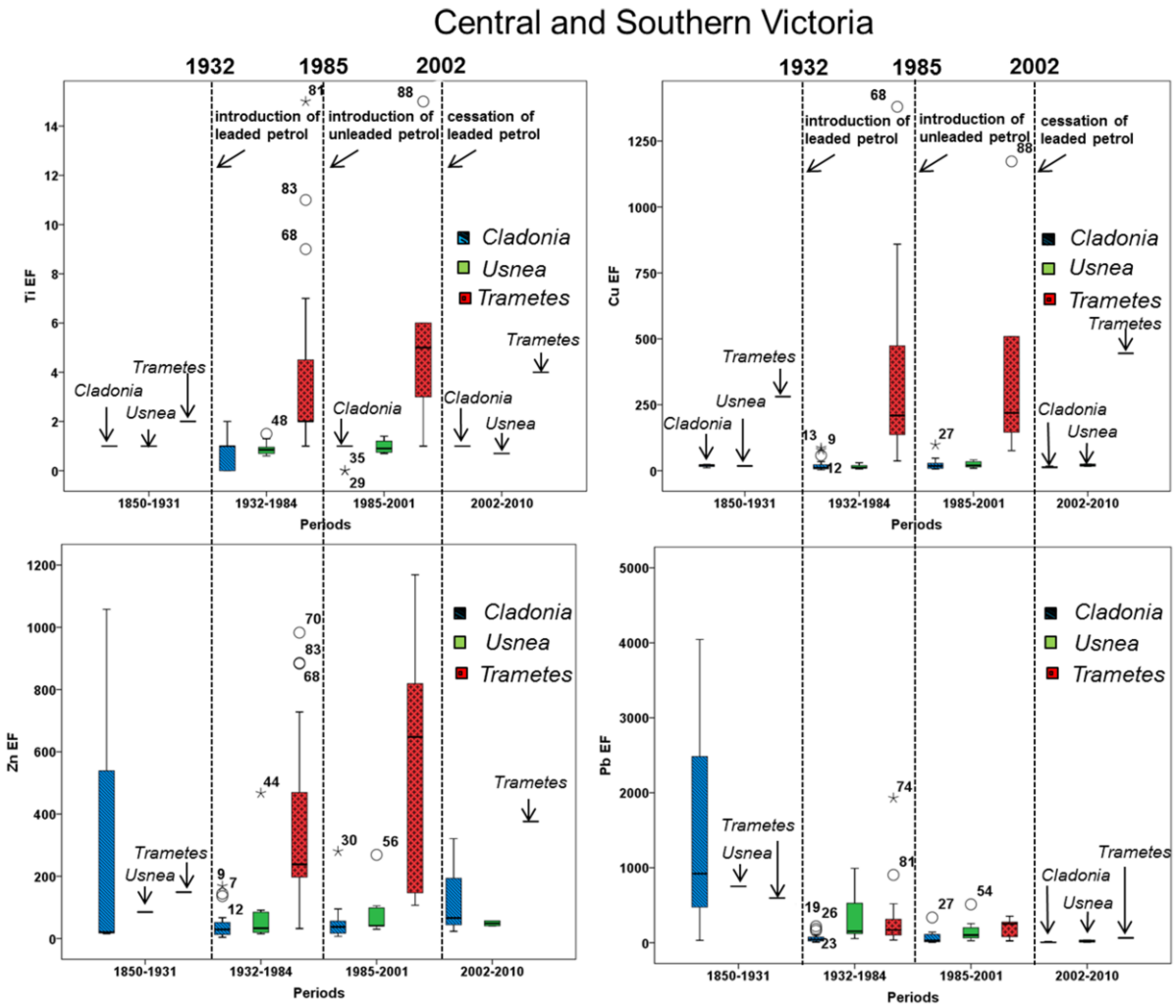

Figure 3. Box-whisker plots for Ti, Cu, Zn and Pb EFs in Victoria *Cladonia*, *Usnea* and *Trametes* samples for four time periods. The boxes define median values and 25th and 75th percentiles of the data while the whiskers represent the 10th and 90th percentiles of the data. Also shown on the figure are the four stages of leaded petrol use/not use in Australia referred to in the text.

In the Sydney *Cladonia* samples the largest Cu EF of 1370, along with relatively high EFs values for Zn and Pb, are observed in the 1897 lichen from Lithgow city, located ~105 km northwest of Sydney CBD (Appendix C, Supplementary Table S7). In addition, two significantly high Pb EFs are determined in a *Cladonia* lichen collected adjacent to Anzac Rifle Range (see map of Wu et al. (2016b)) in 2001 (5211) and in an *Usnea* lichen sampled from near the Zig-Zag railway in 1984 (7042) (Appendix C, Supplementary Table S7–S8). The high *Cladonia* EFs for Zn and Pb of 1058 and 4046, respectively (Appendix C,

Supplementary Table S10) were collected from Mount Macedon of Victoria in 1886, a place associated with gold mining activity.

Cluster and Principal Component Analysis

Cluster analysis (CA) was used to investigate the relationships between metals for the lichen and fungi samples. The resulting dendrograms from the analysis reveal two main clusters of elements in the Sydney and Victoria herbarium dataset, as can be seen in Figures 4 and 5, respectively. The first, Cluster 1, is formed by Ti, Cr, Cu, Ni, Zn and Pb. The second, Cluster 2, is formed by Al and Fe. For the *Trametes* Sydney additional clades are visible within Cluster 1, whereby Cr, Ni, Ti and Pb are grouped and Cu and Zn are grouped. However, the short length of the line joining these clades together in Cluster 1, suggests limited difference between them.

The results of principal component analysis (PCA) for all examined elements are presented in Tables 3 and 4. Trace metals in *Cladonia* lichens from Sydney and Victoria group into a two-component model that accounts for more than 70% of all the data variation, while all *Usnea* lichens group into a three-component model. In contrast, only a one-component model is produced for the Sydney and Victoria *Trametes* fungi. In the Sydney area, the first principal component (PC1) for *Cladonia* shows significant loadings of Al, Fe, Ti, Cr, Ni and Zn (Table 3). The second principal component (PC2) is correlated primarily with Cu and Pb. For the Sydney *Usnea* lichens, Cu, Ni, Zn and Pb are included in the first principal component; PC2 includes Al and Fe, whereas PC3 consists of Al, Ti and Cr. The Sydney *Trametes* fungi data show that the only one principal component is characterised by high loadings of all studied elements. In central and southern Victoria, the results for the first factor for *Cladonia* lichens are the same as for Sydney and explain 56% of the total variance in the dataset (Table 4). The second factor is dominated by Pb and Zn. For the *Usnea* lichens from Victoria area, the first factor has high loadings for Al, Fe, Ti, Cr, Cu and Ni. The second factor contains only Pb, whereas the third factor has a significant component of Zn. In the *Trametes* fungi there is only one factor that includes all the elements.

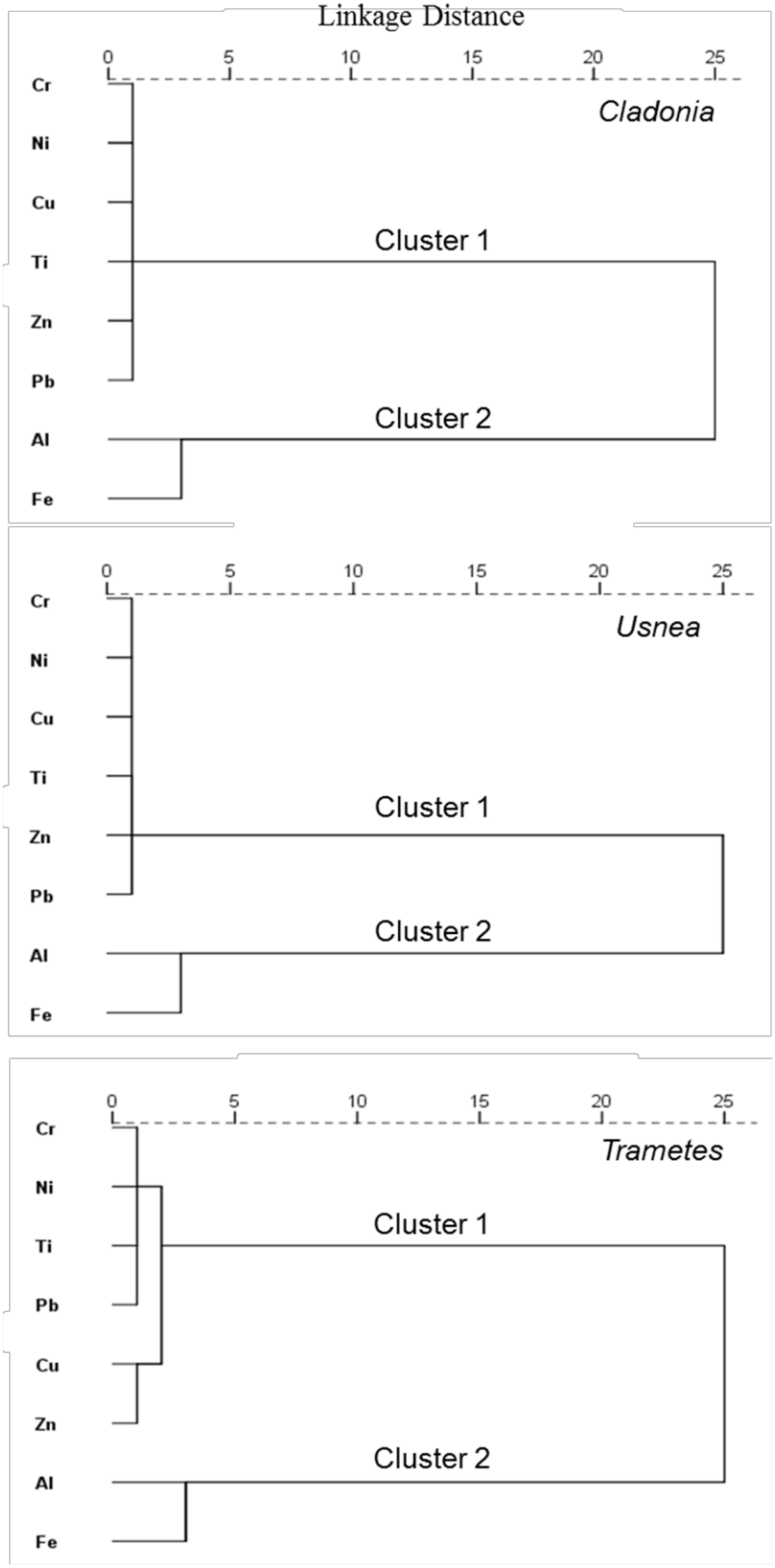

Figure 4. A dendrogram of the measured elements in *Cladonia*, *Usnea* and *Trametes* samples from the Greater Sydney area.

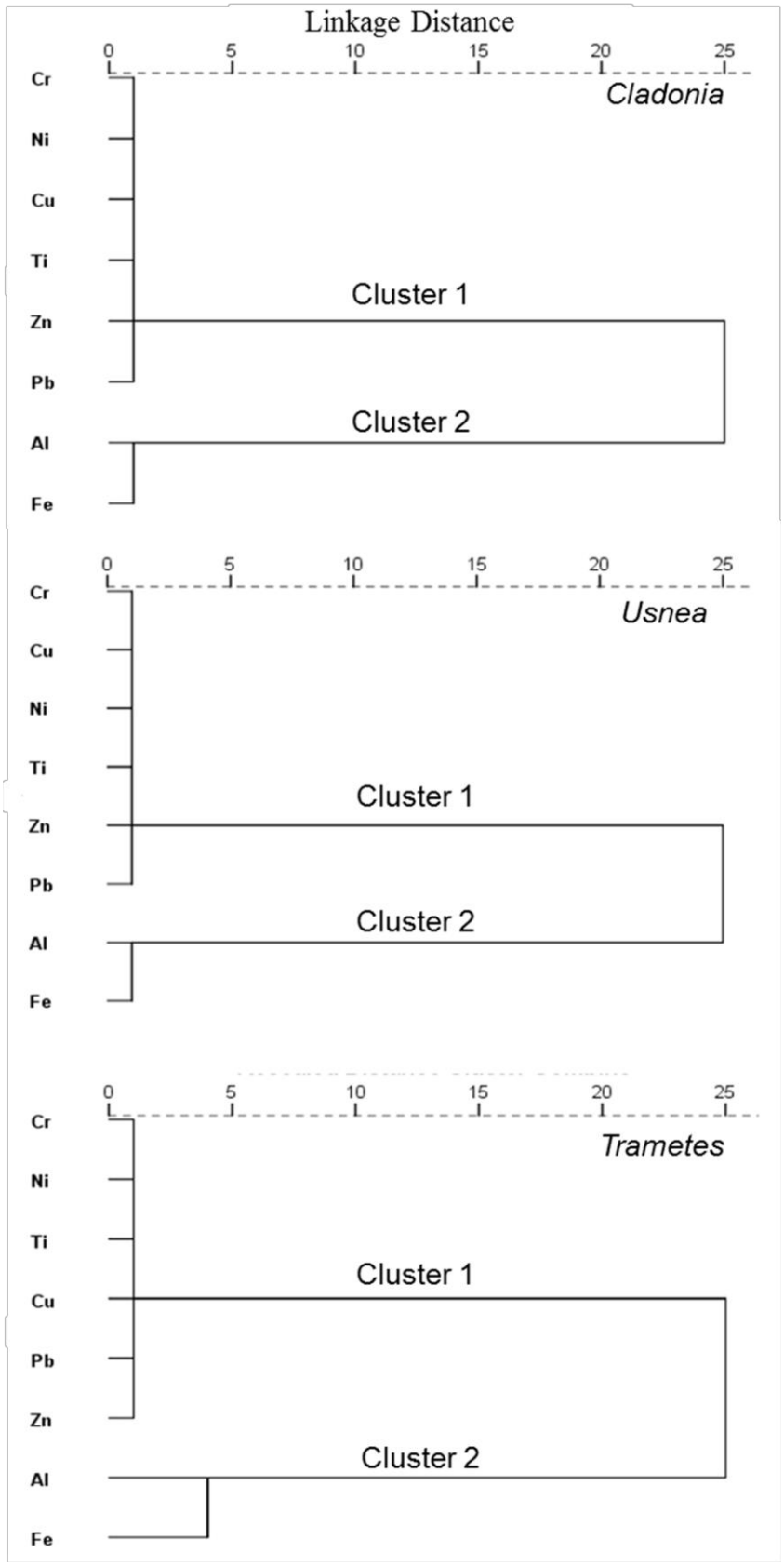

Figure 5. A dendrogram of the measured elements in *Cladonia*, *Usnea* and *Trametes* samples from central and southern Victoria.

Table 3. Rotated component matrix of three factor model for lichens and fungi from the Greater Sydney area

Cladonia			*Usnea*				*Trametes*	
	PC1	PC2		PC1	PC2	PC3		PC1
Al	**0.949**	-0.056	Al	-0.332	***0.669***	***0.564***	Al	**0.983**
Fe	**0.934**	0.082	Fe	0.185	**0.917**	0.173	Fe	**0.789**
Ti	**0.784**	-0.133	Ti	0.064	0.220	**0.880**	Ti	***0.638***
Cr	**0.928**	0.180	Cr	0.304	-0.055	**0.889**	Cr	**0.962**
Cu	0.041	***0.594***	Cu	**0.757**	0.223	0.113	Cu	**0.955**
Ni	**0.877**	0.128	Ni	***0.533***	0.739	-0.128	Ni	**0.878**
Zn	**0.746**	0.077	Zn	**0.896**	0.316	0.008	Zn	**0.901**
Pb	0.024	**0.822**	Pb	**0.712**	-0.234	0.299	Pb	**0.944**
Variance (%)	56	14		30	26	25		79

Elements with correlation values higher than 0.7 are presented in **bold**; values higher than 0.5 and lower than 0.7 in **bold** and in *italics*; values lower than 0.5 in regular font.

Table 4. Rotated component matrix of three factor model for lichens and fungi from central and southern Victoria.

Cladonia			*Usnea*				*Trametes*	
	PC1	PC2		PC1	PC2	PC3		PC1
Al	**0.959**	0.171	Al	**0.936**	0.201	0.035	Al	**0.903**
Fe	**0.971**	0.130	Fe	**0.920**	0.260	0.025	Fe	**0.962**
Ti	**0.873**	0.332	Ti	**0.897**	0.155	-0.052	Ti	**0.740**
Cr	**0.960**	-0.026	Cr	***0.637***	0.493	-0.132	Cr	**0.921**
Cu	0.240	0.434	Cu	***0.656***	0.499	0.223	Cu	**0.845**
Ni	**0.920**	-0.099	Ni	**0.886**	-0.060	0.024	Ni	**0.760**
Zn	-0.119	**0.723**	Zn	0.005	0.010	**0.986**	Zn	**0.911**
Pb	0.089	**0.877**	Pb	0.094	**0.975**	0.008	Pb	**0.795**
Variance (%)	56	21		52	20	13		74

Elements with correlation values higher than 0.7 are presented in **bold**; values higher than 0.5 and lower than 0.7 in **bold** and in *italics*; values lower than 0.5 in regular font.

Discussion

The information gained from statistical analysis of the lichen and fungi data can be used to identify the possible emission sources of historical and contemporary atmospheric trace metal fallout in Sydney and Victoria. Potential sources include lithogenic and anthropogenic sources, such as mining and metal production, varied industrial activities and vehicle exhausts.

Apportionment of sources

Lithogenic sources

Enrichment factors <5 for Fe and Ti in the lichen and fungi samples (Figure 1) indicate a lithogenic, or natural, origin for these elements. The higher Ti EFs in the fungi, relative to the lichens, may be due to the greater impact of suspended soil dust on the former (e.g. (Szczepaniak and Biziuk, 2003; Giordano et al., 2005; Weeks et al., 2006). Aluminium was used as the denominator in the EF calculations, based on the assumption that it is a conservative element, and so it too is assumed to have a lithogenic source. Aluminium and Fe

are strongly clustered (Cluster 2 in Figures 4–5) and correlated (Tables 3–4) in the archival samples suggesting that lithogenic metal inputs have contributed to atmospheric metal contamination in Sydney and Victoria over the sampling period. The strong correlations between these lithogenic elements are coincident with the results reported in other lichen, moss and herb studies (Bargagli et al., 2002; Basile et al., 2008; Agnan et al., 2013; de Paula et al., 2015). The median Zn concentrations in Sydney *Cladonia*, *Usnea* and *Trametes* were 18 mg/kg (range 8–266 mg/kg), 15 mg/kg (range 4–69 mg/kg) and 19 mg/kg (range 7–68 mg/kg), respectively (Table 1). In central and southern Victoria, median Zn concentrations for the three genera were: *Cladonia* 11 mg/kg (range 4–201 mg/kg), *Usnea* 14 mg/kg (range 4–77 mg/kg), and *Trametes* 22 mg/kg (range 5–139 mg/kg) (Table 1). Zinc is a known micronutrient required by plants (Ross, 1990; Akbulut et al., 2008). Previous plant studies have reported that the normal concentrations of Zn ranged from 10–100 mg/kg in plants (Allen, 1989; Ite et al., 2014). Zn concentrations of <100 mg/kg in the lichen and fungi samples studied thus lie within the normal range of Zn metal levels expected.For example, Zn concentrations ranged from 4 to 77 mg/kg were observed in all Victorian *Usnea* lichens, indicating natural inputs. Moreover, in the PCA, the third (Zn) component as single significant element for the Victorian *Usnea* samples accounts for 13% of the total variance (Table 4), suggesting that natural inputs of Zn are an important source.

Anthropogenic sources

On a global basis, elements including Ni, Cu, Pb and Zn, are usually considered to be related to anthropogenic sources (e.g. Nriagu, 1989). In Australia, anthropogenic sources of atmospheric metal contamination have included metal mining and production, general industrial activities and vehicular traffic.

Mining and metal processing

Metal mining and production is considered to be one of the important sources of atmospheric metal contamination in the world (e.g. Nriagu and Pacyna, 1988). In Australia, investigations of various environmental media such as soil, sediment, aerosol, dust and water from mining and smelting communities have demonstrated extensive environmental contamination (Baghurst et al., 1992; Gulson et al., 1994; Boreland et al., 2002; Taylor et al., 2010; Mackay et al., 2013; Dong et al., 2015; Kristensen and Taylor, 2016). High Pb and moderate to high Zn EFs were measured in the Victorian samples and, to a lesser extent, the Sydney samples during the period of 1850–1931 (Table 2; Figures 2–3). These values are, therefore, likely attributed to the commencement of early metal mining and production in Australia in the 1840s (Mudd, 2007). For example, high Pb (922 and 4046) and Zn (20 and 1058) EFs were

observed in two *Cladonia* lichens collected from Mount Macedon in 1885 and 1886 (Appendix C, Supplementary Table S10), an area associated with gold mining activity at this time (Gerasimon and Studios, 2016). Lead isotopic tracing has also indicated that gold mining was a significant source of Pb in lichen archive samples from the Mount Macedon area from 1885 to 1900 (Chapter Three) (Wu et al., 2016a). In addition, significantly high EFs for Cu, Pb and Zn are identified in samples collected adjacent to active mining areas during the sampling period (Appendix C, Supplementary Tables S7–S12). For example, the *Cladonia* lichen sample collected in Lithgow city (the north-western edge of the Greater Sydney sampling site, see map of Chapter Two (Wu et al., 2016b)) in 1897 has a Cu EF of 1370 with accompanying high Pb and Zn EFs (Appendix C, Supplementary Table S7). Since the late 1830s Lithgow has had a history of coal mining, copper production and other industrial activities (e.g. steel works and copper smelters) (Cremin, 1989). A recent study showed that Cu, Zn, Hg and Pb concentrations are enriched in Lithgow surface soils compared with the background values (Rouillon et al., 2013). The higher enrichment of Cu and Zn in *Trametes* samples relative to the *Cladonia* and *Usnea* samples suggests that the fungi may be more sensitive to some metal contaminants than lichens. White-rot fungi of *Trametes* genera can accumulate micronutrients such as Cu and Zn for development and growth from the environment (Viraraghavan et al., 2011).

Industrial activities

Apart from metal mining and processing, local industries such as smelting, waste incineration and coal combustion have contributed to environmental metal contamination on a global scale (Nriagu and Pacyna, 1988; Chiaradia et al., 1997a; Chiaradia et al., 1997b; Monna et al., 1997; Díaz-Somoano et al., 2009). Copper, Pb and Zn show the highest EFs in the fungi and lichen samples (Figure 1), and therefore, form a significant anthropogenic atmospheric input. High Cu, Pb and Zn EFs have also been measured in wetland surface sediments from the Trenerry Reserve, 9 km southeast of Sydney CBD (Connor and Thomas, 2003), supporting these results. In PCA, Cu, Pb and Zn comprise the only components of PC2 in *Cladonia* lichens and these elements along with Ni, form the components of PC1 for Sydney *Usnea* lichens (Tables 3–4). The Cu–Pb–Zn group has been identified in many studies as that associated with the heavy metal and chemical industries (e.g. metal smelting or processing, coal combustion, coal-fired power stations) (Herpin et al., 1997; Harrison and Yin, 2000; Quiterio et al., 2004; Yongming et al., 2006; Khan et al., 2010; Cloquet et al., 2015). Over the period of sample collection, there were significant numbers of metal foundries, paint manufacturers, small smelters, oil refineries, incinerators, coal-fired power stations and gas works operating within a 150 km radius of Sydney and Melbourne city (Chapters Two and Three) (Davis and Gulson,

2005; Marx et al., 2010; Cohen et al., 2012; Birch et al., 2015; Wu et al., 2016a; Wu et al., 2016b). These industries would have contributed to atmospheric metal contamination in the two study areas.

Leaded petrol emission

Among the anthropogenic inputs, automobile exhausts from the use of leaded petrol are a significant source of atmospheric Pb fallout in the world (Nriagu and Pacyna, 1988; Bollhöfer and Rosman, 2000, 2001; McConnell et al., 2014; Ndungu et al., 2016). In Australia, leaded petrol was introduced in 1932 and was phased-out in 2002 (Cook and Gale, 2005). More than 240,000 tonnes of Pb was released to the atmosphere during this period (Kristensen, 2015). A large proportion of Pb used in Australian petrol was sourced from the Broken Hill and Mount Isa mines (Gulson et al., 1983). Relatively high median EFs of Pb were observed in Sydney and Victorian herbarium samples during the period of 1932–1984 (Table 2; Figures 2–3), corresponding to the period of maximum leaded petrol usage in the states of New South Wales and Victoria (Kristensen, 2015). Furthermore, a peak in median EF values is observed in the periods of leaded petrol usage for the Sydney samples (Table 2). Using the Pb isotopic compositions of lichens, fungi, air filters, marine sediments, rocks and soils, leaded petrol has been identified to be a significant contributor of atmospheric Pb deposition in the Sydney area (Chapter Two) (Gulson et al., 1983; Chiaradia et al., 1997b; Larsen et al., 2012; Wu et al., 2016b). In the PCA, the second (Pb and Zn) component for the Victorian *Cladonia* samples accounts for 21% of the total variance (Table 4) suggesting that anthropogenic sources have contributed to atmospheric metal contamination. In addition to metal mining and industrial activities, Pb and Zn can be attributed to traffic-related sources such as leaded petrol, braking lines and tire wear (Thorpe and Harrison, 2008). Elevated Zn in the 2006 *Cladonia* lichen collected close to a picnic site and its car park, northwest of Melbourne city (Appendix C, Supplementary Table S4), indicate that vehicle related inputs of Zn are a relevant source.

Conclusion

The measurement of a suite of elements (Al, Fe, Ti, Cr, Cu, Ni, Zn, Pb) from archival lichens and fungi collected over a period of 150 years has shown to be valuable for reconstructing historical trends in atmospheric metal deposition in Sydney and Victoria. The results show that typical lithogenic elements (e.g. Al, Fe and Ti) in most lichens and fungi have low EF values (EFs <5) and present strong correlations, indicating their input from natural sources. The minor elements Pb, Cu and Zn showed greater enrichment (EFs >10) than other metals, were highly correlated in PCA and CA, and are interpreted to be mainly from anthropogenic sources. Relatively high Cu, Zn and Pb median EFs were measured in the samples from the

period of 1850–1931, compatible with prevailing anthropogenic inputs such as industrial activities and metal mining and processing. From 1932 to 2001, leaded petrol, industrial emissions and traffic sources (e.g. brake lining and tire wear) have contributed to atmospheric Cu-Pb-Zn contamination, following the introduction of leaded petrol in Australia in 1932 and further industrialisation. Herbarium samples collected between 1985–2010 show relatively high Zn and Pb enrichment suggesting anthropogenic metal inputs have persisted in the atmosphere even though unleaded petrol was mandated in Australia in 1985, more stringent environmental regulations have been put in place and there has been a general slowdown in industrial activities in the two regions during this period. The data indicates greater enrichment of Cu and Zn in the *Trametes* fungi samples relative to the lichens in both study areas. This study shows that lichen and fungi can act as powerful proxies for recording historic and current metal contamination in urban and pristine environments.

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CHAPTER 5

Paper Four

Recycling of industrial lead contamination during Australian wildfires

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The paper measures, characterises and identifies concentrations and sources of remobilised lead in ash from four Australian wildfires using stable lead isotopes. The research reveals that remobilisation of lead in ash residue at four wildfire sites in close proximity to four major Australian cities can be ascribed to deposition from former industrial lead. This study provides confirmation that wildfires can redistribute and re-release historic lead pollutants into contemporary environments where they may pose a risk to environmental systems and to human health.

Recycling of industrial lead contamination during Australian wildfires

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Abstract: This study examined the recycling of lead (Pb) from wildfires, its source and potential contribution to environmental contamination. Ash from wildfires was collected from four Australian sites following uncontrolled fires during 2012 to 2013 close to major urban populations in Sydney (New South Wales), Hobart (Tasmania) and Adelaide (South Australia). The samples were analysed for their total Pb concentration and Pb isotopic composition to determine the sources of Pb and the extent, if any, of industrial contamination and its recycling into the ecosystem. Median ash concentrations (23 mg/kg) released from a wildfire close to Australia's largest city, Sydney (Duffys Forest), exceeded local natural Pb soil and rock values (7 mg/kg), indicating contamination. By contrast, median ash Pb concentrations from wildfires from the less populated locations of Hobart, Adelaide and NSW Central Coast (Woy Woy) were below local background values. Lead isotopic compositions of Duffys Forest wildfire ash demonstrate that anthropogenic inputs from legacy leaded petrol depositions were the predominant source of contamination. Despite the cessation of leaded petrol use in Australia in 2002, historic petrol Pb deposits continue to be a substantial source of contamination in ash: petrol Pb contributed 35% of the Pb in the Woy Woy ash, 73% in Duffys Forest ash, 39% in Forcett ash and 5% in Cherryville ash. The remobilisation of legacy industrial Pb depositions by wildfires results in it being a persistent and problematic contaminant in contemporary environmental systems.

Keywords: Pb isotopic composition, ash, leaded petrol, contamination

Introduction

The release of metals during wildfire events and their potential to release and redistribute environmental contaminants have received increasing research interest over the last two decades (e.g. Kashparov et al., 2000; Certini, 2005; Huang et al., 2011; Silva et al., 2015). The re-release of contaminants is supported by recent analysis of metal remobilisation (Cu, As, Zn, Hg and Pb) from pyrogenic emissions measured in ash, air filters, soil cores, foliage and lake sediments (Biswas et al., 2007; Pereira and Úbeda, 2010; Odigie and Flegal, 2011, 2014; Kristensen et al., 2014; Campos et al., 2015; Odigie et al., 2015). For example, total Hg concentrations in aerosols increased following forest fires in North America (Obrist et al., 2007; Friedli et al., 2009). With respect to Pb, Odigie and Flegal (2011) concluded that elevated Pb concentrations measured in ash produced from a wildfire in Santa Barbara County, California, were, in part, due to the pyrogenic remobilization of historic, industrial Pb depositions. Subsequent Pb isotopic measurements of ash released during the Angeles National Forest wildfire (southern California, USA) and of lake sediments impacted by forest fires in Chile have demonstrated that Pb depositions from previous industrial emissions contribute to environmental Pb contamination in those areas (Odigie and Flegal, 2014; Odigie et al., 2015).

The emission and recycling of atmospheric Pb originating from natural and anthropogenic sources remains a contemporary issue with respect to global Pb contamination (e.g. McConnell et al., 2014). This is due, in part, to the known toxicity of Pb in humans (NTP, 2012), and its persistence as a global contaminant with industrial Pb still identifiable in contemporary Antarctic ice cores and ocean waters (McConnell et al., 2014; Ndungu et al., 2016). The application of Pb isotopic compositions for tracing Pb contamination has been demonstrated in multiple environmental and human research studies (e.g. Komárek et al., 2008; Søndergaard et al., 2010; Soto-Jimenez and Flegal, 2011), and is further utilised in this study.

Australia is one of the world's leading producers and exporters of Pb and other base metals (USGS, 2015), with a number of large Pb-Zn mining and smelting sites currently producing significant volumes of industrial Pb emissions (Csavina et al., 2014; Taylor et al., 2014; Dong et al., 2015; Kristensen and Taylor, 2016). The collective atmospheric Pb emissions from mining or smelting operations at Broken Hill (mining only, New South Wales), Port Pirie (smelting only, South Australia), Olympic Dam (mining and smelting, South Australia), Mount Isa (mining and smelting, Queensland), McArthur River (mining only, Northern Territory), Cannington Mine (mining only, Queensland) and Rosebery (mining only,

Tasmania) were estimated to be 202 tonnes for the reporting period 2013/2014 (NPI, 2015). By comparison, the use of leaded petrol as an automotive fuel in Australia between 1932 and 2002 (Cook and Gale, 2005) contributed ~ 240,000 tonnes of Pb to the ambient environment (Kristensen, 2015). Despite the elimination of leaded petrol in Australia in 2002, the legacy of historic leaded petrol emissions remains a persistent source of Pb found in contemporary particulate aerosols (e.g. PM2.5), soils, lichens and fungi (Cohen et al., 2011; Laidlaw and Taylor, 2011; Wu et al., 2016). In addition, anthropogenic Pb emitted from other industrial processes (e.g. base metal mining and smelting, steel works and coal burning) has also contributed, albeit to a lesser extent, to environmental Pb contamination in Australia (e.g. Chiaradia et al., 1997a; Gulson et al., 2004).

Kristensen et al. (2014) investigated the remobilisation of natural and historic industrial Pb depositions in ash from three 2011 Australian wildfires in two states (Western Australia and Victoria). Natural sources and historic leaded petrol emissions, as well as additional unidentified sources, were shown to be the sources of Pb in wildfire ash deposits in those states. However, the effect of wildfires on the recycling of Pb more broadly across Australia has not been addressed. Therefore, the objectives of this study were to: (1) evaluate Pb concentrations and isotopic compositions of ash produced by four Australian wildfires: Woy Woy, Central Coast of New South Wales (NSW), Duffys Forest (near Sydney, NSW), Forcett (near Hobart in southern Tasmania), and Cherryville (near Adelaide in western South Australia); and (2) assess the contribution of recycled natural and industrially-sourced Pb and its potential risk of harm to the environment.

Materials and Methods

Sample collection sites

This study quantifies Pb in ash (n = 68), rock (n = 10), surface soil (0–2 cm; n = 10) and deep soil (>30 cm; n = 4) collected at four wildfire-affected sites: Woy Woy, Duffys Forest, Forcett and Cherryville (Figure 1) that took place in Australia between 2012 and 2013 (Appendix D, Supplementary Table S1). Ash samples were collected within three weeks of the wildfires starting and prior to any rainfall to avoid leaching of Pb from the ash.

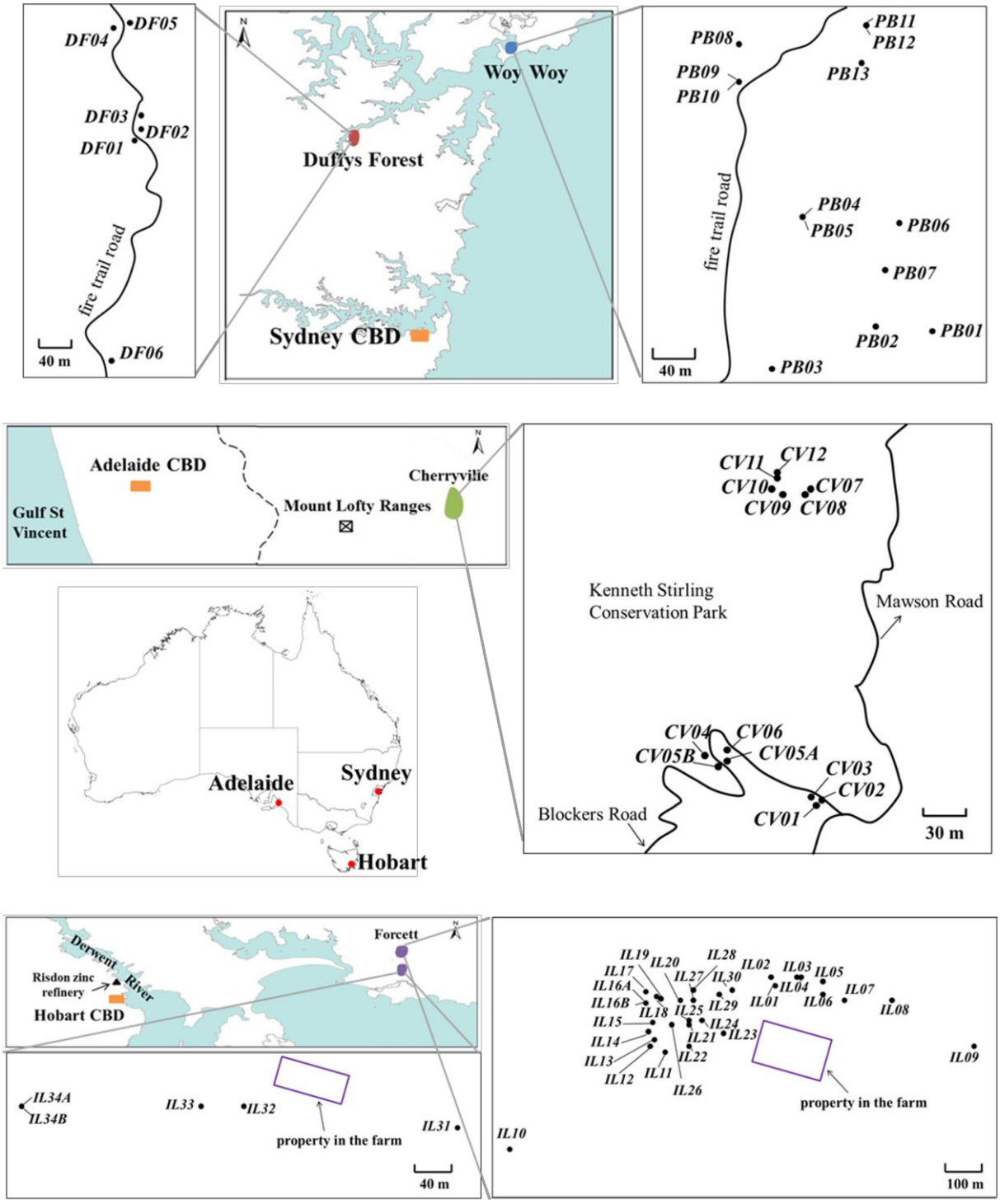

Figure 1. Location maps for ash sample collection at Woy Woy (n = 13), Duffys Forest (n = 6), Cherryville (n = 13) and Forcett (n = 36) wildfire sites close to cities of Sydney Adelaide and Hobart, Australia. The orange-filled squares represent the three Australian cities; the black-filled triangle in the Forcett panel represents the Risdon zinc smelter; the black square with a cross in the Cherryville panel represents the Mount Lofty Ranges area. The map of Australia shows the locations of Sydney, Adelaide and Hobart.

The Woy Woy wildfire in Bouddi National Park, some 79 km north of Sydney, destroyed at least 90 hectares (ha) of eucalyptus forest in the spring of 2012 (SMH, 2012). The Duffys Forest wildfire occurred in a forested area, 28 km north of Sydney, in October 2012 and

affected ~ 310 ha of eucalyptus forest (NSW RFS, 2012). The local soils of Woy Woy and Duffys Forest areas are formed from the Permian and Triassic Wianamatta shales and the Triassic-aged Hawkesbury sandstone of the Sydney Basin (Mayne et al., 1974).

The Forcett wildfire of January 2013, some 30 km southeast of Hobart, Tasmania, burnt approximately 23,960 ha (Boylan et al., 2013). The selected sampling area is dominated by Eucalyptus forest and woodland, which is surrounded by farming areas. The parent bedrock of Forcett soil is Palaeozoic and Permian basalt (Burrett and Martin, 1989; Wang et al., 1996).

The South Australian wildfire which took place in May 2013 at Cherryville, a rural area within the Adelaide Hills, 16 km east of Adelaide city, burnt approximately 650 ha. The soils of the Cherryville area are predominantly formed upon Upper Proterozoic, Cambrian and Ordovician rocks (Drexel et al., 1993).

Sampling procedure

The grey-white ash samples (Appendix D, Supplementary Figure S1) of the burnt areas were collected at the base of large, old *Eucalyptus* trees in order to avoid mixing and contamination with surface soils, litter, gravel and stones. Furthermore, old and large trees are more likely to have taken up Pb from historic leaded petrol depositions compared to younger and smaller trees that have grown in the period following the introduction of unleaded petrol in Australia in 1985 (Kristensen et al., 2014). Grey-white ash was sampled as light coloured (grey or white) ashes are reported to contain more inorganic compounds than dark coloured (black) ashes (Knicker, 2007). Using the Biswas et al. (2007) and Keizer et al. (2008) methods for assessing fire severity, the proportion of burned tree canopy cover (40-100%) and the grey-white colour of the ashes suggest a moderate-to-high fire severity for all sampling sites.

Soil samples were collected to establish surface (0-2 cm) and subsurface (> 30 cm) soil Pb concentrations and isotopic compositions from soil pits in non-burnt areas adjacent to the sampling sites using established procedures (Taylor et al., 2010). Rock samples were also collected from the same areas to help establish natural crustal compositions in the sample areas. Ash, soil and rock samples were placed in plastic bags for processing and analysis at the National Measurement Institute (NMI) laboratory, Sydney. Prior to those analyses, ash and soil samples were air-dried, homogenized and sieved through a 2 mm mesh sieve to remove stones or coarse organics. Rock samples were crushed and ground in an agate ball mill to a fine powder.

Analytical methods

Approximately 0.5 g of ash, 1 g of soil and milled rock samples were digested in 3 mL, trace metal grade HNO_3 and 3 mL HCl (NMI, 2014). Procedural blanks, matrix spike and duplicates were processed and analysed concurrently. Total (acid digestible) Pb concentrations and Pb isotopic compositions were measured using a Perkin Elmer Elan DRC II, inductively coupled plasma mass spectrometer (ICP-MS). Procedural blanks for the ash, soil and rock samples were <0.01 mg/kg Pb. The sample analyses were bracketed with concurrent analyses of Certified Reference Material NIMT/UOE/FM/001 (peat bog-low ash, n = 8), Standard Reference Material 1547 (peach leaves, n = 8), NMI internal reference materials AGAL-10 (river sediment, n = 8) and AGAL-12 (biosoil, n = 8). Recovery rates (mean ± SD) of Pb were 99 ± 0.3% for CRM NIMT/UOE/FM/001, 101 ± 0.1% for SRM 1547, 100 ± 0.4% for AGAL-10 and 100 ± 4% for AGAL-12. Analytical instrumental drift was corrected with indium as an internal standard. In addition, data for Pb isotopic compositions were optimised at 20 or 10 ppb levels and were bracketed by NIST SRM981 (common Pb standard) to correct for mass fractionation. One ash sample (IL_ASH_22) was analysed eight times (n = 8) returning a relative standard deviation (RSD) for Pb concentration of ± 4%, and Pb isotopic composition of 0.23%, 0.17%, 0.14% ($^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, respectively). Repeat measures (n = 8) of CRM NIMT/UOE/FM/001 were undertaken to assess the accuracy and reproducibility of Pb isotope measurements at the NMI. The certified value for CRM NIMT/UOE/FM/001 for the $^{206}Pb/^{207}Pb$ ratio is 1.176 ± 0.0004, comparable to the average $^{206}Pb/^{207}Pb$ ratio of 1.177 ± 0.0017 in our analyses. The RSDs were also within ± 3% for Pb concentration, and 0.05%, 0.11%, 0.04% for the isotope ratios $^{204}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, respectively.

The median Pb concentrations and isotopic compositions, recovery rates and three isotope plots were calculated using Microsoft Excel. Statistical differences were analysed using the Kruskal-Wallis test. Box plots were undertaken using SPSS software, version 21.0 in order to assess the relationship between the Pb concentrations and isotopic compositions of ash samples from the four wildfire sites.

Results and Discussion

Sample Pb concentrations and isotopic compositions in wildfire ash, local soils and rocks are provided in Appendix D, Supplementary Table S1 and presented below according to their geographic locations.

Woy Woy and Duffys Forest, NSW

Given the similarity in base-rock geology and relative proximity of the Woy Woy and Duffys Forest areas, the data from these sites are examined together. Ash samples collected from Woy Woy site had a median Pb concentration of 6 mg/kg (ranging from 0.5 to 41 mg/kg), while median Pb concentrations in Duffys Forest ash were 24 mg/kg (ranging from 10 to 72 mg/kg) (Figure 2a). Twelve of the 13 Woy Woy ash samples had Pb concentrations < 10 mg/kg, although the samples show a relatively wide range in $^{206}Pb/^{207}Pb$ ratios (1.075–1.176) (Figure 2b). By contrast, the Duffys Forest samples show relatively small variation in $^{206}Pb/^{207}Pb$ ratios, despite the relatively large range in Pb concentrations (Figure 2b). The Pb isotopic compositions of ash from the two sites overlap, with median $^{206}Pb/^{207}Pb$ ratios of 1.139 (ranging from 1.104 to 1.176) for Woy Woy and 1.109 (ranging from 1.099 to 1.124) for Duffys Forest (Appendix D, Supplementary Table S1; Figure 2b). The Pb isotopic compositions of ash samples extend from the field of local rocks towards lower isotopic compositions for Woy Woy, while the isotopic data of Duffys Forest are significantly lower than local background samples (Figure 3).

Natural crustal Pb was determined by analysis of local rock and deep soil samples. Lead concentrations of surface soils from Woy Woy and Duffys Forest sites (n = 6) ranged from 3 to 25 mg/kg (Appendix D, Supplementary Table S1). Surface soil Pb concentrations were similar to those of the corresponding subsurface soil samples. However, the isotopic compositions of surface soils were significantly higher than those measured in corresponding subsurface (deep) soils and unweathered rocks collected from areas adjacent to the ash sampling sites (Figure 4).

Forcett, Tasmania

Total extractable Pb concentrations in ash samples from Forcett ranged from 0.6 to 80 mg/kg with a median value of 6 mg/kg (Figure 2a). The $^{206}Pb/^{207}Pb$ ratios (1.075–1.208; median of 1.166) were slightly more variable compared to those from the NSW sites (Appendix D, supplementary Table S1; Figure 2b). Figure 3 shows that 34 of the 36 Forcett ash samples had Pb concentrations < 24 mg/kg, with a relatively wide range in $^{206}Pb/^{207}Pb$ ratios (1.104–1.208). Lead concentrations in two Forcett ash samples were markedly elevated: IL20: 44 mg/kg; IL27: 80 mg/kg (Appendix D, Supplementary Table S1). The relatively high Pb concentrations in these two samples were above the values in local background samples and may have resulted from contamination from adjoining farming activities (Figures 1; Figure 3).

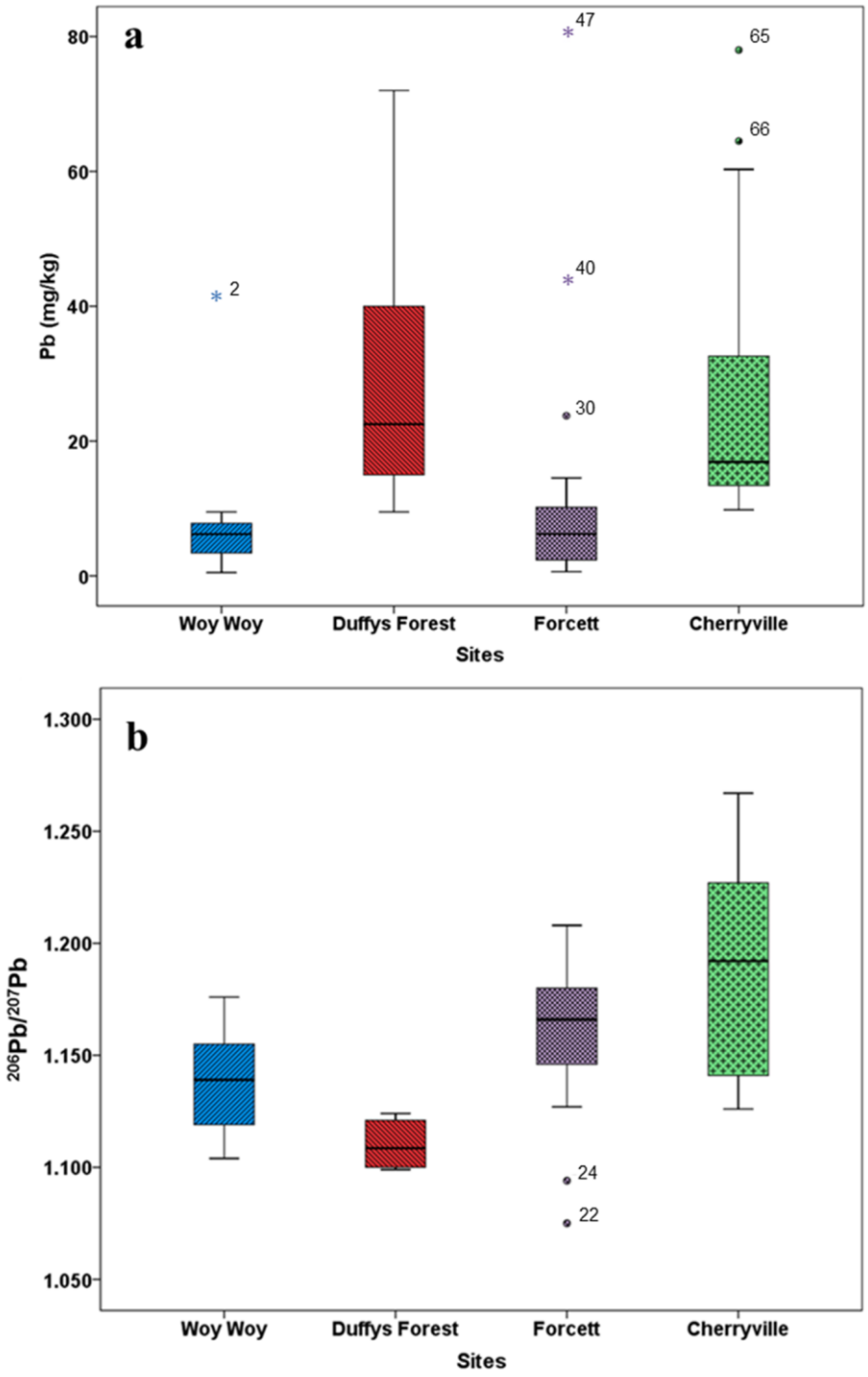

Figure 2. Box-whisker plots for Pb concentration (mg/kg; Figure 2a) and Pb isotopic compositions ($^{206}Pb/^{207}Pb$; Figure 2b) in ash samples for four sampling sites. The boxes define median values and 25th and 75th percentiles of the data while the whiskers represent the 10th and 90th percentiles of the data. The asterisks represent extreme outliers (3*IQR (Interquartile range) from the rest of the scores); the dots represent mild outliers (1.5*IQR from the rest of the scores).

Forcett surface soil Pb concentrations were higher than those of the corresponding subsurface soil samples (Appendix D, Supplementary Table S1). Surface soils (0–2 cm depth, n = 2) have $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotopic compositions of 1.175–1.191 and 2.465–2.458, respectively (Appendix D, Supplementary Table S1). By contrast, lead isotopic compositions

of natural crustal Pb in deep soil and rock samples ($^{206}Pb/^{207}Pb$ = 1.204–1.211 and $^{208}Pb/^{207}Pb$ = 2.470–2.509) collected from an unburnt area in close proximity to Forcett site were higher than surface soil samples (Figure 5).

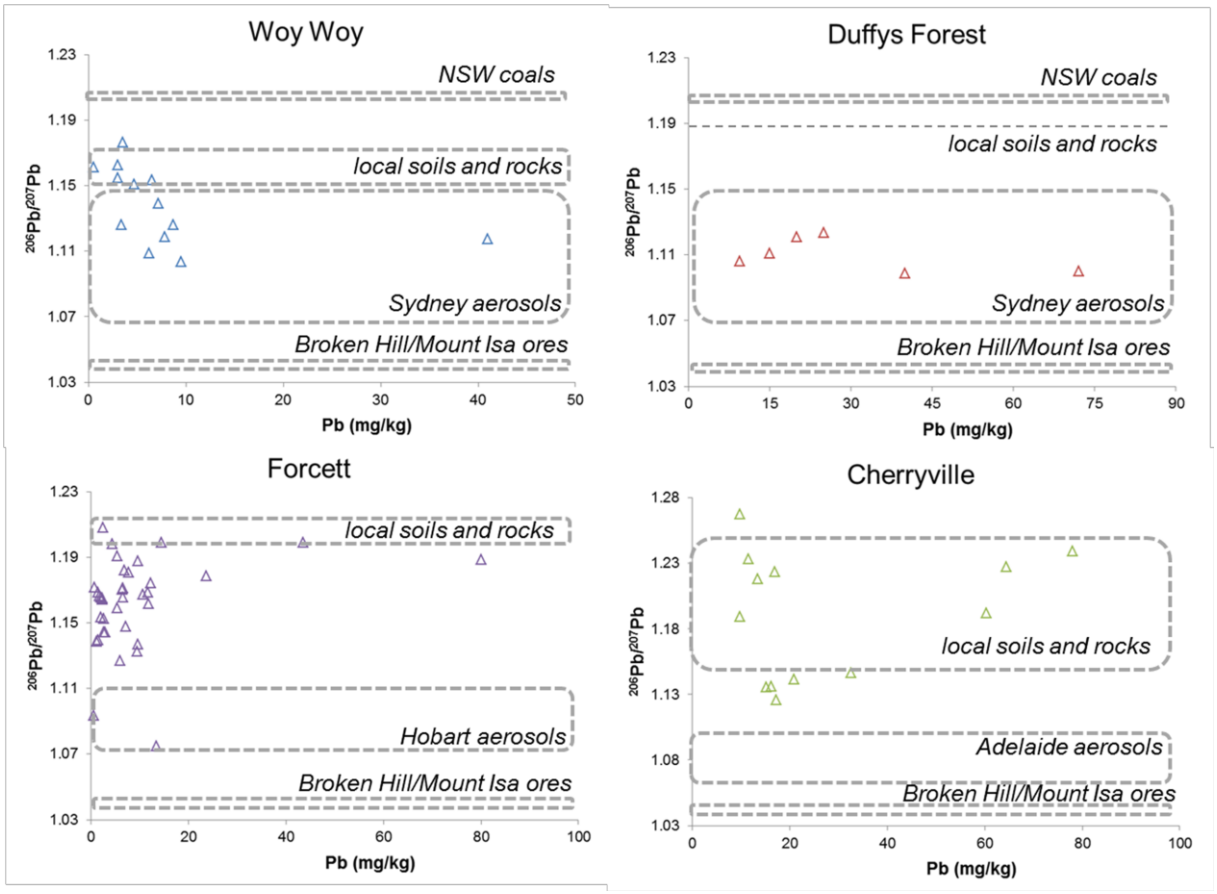

Figure 3. Plots of $^{206}Pb/^{207}Pb$ ratios versus Pb concentrations for ash samples collected from four wildfire sites. The Pb isotopic compositions for Broken Hill/Mount Isa mines, local soil and rock samples, urban aerosols and NSW coals are shown on the figure. Data for the local soils and rocks from this study are given in Appendix D, Supplementary Table S1. Data sources for Broken Hill/Mount Isa mines, urban aerosols and NSW coals are presented in Appendix D, Supplementary Table S2.

Cherryville, South Australia

Ash samples from the Cherryville wildfire show a relatively wide range in Pb concentrations, from 10 to 78 mg/kg (median – 17 mg/kg), and a large range in $^{206}Pb/^{207}Pb$ ratios: 1.126–1.267 (median – 1.192; Appendix D, Supplementary Table S1; Figure 2). In Cherryville, three of the 13 ash samples had notably high Pb concentrations (CV09: 78 mg/kg; CV10: 65 mg/kg; CV11: 60 mg/kg). These samples were collected from a hillslope area of forest not adjacent to any buildings or other obvious anthropogenic structures. The relatively high total Pb levels measured in these three samples were also above local deep soil and rock Pb concentrations (ranging from 3 to 31 mg/kg) indicating a local anomaly (Figures 1; Figure 3; Appendix D, Supplementary Table S1).

Lead concentrations of Cherryville surface soils exceeded those of the corresponding deep soil samples (Appendix D, Supplementary Table S1). Unweathered rock and deep soil samples (40-50 cm depth, n = 3) collected adjacent to the Cherryville site have $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ isotope ratios of 1.163–1.247 and 2.469–2.625, respectively (Appendix D, Supplementary Table S1). The measured $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the two surface soil samples ($^{206}Pb/^{207}Pb$ 1.110–1.213; $^{208}Pb/^{207}Pb$ 2.441–2.575) vary widely and partly overlap with subsurface soil and rock isotopic data, reflecting a mixture of natural and anthropogenic Pb inputs (Figure 6).

Sources of lead in Woy Woy and Duffys Forest ash, NSW

The lead isotopic compositions of Woy Woy and Duffys Forest ash plot along an approximately linear array between a high Pb isotopic end member, represented by natural crustal Pb and a lower Pb isotopic end-member, represented by Broken Hill/Mount Isa ores, the predominant source of lead used in Australian petrol (Figure 4). Lead isotopic compositions of coals and coal fly ash from NSW plot away from the linear array defined by the ash samples, local bedrock and soils and Broken Hill/Mount Isa ores, suggesting a minimal contribution to ash Pb isotopic compositions (Figure 4). Surface soil isotopic compositions have lower Pb isotope ratios than the deep soil/rock samples (Figure 4). This suggests that surface soils are a mixture of subsoil and an atmospherically deposited source of lead with a lower Pb isotopic composition, such as Broken Hill/Mount Isa ore-type material.

Archival air filters (‘Sydney aerosols’ in Figure 4) from Sydney Central Business District (CBD) collected between 1978–1999 (Facchetti, 1989; Chiaradia et al., 1997b; Bollhöfer and Rosman, 2000; Kristensen et al., 2016) are used as a proxy for petrol and industrial Pb emissions during that period (Appendix D, Supplementary Table S2; cf. Kristensen et al., 2016). The Pb isotopic compositions of the air filters also generally lie between the local rocks and subsoils and Broken Hill/Mount Isa ore compositions (Figure 4). The tight linear array of the air filter samples are rotated towards the NSW coal samples at higher Pb isotopic compositions, which may indicate a minor influence from coal combustion.

The city of Sydney has a well-established history of environmental Pb contamination following the commencement of urbanisation and industrialisation in the 19th century and the introduction of leaded petrol in 1932 (Cook and Gale, 2005; Birch et al., 2015). Previous studies of isotopic compositions of air filter samples and archival lichens has indicated petrol emissions were the dominant anthropogenic source of Pb (Cohen et al., 1994; Cohen et al.,

1996; Chiaradia et al., 1997b; Bollhöfer and Rosman, 2000; Wu et al., 2016). Although lower allowable concentrations of Pb in petrol additives were introduced in Australian metropolitan areas from the 1970s, and Pb additives were finally removed from automobile fuel in 2002, the research literature shows that the additives have remained a persistent source of regional contamination in the region (Connor and Thomas, 2003; Cohen et al., 2011; Cohen et al., 2012; Larsen et al., 2012; Wu et al., 2016).

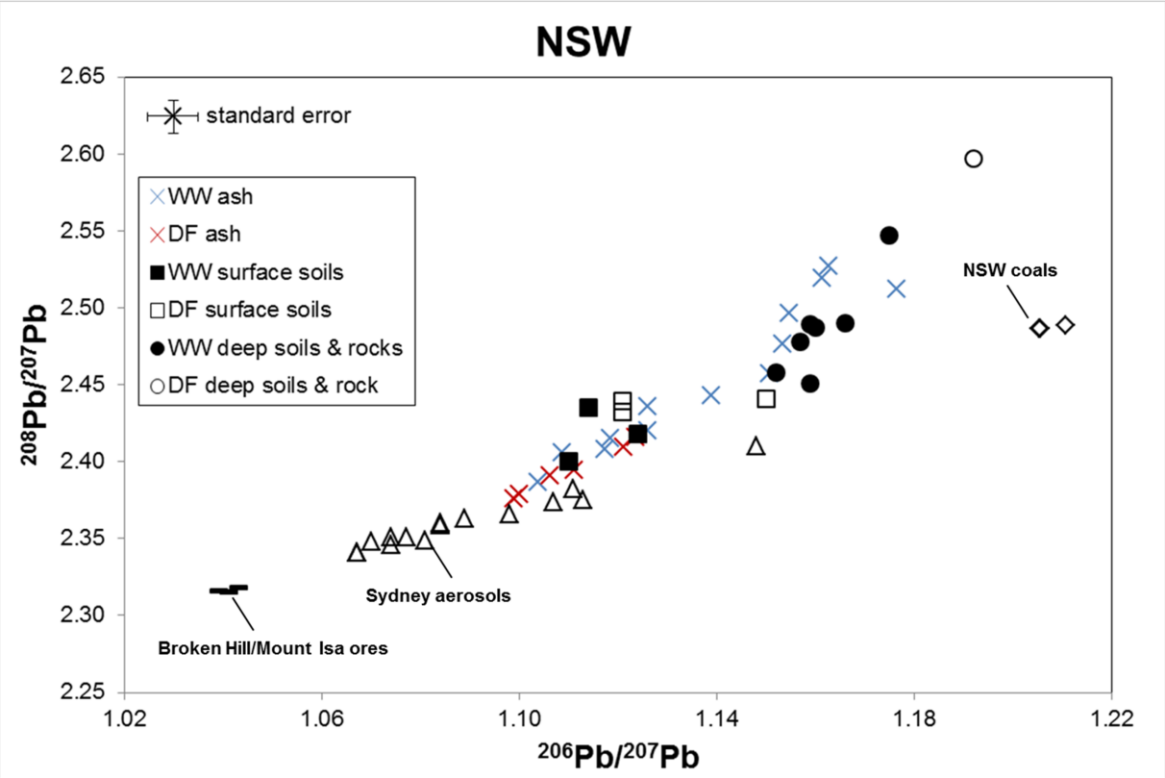

Figure 4. Pb isotopic compositions ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$) of ash data collected from the Woy Woy (WW) and Duffys Forest (DF) wildfire sites. The standard error for the Pb isotopic compositions are: $^{206}Pb/^{207}Pb$: 0.006 and $^{208}Pb/^{207}Pb$: 0.011. Data sources for Sydney aerosols (1978－1999), Australian ores and NSW coals are presented in Appendix D, Supplementary Table S2.

Given the proximity of the Woy Woy and the Duffys Forest ash sites to the city of Sydney, the Pb concentrations measured in the ash samples are likely to have been dominated by historic depositions of petrol Pb emissions in the Sydney region (Wu et al., 2016). Previous research has shown that Broken Hill and Mount Isa Pb ores have been used predominantly to manufacture Pb in petrol and industrial raw materials and feedstock (Woodward et al., 1965; Chiaradia et al., 1997b; Marx et al., 2010; Townsend and Seen, 2012). Relevantly, these ores have characteristically low isotopic compositions (Supplementary Table S2), consistent with those of leaded petrol sold in Sydney which were collected from 1978 to 1981 and the 1990s (Gulson et al., 1983; Kristensen et al., 2014). Relevantly, lead concentrations in Duffys Forest

ash were significantly higher (p <0.05, Kruskal-Wallis test) than those in ash from Woy Woy. This is not unexpected given the proximity of the Duffys Forest to the city of Sydney, which was a major source of atmospheric petrol Pb (Kristensen, 2015).

With respect to the other likely significant sources of Pb, i.e. industrial activity, coal and coal fly ash, there is only limited Australia Pb isotopic data (Chiaradia et al., 1997a; Gulson et al., 2004; Díaz-Somoano et al., 2009). The available Pb isotopic compositions of NSW coals and coal fly ash indicate they have high isotopic compositions compared to those of Broken Hill/Mount Isa Pb ores (Figure 3; Appendix D, Supplementary Table S2). A significant contribution from these sources is not required to explain the isotopic composition of the ash samples.

Sources of Pb in Forcett ash, Tasmania

Figure 5 shows that Forcett ash samples plot between high isotopic end members represented by local soil and rock and a lower isotopic end member represented by Hobart aerosols dating from 1994 to 2000. This overlap indicates that natural crustal Pb inputs and historic industrial and petrol depositions are the primary sources of ash Pb remobilised from the 2013 Forcett wildfire. The Pb isotopic compositions of Hobart leaded petrol samples measured in 1999 were consistent with those of Hobart aerosols at that time (Appendix D, Supplementary Table S2). The similarity between Hobart leaded petrol data and aerosol isotopic compositions substantiates our assumption that local aerosol Pb data reflects depositions from leaded petrol emissions in this region (Bollhöfer et al., 2005). This assumption is evidenced by Hobart aerosol Pb isotopic ratios in 1994 and 1999/2000: $^{206}Pb/^{207}Pb$ 1.068–1.112; $^{208}Pb/^{207}Pb$ 2.340–2.375 (Bollhöfer and Rosman, 2000; Bollhöfer et al., 2005). These aerosol values are similar to those of surface soils ($^{206}Pb/^{207}Pb$ 1.175–1.191; $^{208}Pb/^{207}Pb$ 2.465–2.458) but not subsurface soil samples from this study, reflecting the influence of anthropogenic industrial Pb inputs (Figure 5). Given the proximity of the site to the Nyrstar zinc smelter in Risdon, Hobart (Figure 1), it is likely that the Pb contamination could also include emissions from this source, which has been operating for nearly 100 years (McLaughlin, 2008; Gregory et al., 2013).

Sediment cores collected from the Derwent River in 2004 had the following ratios: $^{206}Pb/^{207}Pb$ 1.074–1.204; $^{208}Pb/^{207}Pb$ 2.346–2.477 (Townsend and Seen, 2012). Some Forcett ash samples have Pb isotopic compositions that correspond to Derwent River sediment dated back to pre-1917, indicating a common Pb source. Townsend and Seen (2012) showed that the Pb isotopic compositions of sediment from the Derwent River (Hobart, Tasmania) dated to the period 1917 to 2004 plot between the primary Pb sources: high isotopic compositions

from Rosebery, Hellyer and Elura ores ($^{206}Pb/^{207}Pb$ 1.159–1.176; $^{208}Pb/^{207}Pb$ 2.439–2.448) that were smelted at the Risdon Nyrstar smelter and lower Pb isotopic values from Broken Hill, Mount Isa and Century mines. Between 1999–2014 the Risdon smelter emitted a total of 9560 kg of Pb into the atmosphere (NPI, 2015). Current annual production of zinc in the smelter is near 280,000 tonnes (Gregory et al., 2013). The Pb depositions from this local industrial point source are likely to have contributed to the Pb absorbed by local vegetation, which was subsequently remobilised in the wildfire ash.

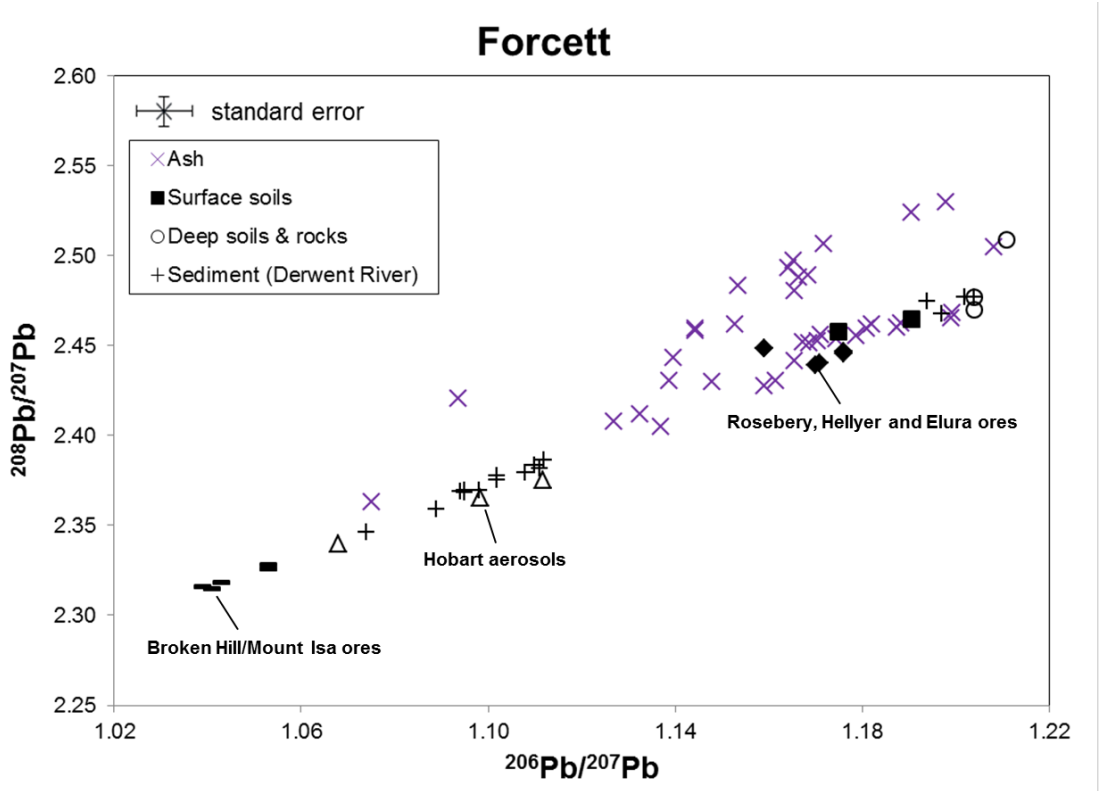

Figure 5. Pb isotopic compositions ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$) of ash data collected from the Forcett wildfire site in Tasmania. The standard error of Pb isotopic compositions is: 0.005 for $^{206}Pb/^{207}Pb$ and 0.006 for $^{208}Pb/^{207}Pb$.Data sources for Hobart aerosols (1994－2000) and Australian ores are presented in Appendix D, Supplementary Table S2.

Sources of Pb in Cherryville ash, South Australia

Potential anthropogenic Pb sources at the Cherryville site including petrol and industrial emissions in Adelaide city, approximately 16 km distant, are given in Supplementary Table S2. The $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{207}Pb$ ratios are plotted in Figure 6. The Adelaide aerosol samples collected in 1994 and during the period of 1997–2004 have relatively low Pb isotopic ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$) compositions (Bollhöfer and Rosman, 2000; Kristensen et al., 2016) compared with those of local background soil and rock samples (Figure 6).

The Pb isotopic compositions in wildfire ash sampled from Cherryville are off-set from local rock and deep soil values toward the Adelaide aerosol isotopic data collected between 1994 to

2004 (Figure 6). The isotopic compositions suggest that the remobilisation of Pb measured in Cherryville ash residues are attributed to natural crustal Pb and industrial/petrol Pb emissions. Analysis of historic wine samples (dating from 1963–2012) from the McLaren Vale and Langhorne Creek regions, south of Adelaide (and within approximately 50 km south of Cherryville site) detail the influence of leaded petrol as a dominant source of anthropogenic Pb depositions in the region (Kristensen et al., 2016). Moreover, most Pb added to petrol sold in Adelaide was sourced from Broken Hill and Mount Isa Pb (Gulson et al., 1981).

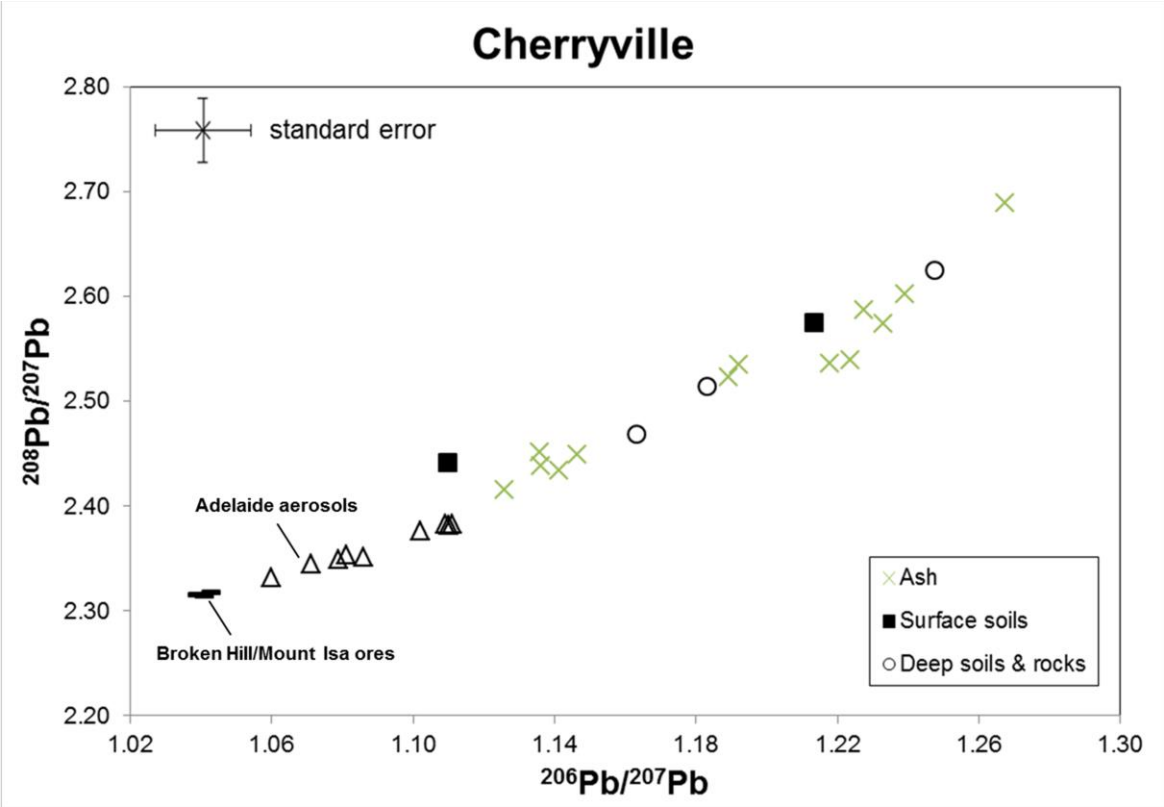

Figure 6. Pb isotopic compositions ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$) of ash data collected from the Cherryville wildfire site in South Australia. The standard error of Pb isotopic compositions is: 0.013 for $^{206}Pb/^{207}Pb$ and 0.022 for $^{208}Pb/^{207}Pb$. Data sources for Adelaide aerosols (1994—2004) and Australian ores are presented in Appendix D, Supplementary Table S2.

In terms of other potential sources, there is a large Pb smelter at Port Pirie in South Australia approximately 200 km north of the sampling site that has been operating since 1889 (Kristensen and Taylor, 2016). Even in recent times the smelter has emitted substantial Pb contaminants with an estimated 743 tonnes being emitted into the atmosphere between 1999 and 2014 (NPI, 2015). Gulson et al. (1996) reported topsoil samples collected from five households in urban Port Pirie area had low Pb isotopic compositions ($^{206}Pb/^{204}Pb$ ratios: 16.3–17.0) as did $^{206}Pb/^{204}Pb$ ratios of topsoil samples (16.5–17.3) collected from five households of urban Adelaide, reflecting anthropogenic Pb inputs from smelter and petrol sources (Gulson et al., 1981). Historically, the feedstocks smelted at Port Pirie were sourced

from the Broken Hill mine (Trengove, 1975), however, in recent years the Pb processed at the smelter has been sourced from multiple sites across Australia (Ohmsen, 2001). Nevertheless, isotopic data from this study data do not suggest that Port Pirie smelter emissions have contributed significantly to the Cherryville ash Pb sources. Moreover, emissions from the Port Pirie smelter were also not identifiable contemporary wines from South Australia (Kristensen et al., 2016), further supporting the contention that Pb emissions from Port Pirie smelter are not a discernible anthropogenic source in that area.

The contribution of leaded petrol to total Pb sources remobilised in ash

Source identification of the ash lead shows that former leaded petrol deposition is a dominant source of Pb contamination found in wildfire ash residue. Average $^{206}Pb/^{207}Pb$ values calculated from analysis of local rock and deep soil at each sampling site along with historic aerosol data from Sydney, Adelaide and Hobart (see Appendix D, Supplementary Table S2) were used to calculate the percentage of leaded petrol using Monna et al. (1997) mixing model. Kristensen et al. (2016) quantified the contribution of leaded petrol in wine samples from South Australia using the 1994 Adelaide aerosol Pb isotopic composition as an end member. The same logic is applied here to calculate the contribution of leaded petrol in Cherryville samples.

These analyses indicate that the proportion of historic petrol Pb in ash samples was as: Woy Woy 35%, Duffys Forest 73%, Forcett 39%, and Cherryville 5%. The results show that although unleaded petrol was introduced in 1985 and leaded petrol was banned in 2002, the legacy industrial Pb is being recycled back into the environment to varying degrees at all of the sites. Moreover, it is not surprising that former petrol Pb emissions are the dominant source of ash Pb at the Duffys Forest site given its proximity to city of Sydney.

The environmental and human health impact of wildfires

These data confirm the emerging paradigm that wildfires promote the recycling of toxic metals stored in ecosystems. Several studies have reported the impacts of wildfires on the transport of Pb from vegetation to the atmosphere, to water bodies and to soil (Demeyer et al., 2001; Stein et al., 2012; Nzihou and Stanmore, 2013). Particulate (ash) movement is considered to be one of mechanisms for metal transfer to the atmosphere during vegetation combustion (Raison et al., 1985). Particulate formulation may lead to metal contamination of the atmosphere, soil and water bodies during fires and also from smoke and ash residues. Karthikeyan et al. (2006) reported the mean Pb concentration in PM2.5 samples collected during wildfires was nearly twice its non-wildfire period value. Ash sampled from the four

recent Australian wildfires evaluated in this study contained Pb concentrations above local background values in several cases. Marked differences were observed close to Sydney, a major source of leaded petrol emissions in the 20th century. These recycled anthropogenic Pb sources have the potential to generate toxic exposures in receiving environments from ash fallout, leaching and erosion (Certini, 2005; Stein et al., 2012). The paucity of information about the association between Australian wildfire toxic metal emissions and mortality (Morgan et al., 2010; Johnston et al., 2011; Roberts, 2013) warrants further study (Odigie and Flegal, 2011, 2014;Odigie et al., 2015; Kristensen and Taylor 2012; Kristensen et al., 2014)

Conclusions

Analysis of Pb concentration and isotopic composition of ash samples from four 2012–2013 Australian wildfires corroborate emerging concerns with respect to the release of industrial Pb during wildfires. Although natural crustal Pb is also remobilised during wildfires, the data shows a concomitant release of anthropogenic Pb sources in significant proportions, particularly close Sydney. Ash samples from Duffys Forest at the outskirts of Sydney show that leaded petrol depositions represent up to 73% of remobilised Pb. Given that wildfires are predicted to increase with climate change, further research is needed to understand the potential impacts from recycling of industrial contaminants on environmental systems.

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CHAPTER 6: DISCUSSIONAND IMPLICATIONS

The aim of this study was to chronicle past and recent depositions and emissions of toxic metals and identify their sources at selected locations across the Australian continent. In order to compile and address this issue, trace metal (Al, Fe, Ti, Cr, Cu, Ni, Zn, Pb) concentrations and Pb isotopic compositions were measured in biological archive samples and ash deposits produced from wildfires. The sample material that formed the focus of this study were two lichen genera (*Cladonia* and *Usnea*) and one fungus (*Trametes*), that had been collected and archived over the past 150 years, In addition, recent ash residues from 2012 and 2013 wildfires were also sampled and subject to total Pb and its isotopic composition analysis.

There have been very few Australian studies that have used lichen and fungi materials for monitoring environmental metal contamination (Zeng et al., 2012; Vitarana, 2013). Similarly, there is a paucity of studies investigating the remobilisation of historic industrial Pb deposition in ash residues released from Australian wildfires and possible risks to environmental and human health (Kristensen et al., 2014). Therefore, this research provides an assessment of toxic metal contamination and accumulation in the Australian environment arising from anthropogenic inputs since the mid-19th century using archived lichen and fungi samples and recent wildfire ash residues.

Large-scale emissions of toxic metals (e.g. Hg, Pb) in the atmosphere as a result of human activities such as mining and mineral processing, coal combustion, the use of leaded petrol and local industry, can pose a risk to environmental and human health (e.g. Nriagu, 1996; Schroeder and Munthe, 1998; Wängberg et al., 2001; Pirrone and Mahaffey, 2005; Nelson, 2007; Needleman, 2008). These toxic emissions not only have adverse impacts on air quality in urban areas (Fenger, 1999; Monaci et al., 2000; Lynam and Keeler, 2006; Duzgoren-Aydin, 2007; Holloway et al., 2012) but also contribute to atmospheric contamination of pristine, remote areas (Candelone et al., 1995; Van Oostdam et al., 2005; Ndungu et al., 2016).

Concerns about the growing list of toxic metals (*inter alia* industrial chemicals) emitted as a result of human activities have reinforced efforts to establish environmental regulations and monitoring in industrialised countries, including Australia. National ambient air quality standards for key hazardous pollutants were established by the National Environment Protection Council (NEPM) in 1998 (NEPM, 1998). The air quality standard for Pb of 0.5 μg/m^3 was set by the Australia Commonwealth government (Federal Government) in 1998 and has remained unchanged until present day (NEPM, 1998). Following the removal of Pb

from petrol in 2002 (Kristensen, 2015), there are no longer drivers for change now that Pb levels in air are very low. There are still locations, predominantly those associated with mining and smelting operations, where Pb in air levels still remain elevated (Gulson et al., 1994; Csavina et al., 2012; Mackay et al., 2013; Dong et al., 2015; Kristensen and Taylor, 2016). In addition, in Australia, there has been a requirement to report emissions of individual pollutants from point sources (e.g. industry, mines) since 1998, under the National Pollutant Inventory (NPI). Reporting data relating to Pb levels in air for all Australian capital cities was only mandated between 1981 and 2001 (Australian State of the Environment Committee, 2001). However, prior to this, environmental protection authorities, related agencies and industrial companies collected some but often sporadic, air quality data. This can be sourced from archive documentation such as the State Pollution Control Commission (SPCC), a New South Wales government agency which was responsible for environmental management in the Sydney Basin (SPCC, 1980). However, these data sources are temporally limited and to the best of the author's knowledge do not go back beyond the early 1970s (see Taylor et al., 2016).

In contrast to the assessment of biological material, there has been considerable research focussed on the sources of toxic metal pollution and their emissions in leaded petrol products, aerosols, surficial sediments, dusts and soils, with data collected from the metropolitan regions within Australia (Gulson et al., 1983; Simpson and Xu, 1994; Liu et al., 1996; Chiaradia et al., 1997b; Birch and Taylor, 1999; Bollhöfer and Rosman, 2000; Matthai and Birch, 2001; Birch and Scollen, 2003; Hawas et al., 2003; Davis and Gulson, 2005; Chan et al., 2008; Townsend and Snape, 2008; Cohen et al., 2011; Laidlaw et al., 2014). These investigations of atmospheric pollution provide *short-term* information on metal emissions and their origins in urban and suburban areas. In Australia there have been only a limited number of studies regarding the *long-term* monitoring of changes in atmospheric metal pollution using peat bog cores, sediment cores and seagrass (Chiaradia et al., 1997a; Gale and Haworth, 2002; Connor and Thomas, 2003; Douglas et al., 2003; De Deckker et al., 2010; Marx et al., 2010; Morelli et al., 2012; Townsend and Seen, 2012; Serrano et al., 2016). As a consequence, the studies in this thesis, use herbarium lichen and fungi archives, and ash production, to detail historic and contemporary emissions of toxic elements from anthropogenic sources in New South Wales, Victoria, Tasmania and South Australia with sub-annual resolution.

6.1 Sources of anthropogenic contamination after European settlement

Since European settlement in 1788, local and regional development of industry and urbanisation within Australia has led to rapid rates of change in pre-existing dynamics of environmental systems (Dodson and Mooney, 2002). Release of toxic metals into the environment increased sharply following the arrival of Europeans, and was associated with anthropogenic activities such as mining, metal production, vehicle emissions and industrial activities (Marx et al., 2010; Townsend and Seen, 2012; Serrano et al., 2016).

6.1.1 Mining and metal production

The history of mining and base metal production in Australia dates back to the 1840s (Drew, 2011). In particular, from the 1880s to 1980s, ore extracted from Broken Hill was regarded as one of the largest mineral resources of industrial Ag, Pb and Zn globally (Solomon, 1988). The ore was smelted at Port Pirie in South Australia (Trengove, 1975). Early mining and mineral processing increased emissions of metals into the environment, and have been identified previously as the source of elevated levels of toxic metals present in the Australian environment during those early years (Marx et al., 2010; Townsend and Seen, 2012; Serrano et al., 2016).

In Chapter Three, significantly high Pb concentrations in lichen samples collected between 1885 to 1889 from the Mount Macedon area of Victoria, were found to be temporally associated with former gold mining activities in this region (Wu et al., 2016a). Chapter Four revealed that these gold mining activities and related emissions from Mount Macedon were also the most likely anthropogenic sources of Cu and Zn pollutants during the same period via the use of Cluster Analysis (CA) and Principal Component Analysis (PCA). High Cu enrichment factors (EFs) of 1370, together with high Pb and Zn EFs have been reported in Lithgow city (central western of New South Wales) as early as 1897, probably as a result of coal mining activities (Chapter Four).

There has been an increase in base metal production within Australia from the early 1900s until the present time (Mudd, 2007). In 2014/2015 emissions, based on NPI estimates of Cu, Zn and Pb pollutants from active mines in Australia were: 400 tonnes, 1100 tonnes and 370 tonnes, respectively (NPI, 2015). Such large-scale toxic pollutants have had demonstrable impacts on environmental and human health in locations in close proximity to the mines (Baghurst et al., 1992; Gulson et al., 1994; Boreland et al., 2002; Taylor et al., 2010; Lesjak et al., 2013; Mackay et al., 2013; Dong et al., 2015; Earl et al., 2015; Kristensen and Taylor, 2016).

6.1.2 The use of leaded petrol

Leaded petrol was introduced into Australia in 1932 (Cook and Gale, 2005) and it has been calculated that 240,510 tonnes of Pb were emitted through the consumption of leaded petrol from automotive vehicles during the 70 years from 1932 to 2002 (Kristensen, 2015). The author notes that leaded fuel has ongoing restricted uses, predominantly for aviation fuel use in piston engines (Anele, 2016). Lead from leaded petrol is the major metal contaminant in urban communities within Australia (Gulson et al., 1983; Cohen et al., 1994; Gulson et al., 1996; Chiaradia et al., 1997b; Chan et al., 1999; Cohen et al., 2002; Cohen et al., 2011). Furthermore, the pervasiveness of petrol emissions on environmental quality was identified in a recent study of Australian wine dating back six decades (Kristensen et al., 2016). Kristensen et al.'s (2016) study showed that leaded petrol emissions had measurable impacts on Pb levels recorded in wine sampled from two wine growing regions close to Adelaide, the capital city of South Australia.

From 1932 to 1970, Pb emissions from petrol consumption steadily increased, but from the mid-1970s, the levels of emissions began to fall following the implementation of regulations that limited the allowable levels of Pb in petrol (Kristensen, 2015). In 1985 the introduction of unleaded petrol further aided the fall in petrol emissions to the environment (Kristensen, 2015). Although the petrol additive regulations had a significant impact on the reduction of Pb emissions into the atmosphere, throughout the 1990s, Pb from petrol continued to be a major atmospheric pollutant (Chapters Two, Three and Four) (Wu et al., 2016a; Wu et al., 2016b). In the Sydney region during the 1990s, data from air filters demonstrated that more than 90% of atmospheric Pb was attributed to leaded petrol emissions (Chiaradia et al., 1997b). Lead isotopic measurements derived from urban aerosols within Australia also demonstrated that petrol Pb emissions have substantially contributed to atmospheric Pb contamination throughout the 1990s (Bollhöfer and Rosman, 2000, 2002).

The use of leaded petrol for automotive use was finally discontinued in 2002. This had a striking effect in terms of reduction and elimination of environmental atmospheric Pb emissions (Australian State of the Environment Committee, 2001; Kristensen, 2015). However, the legacy of historic leaded petrol emissions and depositions can still be determined, identified and traced in the environment (Larsen et al., 2012; Kristensen et al., 2014; Laidlaw et al., 2014). Lead concentrations measured in Sydney residential soils were probably derived from the resuspension of previous leaded petrol depositions (Laidlaw et al., 2014). This interpretation is consistent with analyses of Pb concentrations in marine surface sediments from Iron Cove and Rose Bay in Sydney Harbour that were attributed to a legacy

of contamination from historic leaded petrol emissions (Larsen et al., 2012). Thus, the legacy of leaded petrol Pb emissions continues to influence the recycling and redistribution of Pb levels in the environment.

The studies of Pb concentrations and Pb isotopic compositions reported in Chapter Two have shown that, during the era of leaded petrol from 1932 to 2002, leaded petrol has been the major contributor of Pb found in archival collections of lichen and fungi from the Greater Sydney region (Wu et al., 2016b). Although median Pb concentrations (1.7–4.8 mg/kg) recorded in contemporary (2000s) samples are significantly lower than those (18.8–21.5 mg/kg) recorded during the leaded petrol period, the isotopic compositions in the 2000s do not return to the pre-leaded petrol values, demonstrating there remains a legacy imprint from previous emissions of leaded petrol in recently collected lichen samples (Wu et al., 2016b).

In Chapter Three, Pb contamination from the use of leaded petrol was further assessed in biological samples collected from central and southern Victoria. The Pb concentrations and Pb isotopic data of lichens and fungi from this region show again that leaded petrol was the most anthropogenic source of atmospheric Pb deposition during the leaded petrol era (Wu et al., 2016a). Similarly, Pb isotopic values of contemporary (post 2002) herbarium collections do not return to the levels recorded in collections made prior to the pre-leaded petrol era (Wu et al., 2016a). Thus, the data simply show that the legacy of Pb derived from petrol emissions persists in the environment and its imprint is clearly evident in Australia's two most populous states of New South Wales and Victoria (Chapters Two and Three) (Wu et al., 2016a; Wu et al., 2016b). The evidence of anthropogenic impact on the environment is further detailed in Chapter Four. Here, the CA and PCA results of trace metals recorded in lichens and fungi reveal vehicle-related emissions (e.g. leaded petrol emissions, brake lining and tire wear) are the most likely anthropogenic sources of high Pb and Zn EFs during the leaded petrol period.

Pb concentrations and isotopic compositions were measured in ash residues collected from four Australian wildfire sites, all in close proximity to the major state capital cities of Adelaide, Sydney and Hobart. Chapter Five demonstrates that the remobilisation of Pb in ash can be attributed to previous deposition of Pb from industrial and from petrol emissions. The persistence of these Pb deposits is comparable to the results of other ash and sediment studies in Australia and elsewhere in the world (Odigie and Flegal, 2011; Kristensen et al., 2014; Odigie and Flegal, 2014; Odigie et al., 2015). In Australia, for example, (Kristensen et al., 2014) concluded that Pb concentrations and isotopic compositions of ash released from three wildfires in 2011 were linked to past contamination from leaded petrol emissions. Similarly,

in North America, the Pb isotopic measurements of ash produced during forest fires, demonstrated that historic petrol Pb emissions have contributed to remobilised Pb contamination (Odigie and Flegal, 2011, 2014). In Chile, Pb levels recorded in a lake sediment core, quantified the amount of Pb released to aquatic ecosystem through wildfires (Odigie et al., 2015). It has also demonstrated that the pyrogenic remobilisation of industrial Pb deposits (e.g. previous leaded petrol emissions) by wildfires in Chile were identifiable via the application of Pb isotopes (Odigie et al., 2015).

6.1.3 Local industries and combustion of coal

In addition to emissions from mining operations and from the use of leaded petrol in motor vehicles, industrial development and coal combustion have proved to be important sources of environmental metal contamination throughout the world (Monna et al., 1997; Brännvall et al., 1999; Farmer et al., 1999; Danihelka et al., 2003; Ettler et al., 2004; Loska et al., 2004; Yongming et al., 2006). In Australia, more than 70% of electricity is produced from coal-fired power stations (Wells and Donaldson, 2005). Numerous heavy industrial operations such as base metal smelters (e.g. Pb-Zn smelters), incinerators and coal-fired power stations are located within a 200 km radius of major capital cities in Australia (Alexander and Metals-EZ, 1992; Roberts and Enright, 2004; Marx et al., 2010; Cohen et al., 2012; Birch et al., 2015). However, environmental assessments of Pb from coal combustion and industrial emissions have not been well-quantified within Australia and there are limited studies that have used data derived from sediments, aerosols and peat bogs to investigate metal contamination (Chiaradia et al., 1997a; Connor and Thomas, 2003; Marx et al., 2010; Cohen et al., 2012; Townsend and Seen, 2012). The methods employed in this thesis have proved to be useful techniques that can be utilised to track and assess environmental metal contamination resulting from coal combustion and industrial applications.

Chapter Two provides evidence that Pb recorded in archival herbarium from the Greater Sydney area has been accumulated from anthropogenic inputs from coal combustion and local industry following early industrialisation and urban expansion (Wu et al., 2016b). Similarly, in central and southern Victoria, Pb levels recorded in herbarium lichen and fungi collections, suggested that both coal combustion and industrial emissions may have contributed to atmospheric Pb deposition (Chapter Three) (Wu et al., 2016a). Copper, Pb and Zn have been shown to be correlated, not only with car-exhaust emissions and mining, but also with industrial activities using CA and PCA (Chapter Four). In the Greater Sydney Basin, similar results have been obtained from sediment cores, confirming yet again that local industry has contributed to environmental metal contamination since the start of European settlement (Connor and Thomas, 2003; Birch et al., 2015). Emissions of Pb from a Zn smelter in close

proximity to Hobart city have probably contributed to remobilised Pb deposits measured in ash samples following the Forcett 2013 wildfire (Chapter Five). The degree of impact of this local smelter on environmental quality has also been measured and identified in recent sediment core and soil studies using analyses of Pb concentrations and isotopic compositions (McLaughlin, 2008; Townsend and Seen, 2012).

6.2 Comparison of lichens and fungi with other archival materials

Lichens and fungi archives have been successfully used in this thesis as environmental proxies for recording and identifying the temporal and spatial trends of atmospheric metal contamination and their potential sources. In addition to the use of herbarium collections of lichen and fungi, other environmental archives, such as aerosols, mosses, peat bogs, ice cores and snow, have been studied as a means of revealing historical changes and trends in heavy metal deposition. A comparison of data sourced from lichen and fungal collections with data from these other archival environmental sources, can provide more information on source-apportionment of atmospheric metal contamination and the patterns of depositions in Australian urban and remote environments.

6.2.1 Aerosols

Measurements of air particulates (Total Suspended Particulate, Particulate Matter <2.5 μm, Particulate Matter <10 μm) have been used by environmental researchers and environmental protection agencies to monitor local and regional atmospheric metal contaminants over long periods of time (Sturges and Barrie, 1989; Schroeder and Munthe, 1998; Bollhöfer and Rosman, 2000, 2001; Widory et al., 2010; ANSTO, 2013; U.S.EPA, 2015; Zhao et al., 2015). As mentioned previously, published data with respect to levels of Pb in air for Australian capital cities are only available from 1981 to 2001 (Australian State of the Environment Committee, 2001), however, there have been some specific studies which have reported air Pb concentration and Pb isotopic composition data over the last two decades for major Australian cities (Chiaradia et al., 1997b; Bollhöfer and Rosman, 2000, 2002; Hawas et al., 2003; Bollhöfer et al., 2005; Gulson et al., 2007; Torre et al., 2007; Chan et al., 2008; Cohen et al., 2011; Kristensen et al., 2016). Although air quality data are also measured by industry in Australia, the availability of this information is limited as the priority is to supply directly to state EPAs according to the requirement of pollution licences granted by state EPAs (Taylor et al., 2014). Previous studies have shown that anthropogenic sources, including metal emissions from mining and metal processing, the use of leaded petrol, coal combustion and industrial activities have all contributed substantially to the levels of atmospheric toxic metals in the northern hemisphere (Cloquet et al., 2006b; Mielke et al., 2010; Pirrone et al., 2010). In addition, similar anthropogenic sources of metal contamination have been determined from

air filter samples in Australia (Cohen et al., 1994; Chiaradia et al., 1997b; Chan et al., 1999; Chan et al., 2008; Cohen et al., 2011; Gulson and Taylor, 2014).

Lead isotopic data for TSP recorded in Sydney air filter samples collected from 1978 to 2004 are reported in Chapter Two (Wu et al., 2016b). In order to chronicle the past history of atmospheric contamination relating to metal emissions prior to 1978, lichen and fungi archives used in this study have proven critical in the reconstruction of historic records of metal emissions in the Greater Sydney area and in central and southern Australia. Previous studies elsewhere in the world showed a close correlation between metals trapped in air filters and metal concentrations recorded in biological archives (Sloof, 1993; Berg and Steinnes, 1997; Jeran et al., 2000; Bari et al., 2001; Farmer et al., 2002; Adamo et al., 2008; Flegal et al., 2010; Farmer et al., 2015). Lead isotopic data from our lichen and fungi studies (see Chapters Two and Three) (Wu et al., 2016a; Wu et al., 2016b) are consistent with the results from Sydney and Melbourne air filters (Bollhöfer and Rosman, 2000, 2002) over the same period of time, indicating that archival lichens and fungi serve as good surrogates for Pb in air data from filters, and can therefore be used to monitor and chronicle historic and contemporary metal emissions in Australia.

6.2.2 Mosses

Mosses lack roots and either have no cuticles, or limited cuticles, and thus are able to accumulate and absorb chemical nutrients directly from the atmosphere (Conti and Cecchetti, 2001; Wolterbeek, 2002) and therefore, mosses have been widely used to monitor exposure to metal emissions and to document metal contamination histories in Europe since the late 1960s (Ruhling and Tyler, 1968; Rühling and Tyler, 1970; Herpin et al., 1997; Weiss et al., 1999c; Farmer et al., 2002; Cloy et al., 2005; Shotbolt et al., 2007; Agnan et al., 2014). A study using moss archives collected in Scotland from 1838 to 2000, showed a significant fall of the $^{206}Pb/^{207}Pb$ ratios from 1.17 in the 1920s to 1.12 during the 1980s (Farmer et al., 2002). This reduction of Pb isotopic compositions was likely attributed to anthropogenic sources of atmospheric metal emissions, including mining, smelting, coal combustion and vehicular emissions from leaded petrol (Farmer et al., 2002). There is a similarity in the apportionment of anthropogenic sources of Pb identified in Scottish moss archives (Farmer et al., 2002) and in that measured in Australian herbarium lichen and fungi collections recorded in this thesis (Wu et al., 2016a; Wu et al., 2016b), indicating that the validity of using lichen and fungi archives for assessing atmospheric metal deposition over time. In northern hemisphere studies, combinations of mosses and lichens have been used to study atmospheric metal contamination (Bargagli et al., 2002; Adamo et al., 2003; Giordano et al., 2005; Basile et al., 2008; Cao et al., 2008; Giordano et al., 2013; Gerdol et al., 2014). Although in Australia there have been

several studies that have utilised mosses to monitor *short-term* atmospheric trace metal emissions (As, Cd, Cu, Pb, Se and Zn) from power stations and a Zn-Pb smelter in Australia (Godbeer et al., 1981; Swaine et al., 1983; Huang and Gulson, 2002). However, there is a lack of quantification of temporal changes in metal deposition using moss (or lichen or fungi) archives. This data gap warrants further studies given the abundance of mosses collected that have been preserved in Australian herbaria.

6.2.3 Peat bogs

Peat bogs acquire chemical nutrients from precipitation rather than from inflow from streams and rivers, thus the layers of peat in which chemicals have been sequestered can be utilised as natural archive of atmospheric deposition of toxic metals (Weiss et al., 1999a). There have been numerous studies of metal contamination of peat bogs over time in North America (Norton et al., 1990; Norton et al., 1997), Europe (Shotyk et al., 1996; Cortizas et al., 2002; Le Roux et al., 2004; Monna et al., 2004; Kylander et al., 2005; Cloy et al., 2008; De Vleeschouwer et al., 2009; Cortizas et al., 2012; Farmer et al., 2015), South America (Espi et al., 1997; Biester et al., 2002), and Australia (Marx et al., 2010). Data from Australian peat bog studies have revealed an increase in Pb emissions during the mid-1850s, associated with the commencement of industrial activities and steadily increasing urbanisation. In Australia, large-scale mining, smelting, coal combustion, leaded petrol consumption and agriculture all contributed to increased levels of Pb recorded in peat bogs (Marx et al., 2010). Elevated high concentrations and enrichment of Cu, Pb and Zn are measured in the lichen and fungi archives from 1850 to 1931 with respect to natural inputs, past mining activities and industrial emissions (Chapters Two, Three and Four) (Wu et al., 2016a; Wu et al., 2016b). The increased emission records of Pb and Zn from 1932 to 1984, and then from 1985 to 2001, suggest that contamination during this period in the Greater Sydney area and central and southern Victoria is highly likely to be related to car-exhaust emissions from the use of leaded petrol and other road transport sources, such as brake lines and tyre wear during the era of leaded petrol. In 2002, Pb ceased to be added to petrol, but the data reveals evidence of atmospheric pollution derived from leaded petrol and industry after this time. The temporal similarity of the Pb isotopic compositions recorded in lichen and fungi in this study and Australian peat bog isotopic data, confirm the validity of utilising herbarium archives to reconstruct historic and contemporary records of environmental metal contamination.

6.2.4 Sediments

On a global scale, lake, river and marine sediments have been used to assess the dominant sources of temporal atmospheric metal pollution (e.g. Nriagu, 1979; Norton et al., 1990; Valette-Silver, 1993; Moor et al., 1996; Weiss et al., 1999b; Outridge et al., 2005; Outridge et al., 2011; Walraven et al., 2014). The data from these studies provide a comprehensive record

of past metal contamination. In Australia, sediment cores have also been used as environmental archives of long-term integrated records and changes in metal deposition (Chiaradia et al., 1997a; Gerritse et al., 1998; Connor and Thomas, 2003; Douglas et al., 2003; Harrison et al., 2003; Birch and Olmos, 2006; USEGG, 2007; De Deckker et al., 2010; Morelli et al., 2012; Townsend and Seen, 2012). A recent study of marine sediments in Moreton Bay, south-eastern Queensland, showed that the increase in concentrations of Pb, Zn, Cd and Ni after 1920 pointed to anthropogenic contributions from industrialisation, urban expansion and land clearing to make way for agriculture (Morelli et al., 2012). In Tasmania, Pb isotope ratios in sediment cores from the Derwent River, decreased from natural background levels when a zinc smelter commenced operating in 1917, clearly indicating local industrial emissions were the principal source of Pb pollution in this region (Townsend and Seen, 2012). Changes in the emissions and isotopic compositions of Pb studied in this thesis over the last 150 years can be ascribed to both anthropogenic and natural inputs (Chapters Two, Three and Four) (Wu et al., 2016a; Wu et al., 2016b). Analysis of marine core sediments that were deposited from 1850 onwards, have shown that large quantities of metals have been released into the marine ecosystem (Morelli et al., 2012). These sediment records are consistent with the results obtained in this thesis using archival lichen and fungi collections. In addition, the decrease in Pb isotope ratios in herbarium archives from the late 1880s, broadly matches the decreasing trends in Pb isotopic compositions recorded in sediment cores within Australia during the same period (Chiaradia et al., 1997a; Townsend and Seen, 2012).

6.2.5 Ice cores and snow

The use of ice cores and snow as environmental archives has proved to be extremely successful and ice cores are excellent proxies for past and current changes in levels of toxic metals in the atmosphere (e.g. Ng and Patterson, 1981; Wolff and Suttie, 1994; Barbante et al., 1998; Rosman et al., 2000; Bargagli, 2008; Liu et al., 2011; Wolff, 2014). Lead was one of the first industrial pollutants found in Greenland ice cores (Murozumi et al., 1969) and is also considered a characteristic contaminant reflecting human impact on the Antarctic continent (Vallelonga et al., 2002; Bargagli, 2006). In addition to Pb, other metals including Cr, Cu, Ag and Zn, all predominantly derived from mining, smelting and industrial activities from the Southern Hemisphere nations of Australia, Chile, Peru, Zaire and Zambia, have been documented in snow and ice cores from Antarctica (Planchon et al., 2002; Vallelonga et al., 2002; Do Hur et al., 2007; McConnell et al., 2014). In the 1990s, Pb isotopes were utilised to identify the anthropogenic sources (e.g. leaded petrol emissions) of Pb contamination in four surface snow blocks collected in Antarctica (Rosman et al., 1994). In a recent study of Antarctic ice cores, low $^{206}Pb/^{207}Pb$ ratios were observed for the period 1890 to 1905 and from

1957 to 1995. These have been attributed to result from Australian mining and smelting operations, for example at Broken Hill in western NSW and Port Pirie in South Australia and from Australia-wide leaded petrol emissions (McConnell et al., 2014). Similar anthropogenic Pb sources were identified in Antarctic snow from 1891 to 1908 and then from 1948 to 1994 (Van de Velde et al., 2005). The lead isotopic compositions measured in this thesis indicate that early mining and metal processing between 1850 and 1931, together with leaded petrol emissions, have been the major source of Pb contamination recorded in herbarium archival material from the Greater Sydney area and central and southern Victoria between 1932 and 2001 (Chapters Two and Three) (Wu et al., 2016a; Wu et al., 2016b). These findings are consistent with the anthropogenic sources identified by McConnell et al. (2014) and Van de Velde et al. (2005) in Antarctic ice cores and snow. The temporal similarity of those anthropogenic sources identified in herbarium archives used here and the Antarctic ice cores and snow published elsewhere, provides a better understanding of the pervasive impacts of anthropogenic Pb (*inter alia* other toxic metals) inputs on the Australian environments.

Environmental contaminants preserved in aerosols, sediments, peat bogs, mosses, ice cores and snow have proven to be invaluable for evaluating the temporal trends of atmospheric contamination across the globe. Here we also highlight the value of lichen and fungi samples as global monitors and archives of temporal changes in atmospheric contamination through their wide geographic distribution. Collections of lichen and fungi archives are easier to access, do not require expensive technical instrumentation or costly manpower (Wolterbeek, 2002), when compared to the effort required to use aerosols or cores from sediments, peat bogs, snow or ice. The advantages of using archival moss collections are similar to those of using lichen, as taxa can be selected that are common throughout study areas, they are long lived and have a morphology conductive to chemical analyses (Sloof, 1993). Thus, indirect monitoring methods, such as analysis of moss, lichen and fungi, can provide valuable insights into environmental metal pollution over a very long period of time, accurately documenting major sources of toxic metals and monitoring the relative environmental health of urban, suburban and remote areas.

6.3 Implications of findings

Archival collections of the lichens, *Cladonia* and *Usnea*, and the fungus *Trametes,* dating back more than 150 years from south-eastern and southern Australia, are shown to be effective proxies for mapping and tracing airborne toxic metal pollution. Following European settlement in Australia in 1788, long-term records of environmental metal contamination arising from natural sources and anthropogenic inputs such as mining, smelting, coal

combustion, use of leaded petrol and industrial activities, have been documented in limited naturally occurring environmental archives.

To the best of the author's knowledge, there have been very few pioneer studies carried out in Australia using lichens and fungi as proxies for monitoring short-term atmospheric metal pollution, compared to the equivalent investigations carried out in the northern hemisphere (Ferry et al., 1973; Garty and Ammann, 1987; Loppi and De Dominicis, 1996; Kalač and Svoboda, 2000; Doucet and Carignan, 2001; Bargagli et al., 2002; Carignan et al., 2002; Adamo et al., 2003; Cloquet et al., 2006a; Komárek et al., 2007; Basile et al., 2008; Newbound et al., 2010; Cloquet et al., 2015).

Despite the existence of large collections of historic lichen and fungi preserved in Australian herbaria dating from the 19th century, lichen and fungi archives had not been used previously to document the history of environmental metal pollution. In contrast, northern hemisphere archival lichens have been widely used to identify the changes in levels of atmospheric metal deposition and to chronicle metal pollution history (Keinonen, 1992; Zschau et al., 2003; Purvis et al., 2007; Flegal et al., 2010; Agnan et al., 2013; Minganti et al., 2014; Abdulmanova and Ektova, 2015). Therefore, the studies in this thesis that have utilised herbarium collections of lichen and fungi collected over the past 150 years, go some way to filling the gap in the literature with respect to recording the chronology of metal contamination since the start of base metal mining and the use of leaded petrol in Australia.

In this thesis, specimens of the fungus *Trametes* were found to have higher Cu and Zn enrichment relative to the lichens *Cladonia* and *Usnea*, suggesting that fungi are more sensitive to some metal contaminants than lichens irrespective of where they were collected (e.g. the Greater Sydney area or central and southern Victoria). Combining historic lichen and fungi data with data from other archives, such as aerosols, peat bogs and sediments, can result in valuable, integrated information on the changes in levels of toxic pollutants and their sources in the different environments over time.

In Chapter Four, the toxic metals Pb, Cu and Zn showed greater enrichment (EFs >10) than other metals (e.g. Cr, Fe, Ti), are highly correlated via the use of PCA and CA, and are interpreted to be mainly from anthropogenic sources (e.g. mining and mineral processing, coal combustion, petrol and local industrial emissions). Further, Pb isotopic compositions measured in the lichen and fungi archives confirmed a high proportion of Pb released from a wide variety of anthropogenic inputs dominated by leaded petrol during the period of 1932–

2002 (Chapters Two and Three) (Wu et al., 2016a; Wu et al., 2016b). Analysis of the data using a combination of statistical analysis and isotopic tracers offers a powerful tool for better understanding and detailing temporal shifts atmospheric metal contaminants in urban and remote environments in Australia.

Lead is no longer added to petrol in Australia, but the results from the ash study imply that historic anthropogenic Pb remains persistent in the environment after these Pb sources (e.g. leaded petrol emissions) have been removed. This finding increases awareness of the legacy exposure risks to Pb arising from petrol and industrial emissions follow the extreme wildfire events in Australia. Potential environmental and health risks associated with metal re-release during extreme wildfire events are of increasing concern in the world, due to the frequency and intensity of wildfires are expected to increase as a result of anticipated climate change (Gillett et al., 2004; Lavorel et al., 2007; Marlon et al., 2009). In addition, there is a paucity of scientific research in terms of the association between wildfire smoke and daily mortality in capital cities of Australia (Morgan et al., 2010; Johnston et al., 2011; Roberts, 2013). Therefore, increased remobilisation of Pb (*inter alia* other toxic metals) from wildfire related events and their potential environmental and health exposure risks warrant further study, particular with respect to the safety of fire service personnel who are subject to the greatest exposure (Dobraca et al., 2015).

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CHAPTER 7: CONCLUSIONS

In this chapter, the main conclusions are presented on the applicability of historic collections of the lichens *Cladonia* and *Usnea*, the fungus *Trametes*, as well as wildfire ash residue, as proxies for monitoring toxic metal contamination and its occurrence in the environment.

7.1 Temporal and spatial patterns of trace metal concentrations in environmental samples

During the period from 1850–1931, significantly high concentrations of Cu, Pb and Zn were measured in archival lichen and fungi samples that had been collected in areas of Australia that had a history of mining and heavy industry, such as Lithgow in New South Wales and Mount Macedon in Victoria. Following the introduction of leaded petrol in 1932, Pb from petrol emissions became a major source of atmospheric contamination, characterised by elevated median concentrations and enrichments of Pb and Zn recorded in lichen and fungi collected between 1932 and 1984 and then from 1985 to 2001. Increased median Pb concentrations and high Pb EFs observed in the Greater Sydney area and central and southern Victoria, were consistent with the timing of maximum Pb emissions from leaded petrol consumption in New South Wales and Victoria. Low levels of Pb were measured in lichen and fungi specimens collected in the post-leaded petrol era (after 2002).

In the Greater Sydney area, the lowest median Pb concentration was recorded in herbarium archives collected from woodland and forest-dominated regions of the Blue Mountains. The highest median Pb value in *Cladonia* lichens was recorded in the more densely populated area of South Sydney, while the highest median concentration of *Usnea* lichens was recorded in the heavily urbanized North Sydney region. This suggested that Pb concentrations in lichens can be used as a tool to differentiate undeveloped and more developed areas. In central and southern Victoria, Pb concentrations of herbarium specimens collected between 1939 and 2001 were similar to those collected both from national parks and from urban and suburban areas, inferring that atmospheric Pb sources were distributed uniformly throughout this region during the sampling period.

The study of toxic elements present in wildfire ash has provided an opportunity to evaluate another potential source of Pb contamination in the environment and biogenic recycling of industrial contamination. Median Pb concentrations in most ash residues collected following wildfire events were lower than lithogenic values recorded in local soil and rock. Wildfire ash from Duffys Forest was the exception as Pb concentrations were an order of magnitude higher than the local natural background Pb values for soil and rock. Contamination at the Duffys

Forest site, which is 28 km from the city of Sydney, is likely to be associated with anthropogenic Pb emissions predominantly from the use of leaded petrol.

7.2. Source apportionment for metal contamination

In environmental studies, Pb isotopes are a widely applied and powerful tool for source identification. In this study, Pb isotopic compositions of environmental samples were combined with statistical analysis such as cluster analysis (CA) and principal component analysis (PCA) to identify the sources of atmospheric metal contamination between the four interval periods. These statistical approaches produced results that are consistent with the Pb isotopes and metal concentration data. During the period from 1850 to 1931, the results indicated that lithogenic inputs from crustal processes, early mining and mineral processing, and industrial activities, were all likely to be major sources of metal contamination. Between 1932 and 1984, car-exhaust emissions from the use of leaded petrol and other road transport sources, such as brake lines and tire wear, have been identified as significant contributors of atmospheric Pb emissions to the environment. Despite the introduction of unleaded petrol in 1985, vehicle emissions continued to be the main anthropogenic source of Pb in the atmosphere from 1985 to 2001. After 2002, historic petrol and industrial Pb deposition has been identified as important sources of atmospheric pollution. In Australia, in spite of the cessation of the addition of Pb to petrol in 2002, there is still the potential for former anthropogenic Pb deposits to be re-released into the surrounding environment during wildfire events.

7.3. The validity of lichen, fungi and ash as proxies for monitoring metal contamination

The environmental data collated in this thesis provides further evidence of the value and potential for the use of archival lichens and fungi as invaluable contaminant biomonitors. Data from lichen and fungi specimens, some collected over 150 years ago, demonstrates that they are sensitive to variations in atmospheric levels of toxic metal contaminants. Quantification of Pb concentration in ash provides a better understanding of the assumption that wildfires can remobilise and recycle toxic metals back into the atmosphere and to the environment.

This study has shown that trace metal concentrations recorded in lichen and fungi archives reflect atmospheric metal emissions and depositions and that resulting data reflect that measured in urban air filter archives (in this case, from Sydney and Melbourne). Furthermore,

the results from this thesis are also mirrored in other archives (e.g. peat bogs, seagrasses, sediment cores, ice cores and snow), both from the Australian continent and from Antarctica. Thus, this study has demonstrated the validity of using historical collections of lichens *Cladonia* and *Usnea*, and *Trametes* fungi as suitable proxies for historic trace metal concentrations and trends in atmospheric ecosystems. With respect to ash deposits yielded from wildfires, the data from this thesis supports the contention that wildfires have clear potential to re-release and redistribute to the environment contaminants previously stored in vegetation.

In summary, chronological trends of metal concentrations determined in lichens, fungi and wildfire ash, followed broadly the pattern of rise and fall in the use of leaded petrol in Australia. Four main periods were identified in this thesis: 1) pre-leaded petrol era, from 1850–1931, when early mining and metal processing was just getting under way Australia; 2) main leaded petrol era, from 1932–1984, particularly the decades when Pb was added to petrol; 3) the introduction of unleaded petrol from 1985–2001, a period of decreasing impact of leaded petrol when the practice of adding lead to petrol was phased out; and 4) a post-leaded petrol era, from 2002 to the present, following the cessation of use of leaded petrol in 2002.

The studies encompassed by this thesis suggest that the potential threat from ongoing exposure to sources of metal contamination, such as active mines and industry, as well as historic industrial deposition, persists in the environment. Given that there are still no established lower safe levels for many toxic metals, this thesis also highlights the need for continued investigation into the history of metal contamination and its effect on environmental systems and human health, commencing with the period of early industrialisation and urbanisation in Australia, and continuing to the present and ongoing emissions from mining, smelting, and local industry on both environmental systems and human health.

APPENDICES

Appendix A: Supplementary Information for Chapter Two

Supplementary Table S1

Supplementary References

Appendix B: Supplementary Information for Chapter Three

Supplementary Table S1

Supplementary Table S2

Supplementary Table S3

Supplementary Table S4

Supplementary Table S5

Supplementary References

Appendix C: Supplementary Information for Chapter Four

Supplementary Table S1

Supplementary Table S2

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Supplementary Table S6

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Supplementary Table S8

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Supplementary Table S11

Supplementary Table S12

Supplementary Table S13

Appendix D: Supplementary Information for Chapter Five

Supplementary Table S1
Supplementary Figure S1
Supplementary Table S2
Supplementary References

Appendix E: Additional research undertaken during PhD candidature.

Published research article – Harvey, P. J., M. P. Taylor, L. J. Kristensen, S. Grant-Vest, M. Rouillon, **L. Wu,** and H. K. Handley. 2015. Evaluation and assessment of the efficacy of an abatement strategy in a former lead smelter community, Boolaroo, Australia, *Environmental Geochemistry and Health*, DOI: 10.1007/s10653-015-9779-8.

This article is included in the supplementary section of the thesis because it represents part of the outputs from my postgraduate research training at the Department of Environmental Sciences, Macquarie University. The issue examined in the article addresses historic lead contamination from smelter operations. It is relevant to the broader question of environmental contamination examined within the body of this thesis. My contribution to the completion of the study included laboratory analysis and evaluation of the data, plus contributions to the writing of the article.

Appendix A: Supplementary Information for Chapter Two

Supplementary Table S1. Lead isotope ratios of important emission sources.

Sample type	Sample [no.]	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	References
Australian ore deposits	Broken Hill	16.00	1.040	2.310	(Townsend et al., 1998)
	Broken Hill	16.00	1.040	2.317	(Chiaradia et al., 1997)
	Broken Hill	16.00	1.039	2.316	(Cooper et al., 1969)
	Mount Isa	16.12	1.043	2.320	(Cumming and Richards, 1975)
	Mount Isa	16.11	1.043	2.318	(Gulson, 1985)
Sydney air filters (AF)	AF 1978 (6)		1.084 ± 0.011 (1.076-1.103)	2.359 ± 0.010 (2.352-2.375)	this study
	AF 1979 (12)		1.111 ± 0.019 (1.086-1.145)	2.382 ± 0.016 (2.363-2.415)	this study
	AF 1980 (12)		1.148 ± 0.013 (1.128-1.164)	2.410 ± 0.010 (2.393-2.428)	this study
	AF 1981 (12)		1.113 ± 0.026 (1.081-1.146)	2.375 ± 0.017 (2.354-2.396)	this study
	AF 1983 (5)		1.074 ± 0.001 (1.073-1.075)	2.346 ± 0.003 (2.342-2.349)	this study
	AF 1987 (11)		1.074 ± 0.004 (1.070-1.082)	2.351 ± 0.003 (2.347-2.356)	this study
	AF 1991 (12)		1.081 ± 0.003 (1.076-1.086)	2.349 ± 0.004 (2.343-2.358)	this study
	AF 1992 (12)		1.077 ± 0.005 (1.067-1.083)	2.351 ± 0.005 (2.338-2.356)	this study
	AF 1993 (11)		1.067 ± 0.002 (1.064-1.071)	2.341 ± 0.003 (2.336-2.345)	this study
	AF 1994 (11)		1.067 ± 0.003 (1.063-1.071)	2.341 ± 0.003 (2.337-2.347)	this study
	AF 1995 (15)		1.070 ± 0.003 (1.067-1.079)	2.348 ± 0.005 (2.342-2.358)	this study
	AF 1996 (6)		1.084 ± 0.001 (1.083-1.086)	2.360 ± 0.004 (2.353-2.365)	this study
	AF 1997 (4)		1.098 ± 0.002 (1.096-1.100)	2.366 ± 0.004 (2.362-2.371)	this study
	AF 1998 (12)		1.107 ± 0.008 (1.096-1.119)	2.374 ± 0.010 (2.358-2.390)	this study
	AF 1999 (2)		1.089 ± 0.037 (1.063-1.114)	2.363 ± 0.031 (2.341-2.384)	this study
	AF 2000 (9)		1.108 ± 0.011 (1.096-1.124)	2.375 ± 0.011 (2.362-2.392)	this study
	AF 2001 (11)		1.136 ± 0.018 (1.120-1.184)	2.399 ± 0.011 (2.387-2.427)	this study
	AF 2002 (12)		1.132 ± 0.007 (1.118-1.140)	2.407 ± 0.009 (2.395-2.422)	this study
	AF 2003 (12)		1.115 ± 0.014 (1.088-1.132)	2.399 ± 0.015 (2.371-2.418)	this study
	AF 2004 (6)		1.111 ± 0.007 (1.098-1.116)	2.398 ± 0.008 (2.385-2.408)	this study

Sydney leaded petrol	Petrol 1978	16.70	1.081	2.353	(Gulson et al., 1983)
	Petrol 1979	17.24	1.113	2.383	(Gulson et al., 1983)
	Petrol 1980	18.63	1.193	2.440	(Gulson et al., 1983)
	Petrol 1981	17.65	1.138	2.392	(Gulson et al., 1983)
	Petrol 1991	16.66	1.077	2.348	Gulson, personal communication
	Petrol 1992	16.51	1.067	2.339	Gulson, personal communication
	Petrol 1993	16.42	1.061	2.334	Gulson, personal communication
	Petrol 1994	16.38	1.059	2.333	Gulson, personal communication
	Petrol 1995	16.52	1.067	2.340	Gulson, personal communication
	Petrol 1996	16.85	1.086	2.362	Gulson, personal communication
	Petrol 1997	17.05	1.110	2.371	Gulson, personal communication
	Petrol 1998	17.54	1.127	2.383	Gulson, personal communication
	Petrol 1999	17.35	1.115	2.376	Gulson, personal communication
Australian Coal	Coal 1		1.2057	2.4865	(Díaz-Somoano et al., 2009)
	Coal 2		1.2053	2.4867	(Díaz-Somoano et al., 2009)

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Appendix B: Supplementary Information for Chapter Three

Supplementary Table S1. Lead concentrations (mg/kg) and isotopic compositions of *Cladonia* lichens collected between 1885 and 2006.

ID	Year	Species	Coordinates (decimal)		Locations	Pb	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
1	1885	*Cladonia sulcata*	-37.38 S	144.57 E	Mount Macedon	439	18.4	1.178	2.462
2	1886	*Cladonia capitellata*	-37.40 S	144.95 E	Mount Macedon	216	18.3	1.175	2.458
3	1887	*Cladonia enantia*	-37.90 S	144.12 E	Oakleigh	3.0	17.6	1.171	2.462
4	1888	*Cladonia fimbriata*	-37.38 S	144.57 E	Mount Macedon	11	17.4	1.164	2.450
5	1889	*Cladonia squamosa*	-37.37 S	144.57 E	Mount Macedon	3.2	18.0	1.151	2.429
6	1934	*Cladonia sp*	-37.92 S	145.42 E	Cardinia Creek, near Clematis	3.9	17.0	1.095	2.373
7	1940	*Cladonia fimbriata*	-37.87 S	145.37 E	Hardy's Gully, Kallista	11	17.2	1.104	2.386
8	1953	*Cladonia squamosa*	-37.87 S	145.35 E	Sherbrooke Forest, Kallista. Below Coles Ridge	2.7	16.7	1.082	2.356
9	1954	*Cladonia fimbriata*	-37.75 S	145.35 E	Lilydale	25	16.7	1.083	2.356
10	1955	*Cladonia P. Browne*	-37.80 S	144.22 E	Brisbane Ranges, Reilly's Creek Gorge	2.6	17.0	1.095	2.366
11	1957	*Cladonia macilenta*	-37.77 S	145.25 E	North Ringwood	7.2	16.7	1.077	2.362
12	1959	*Cladonia fimbriata*	-37.62 S	145.70 E	On the lower slopes of Mount Vinegar	4.8	16.5	1.076	2.350
13	1960	*Cladonia sp*	-37.43 S	144.40 E	Blackwood Ranges	2.6	16.6	1.078	2.358
14	1961	*Cladonia gracilis*	-37.85 S	144.17 E	Brisbane Ranges	1.3	16.6	1.080	2.360
15	1963	*Cladonia P. Browne*	-37.77 S	144.10 E	Moorabool River 3 km SW Eggerton	1.8	16.5	1.067	2.340
16	1964	*Cladonia pleurota*	-37.57 S	144.40 E	Lerderderg River	7.6	16.3	1.061	2.341
17	1965	*Cladonia P. Browne*	-37.52 S	144.07 E	Moorabool Reservoir	6.3	16.9	1.089	2.368
18	1967	*Cladonia staufferi*	-37.27 S	145.02 E	Spion Kopje 0.8 km W of Mount Nelse North	2.6	17.5	1.125	2.403
19	1968	*Cladonia P. Browne*	-37.97 S	144.50 E	Brisbane Ranges, Little River, Reilley's Creek Gorge	6.0	17.6	1.130	2.427
20	1969	*Cladonia P. Browne*	-37.27 S	144.40 E	Lauriston Reservoir, Macedon Ranges	1.9	16.9	1.098	2.378
21	1970	*Cladonia pertricosa*	-37.37 S	144.60 E	Camels Hump, Mount Macedon	6.7	16.8	1.087	2.363
22	1971	*Cladonia P. Browne*	-37.82 S	144.23 E	24 km SW of Bacchus Marsh, Brisbane Ranges	1.5	17.0	1.098	2.381
23	1972	*Cladonia sp*	-37.95 S	144.41 E	Victoria, You Yangs	11	17.0	1.098	2.383
24	1974	*Cladonia P. Browne*	-37.55 S	144.37 E	Near Mount Blackwood	3.6	17.3	1.115	2.389
25	1976	*Cladonia sp*	-37.95 S	144.42 E	You Yangs. N and NE of Branding Yard Hill	7.3	17.3	1.116	2.389
26	1978	*Cladonia P. Browne*	-37.97 S	144.50 E	Brisbane Ranges in vicinity of Little River Picnic Area	14	17.2	1.112	2.382
27	1981	*Cladonia fimbriata*	-37.45 S	144.60 E	Mount Macedon - Wooden Road	5.0	17.6	1.126	2.393
28	1982	*Cladonia sp*	-37.73 S	145.26 E	Jumping Creek National Park, Warrandyte	13	17.2	1.106	2.377

29	1985	*Cladonia floerkeana*	-37.82 S	145.23 E	Antonio Park, Ringwood, 23 km W of Melbourne	70	16.9	1.092	2.366
30	1986	*Cladonia P. Browne*	-37.82 S	144.28 E	Brisbane Ranges National Park.	1.9	16.6	1.083	2.362
31	1993	*Cladonia enantia*	-38.45 S	144.12 E	Ironbark Gorge, Bambra Rd, Aireys Inlet, Anglesea	3.5	17.5	1.129	2.413
32	1994	*Cladonia ramulosa*	-37.42 S	145.70 E	3 km SSW of Buxton, Buxton Silver Gum Reserve	3.1	16.7	1.085	2.354
33	1995*	*Cladonia ochrochlora*	-37.41 S	144.36 E	South of Blackwood, Trentham	4.8	16.9	1.087	2.365
34	1996	*Cladonia fimbriata*	-37.73 S	145.67 E	One Tree Hill (Mount Donna Buang excursion)	18	17.1	1.099	2.373
35	1997	*Cladonia humilis*	-37.39 S	144.25 E	Wombat State Forest, Babbington Hill	0.8	17.2	1.102	2.379
36	1998	*Cladonia furcata*	-37.33 S	144.67 E	Brock Monument, Woodend-Wallen Road	2.0	16.9	1.092	2.362
37	2000	*Cladonia humilis*	-37.68 S	144.31 E	Parwan Valley, White Elephant Reserve	0.5	17.5	1.135	2.407
38	2001	*Cladonia P. Browne*	-37.70 S	144.32 E	Parwan Valley, White Elephant Reserve	0.7	17.4	1.112	2.381
39	2002	*Cladonia rigida*	-37.35 S	144.67 E	Black Range, 5 km W of Romsey	0.8	17.4	1.101	2.377
40	2005	*Cladonia scabriuscula*	-37.47 S	144.28 E	Wombat State Forest, New Sultan Mine Track	0.4	17.8	1.147	2.443
41	2006	*Cladonia confusa*	-37.33 S	144.12 E	1-1.2 km S from Bryces Flat picnic ground and carpark	0.2	18.0	1.140	2.384

Sample marked with (*) was processed eight times—see text for discussion.

Supplementary Table S2. Lead concentrations (mg/kg) and isotopic compositions of archived *Usnea* lichens collected between 1900 and 2008.

ID	Year	Species	Coordinates (decimal)		Locations	Pb	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
1	1900	*Usnea scabrida*	-37.37 S	144.57 E	Mount Macedon	36	17.7	1.143	2.418
2	1940	*Usnea scabrida*	-37.87 S	145.30 E	Ferntree Gully	15	16.8	1.088	2.377
3	1944	*Usnea scabrida*	-37.35 S	144.15 E	Daylesford	16	16.9	1.092	2.374
4	1961	*Usnea scabrida*	-37.47 S	144.50 E	Bullengarook	11	16.2	1.048	2.324
5	1963	*Usnea meridionalis*	-37.92 S	144.12 E	Moorabool River	5.0	16.7	1.079	2.356
6	1966	*Usnea scabrida*	-37.38 S	144.57 E	Mount Macedon, 4.8 km along Woodend Road	24	16.6	1.074	2.352
7	1967	*Usnea*	-37.37 S	144.58 E	Camels Hump, Mount Macedon	17	16.7	1.080	2.353
8	1968	*Usnea scabrida*	-37.37 S	145.75 E	Cooks Mill on eastern side of the Cathedral Range	9.8	16.8	1.088	2.366
9	1971	*Usnea inermis*	-37.77 S	144.27 E	Brisbane Ranges, about 24 km SW of Bacchus Marsh	4.8	16.9	1.091	2.377
10	1975	*Usnea baileyi*	-37.07 S	145.08 E	Eastern foothills of Pine Mountain, 12 km SE of Walwa	9.7	17.2	1.110	2.384
11	1977	*Usnea*	-37.35 S	144.12 E	Western highlands, Daylesford, Caravan Park - Victoria Park	21	17.4	1.116	2.386
12	1980	*Usnea scabrida*	-37.67 S	145.52 E	Coranderrk Bushland Reserve, 4 km SSE of Healesville	42	17.1	1.101	2.373
13	1981	*Usnea*	-37.37 S	144.57 E	Mount Macedon, 5 km SE of Woodend	58	17.7	1.133	2.395
14	1983	*Usnea*	-37.38 S	145.37 E	Two Mile Creek, Glenburn-Flowerdale Road, 21 km SSW of Yea	18	17.1	1.098	2.373
15	1984	*Usnea*	-37.38 S	144.30 E	Daylesford-Trentham via Domino Road, 5 km WSW of Trentham	86	16.7	1.077	2.354
16	1986	*Usnea*	-37.70 S	145.67 E	Mount Donna Buang, 5 km NNW of Warburton	20	16.8	1.080	2.352
17	1993	*Usnea*	-37.50 S	144.57 E	E side of Mount Gisborne Road, at `Windrush' (Millar property)	26	16.9	1.084	2.355
18	1994	*Usnea molliuscula*	-37.52 S	145.87 E	Lake Mountain Alpine Reserve	7.1	16.8	1.086	2.358
19	1996	*Usnea subalpina*	-38.22 S	144.36 E	Observation Road, Armstrong Creek Catchment, O'shannessy	1.4	16.9	1.102	2.377
20	1997	*Usnea molliuscula*	-37.06 S	144.21 E	Summit of Mount Alexander, Castlemaine	3.0	17.2	1.126	2.398
21	1999	*Usnea dasaea*	-37.32 S	144.11 E	SW of Hepburn, Tipperary Track, S of Bryces Flat	1.9	16.7	1.089	2.356
22	2001	*Usnea*	-37.56 S	145.88 E	Yarra Ranges National Park, Cumberland Scenic Reserve	0.7	16.9	1.094	2.363
23	2006	*Usnea scabrida*	-37.66 S	144.51 E	Long Forest Nature Conservation Reserve, Bermagui Track Djerriwarrh	1.3	17.3	1.115	2.386
24	2008	*Usnea subeciliata*	-37.48 S	145.82 E	Yarra Ranges National Park	0.4	17.6	1.135	2.402

Supplementary Table S3. Lead concentrations (mg/kg) and isotopic compositions of archived *Trametes* fungi collected between 1852 and 2006.

ID	Year/Month	Species	Coordinates (decimal)		Locations	Pb	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
1	1852	*Trametes versicolor*	-37.50 S	145.00 E	Port Phillip	14	17.7	1.180	2.463
2	1932	*Trametes ochracea*	-37.92 S	145.35 E	Belgrave	3.2	17.0	1.096	2.381
3	1939	*Trametes versicolor*	-37.82 S	144.92 E	Pole Yard, Fishermans Bend	15	17.0	1.098	2.374
4	1947Mar	*Trametes versicolor*	-37.93 S	145.45 E	Emerald	10	16.6	1.071	2.346
5	1947Aug	*Trametes velutina*	-37.67 S	145.73 E	Acheron Way	1.9	16.6	1.080	2.359
6	1949	*Trametes ochracea*	-37.70 S	145.72 E	Cement Creek	7.7	16.9	1.086	2.364
7	1951	*Trametes ochracea*	-37.47 S	144.32 E	Blackwood	2.3	16.6	1.074	2.356
8	1953May	*Trametes ochracea*	-37.80 S	145.32 E	Kilsyth	2.3	16.6	1.073	2.349
9	1953Aug	*Trametes velutina*	-37.77 S	144.95 E	Royal Park, Melbourne	5.2	16.8	1.083	2.364
10	1954	*Trametes ochracea*	-37.92 S	145.45 E	Emerald Lake	3.3	16.6	1.076	2.355
11	1957	*Trametes velutina*	-37.82 S	145.02 E	Glenferrie	24	16.6	1.076	2.353
12	1958	*Trametes versicolor*	-37.92 S	145.12 E	Clayton	8.8	16.6	1.075	2.360
13	1959	*Trametes ochracea*	-37.82 S	145.12 E	Box Hill	7.2	16.6	1.076	2.353
14	1960	*Trametes ochracea*	-37.87 S	145.02 E	Caulfield	18	16.2	1.052	2.327
15	1962Jun	*Trametes ochracea*	-37.87 S	145.78 E	Powelltown, Mackley's (Mackley Creek) Road	0.7	16.8	1.090	2.372
16	1962Jul	*Trametes lactinea*	-37.85 S	145.47 E	Woori Yallock, near Warburton Rd bridge	4.2	17.1	1.104	2.384
17	1963	*Trametes ochracea*	-37.82 S	144.95 E	Ingles St store, South Melbourne	23	16.9	1.097	2.378
18	1964	*Trametes versicolor*	-37.83 S	144.98 E	Melbourne, suburb of South Yarra, Royal Botanic Gardens	8.0	16.7	1.082	2.365
19	1967	*Trametes velutina*	-37.82 S	144.97 E	Flinders Lane, Melbourne city	19	16.7	1.085	2.365
20	1969	*Trametes versicolor*	-37.87 S	145.35 E	Sherbrooke Forest,Kallista	2.0	16.8	1.093	2.375
21	1974	*Trametes ochracea*	-37.92 S	145.00 E	East Brighton	4.9	17.2	1.115	2.378
22	1975	*Trametes versicolor*	-37.67 S	145.73 E	Acheron Way	1.8	16.9	1.093	2.368
23	1976Jul	*Trametes versicolor*	-37.92 S	145.33 E	Ferntree Gully National Park, Dandenong Ranges	0.5	17.4	1.108	2.382
24	1976Nov	*Trametes hirsuta*	-37.65 S	145.53 E	Sir Colin MacKenzie Wildlife Sanctuary, Badger Creek	1.3	17.0	1.105	2.376
25	1978	*Trametes ochracea*	-37.70 S	145.73 E	Cement Creek, 5 km N of Warburton	1.6	17.3	1.121	2.388
26	1980	*Trametes hirsuta*	-37.99 S	145.04 E	Port Phillip Bay, suburb of Beaumaris	3.4	17.4	1.122	2.389
27	1994	*Trametes versicolor*	-37.80 S	145.02 E	Melbourne, Yarra Bend	3.0	16.8	1.085	2.363
28	1995	*Trametes Fr.*	-37.84 S	145.10 E	Wattle Park	1.6	16.8	1.086	2.361
29	1996Jul	*Trametes versicolor*	-37.82 S	144.97 E	Melbourne, South Yarra, Royal Botanic Gardens	2.0	17.7	1.135	2.401
30	1996Jul	*Trametes versicolor*	-37.72 S	145.15 E	Melbourne, outer suburb of Eltham, private houseblock	5.0	17.2	1.103	2.384
31	1999	*Trametes versicolor*	-37.50 S	145.25 E	Kinglake National Park, Lyrebird Circuit Walk	0.2	17.4	1.104	2.378
32	2006	*Trametes hirsuta*	-37.99 S	145.05 E	Beaumaris, foreshore reserve	0.7	16.7	1.086	2.355

Supplementary Table S4. Lead concentrations (mg/kg) and isotopic compositions of river surface sediments, surface soils and deep soil.

Sample ID	Coordinates (decimal)		Locations	Pb	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
MEL_Sediment_1	-37.73 S	145.64 E	Yarra Ranges National Park	14	18.8	1.185	2.472
MEL_Sediment_2	-37.73 S	145.64 E	Yarra Ranges National Park	12	18.8	1.192	2.477
MEL_Sediment_3	-37.83 S	145.38 E	Dandenong Ranges National Park	23	18.3	1.167	2.457
MEL_Sediment_4	-37.83 S	145.38 E	Dandenong Ranges National Park	20	18.2	1.167	2.455
MEL_Soil_1_0-2	-37.63 S	145.78 E	Yarra Ranges National Park	13	17.8	1.139	2.420
MEL_Soil_2_0-2	-37.59 S	145.85 E	Yarra Ranges National Park	18	17.9	1.147	2.420
MEL_Soil_3_0-2	-37.73 S	145.64 E	Yarra Ranges National Park	21	18.3	1.172	2.461
MEL_Soil_4_0-2	-37.73 S	145.64 E	Yarra Ranges National Park	32	17.5	1.131	2.414
MEL_Soil_5_0-2	-37.83 S	145.38 E	Dandenong Ranges National Park	300	17.7	1.139	2.420
MEL_Soil_6_0-2	-37.83 S	145.38 E	Dandenong Ranges National Park	31	17.8	1.136	2.422
MEL_Soil_2_40-50	-37.59 S	145.85 E	Yarra Ranges National Park	8.4	19.1	1.216	2.497

Supplementary Table S5. Lead isotopic compositions of relevant sources.

Sample types	Samples	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	References
Major Australian ore deposits	Broken Hill	1.041	2.315	(Gulson, 1984)
	Broken Hill	1.039	2.316	(Gulson, 1984)
	Mount Isa	1.043	2.318	(Gulson, 1985)
Melbourne aerosols	1994	1.0676	2.3416	(Bollhöfer and Rosman, 2002)
	1994	1.0681	2.3448	
	1994	1.0671	2.3524	
	1995	1.0692	2.3389	
	1995	1.0714	2.3445	
	1995	1.0716	2.3420	
	1998	1.1022	2.3688	
	1998	1.0994	2.3680	
	1998	1.0997	2.3683	
	1998	1.0904	2.3683	
	1998	1.0963	2.3730	
	1998	1.1008	2.3681	
Wattle Gully distal slates	B389 WR	1.206	2.508	Unpublished data relates to
	B390 WR	1.181	2.476	
	B391 WR	1.214	2.516	(Gulson et al., 1988)
	B392 WR	1.210	2.508	
	B393 WR	1.223	2.519	
	B389 WR	1.205	2.507	
Bendigo and Ballarat galena	C481 Gn	1.153	2.434	Unpublished data relates to
	C489 Gn	1.152	2.438	
	C488 Gn	1.152	2.437	(Gulson et al., 1988)
	C487 Gn	1.151	2.433	
	C486 Gn	1.150	2.434	
	C507 Gn	1.153	2.436	
	C485 Gn	1.152	2.434	
	C484 Gn	1.153	2.435	
	C482 Gn	1.153	2.435	
	C483 Gn	1.152	2.434	
Sydney lead petrol	1991	1.077	2.348	(Wu et al., 2016)
	1992	1.067	2.339	
	1993	1.061	2.334	
	1994	1.059	2.333	
	1995	1.067	2.340	
	1996	1.086	2.362	
	1997	1.110	2.371	
	1998	1.127	2.383	
	1999	1.115	2.376	
Sydney air filters	1991	1.081	2.349	(Wu et al., 2016)
	1992	1.077	2.351	
	1993	1.067	2.341	
	1994	1.067	2.341	
	1995	1.070	2.348	
	1996	1.084	2.360	
	1997	1.098	2.366	
	1998	1.107	2.374	
	1999	1.089	2.363	

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Appendix C: Supplementary Information for Chapter Four

Supplementary Table S1. Trace metal concentrations of *Cladonia* lichens collected from the Greater Sydney area between 1885 and 2009.

Year	Species	Locations	Al	Fe	Ti	Cr	Cu	Ni	Zn	Pb[a]
1885	*C. furcata*	Ross Cave, Mt Victoria	160	155	6	0.35	1.4	0.29	59	7
1894	*C. cervicornis*	Eastern Creek, Near Blacktown	863	961	16	0.99	2.8	0.74	25	5
1897	*C. fimbriata*	Lithgow	225	239	6	0.25	96	0.43	16	32
1898	*C. floerkeana*	Penshurst	1470	1683	26	1.47	4.6	0.69	31	7
1899	*C. floerkeana*	Sydney	203	373	10	0.31	1.6	0.15	11	10
1900	*C. floerkeana*	Randwick	564	678	38	0.48	5.5	0.31	19	27
1902	*C. floerkeana*	Hurstville	550	491	27	0.53	2.8	0.28	15	10
1903	*C. fimbriata*	Oatley	426	454	22	0.41	3.9	0.36	18	14
1906	*C. pertricosa*	Gladesville	541	574	28	0.58	3.0	0.34	18	8
1907	*C. humilis*	Gladesville	785	1001	45	0.99	4.2	0.70	24	13
1908	*C. fimbriata*	Wahroonga, near Sydney	1290	1271	31	1.31	4.1	0.66	18	20
1909	*C. furcata*	Near Manly, Sydney	969	1589	35	1.61	4.8	0.74	39	17
1910	*C. fimbriata*	Penshurst.	1633	2936	80	2.02	6.6	0.96	16	79
1911	*C. sulcata*	Gladesville	4104	4746	87	4.57	16	3.43	266	6
1914	*C. pertricosa*	Balmoral, Sydney	984	1419	58	1.34	6.8	0.91	21	19
1971	*Cladonia*	23 km N of Sydney	477	511	22	0.47	2.0	0.43	21	21
1974	*C. sp*	Bradley's Head, Sydney	148	221	10	0.06	2.2	0.29	16	19
1977	*C. ramulosa*	Jamieson Valley, Blue Mtns	151	52	6	0.64	0.8	0.12	13	4
1978	*C. cervicornis*	Old Great Northern Rd	258	608	6	0.31	1.2	0.31	9	26
1980	*C. kuringaiensis*	Grosvenor Track	468	878	17	0.83	4.7	0.89	47	55
1981	*C. floerkeana*	Near McCarrs Creek	304	248	10	0.16	2.1	0.19	10	10
1982	*C. furcata*	Epping, near Devlins Creek	526	681	27	1.27	5.4	1.09	32	73
1983	*C. praetermissa*	Towler Bay. 30 km N of Sydney	775	639	12	0.78	3.3	0.69	24	42
1984	*C. sulcata*	Mona Vale Rd, 18 km N of Sydney	337	363	22	0.31	2.0	0.40	35	16
1985Feb	*C. kuringaiensis*	Glaston Gorge near Sydney	204	187	11	0.16	1.3	0.25	10	25
1985Mar	*C. floerkeana*	Yeoman's Bay	731	642	32	0.53	2.0	0.22	8	17
1985July	*C. pertricosa*	Erskine Creek, Blue Mtns	109	109	5	bdl	1.1	0.17	8	15
1986	*C. fruticulosa*	Toby`s Glen, Blue Mtns	1463	1032	22	1.63	1.8	0.81	9	18
1987Mar	*C. floerkeana*	Jenolan Caves, Blue Mtns	1095	782	28	0.94	3.3	0.47	18	3
1987Sep	*C. sulcata*	Hazelbrook, Blue Mtns	132	233	4	0.09	1.3	0.09	12	4
1988	*C. floerkeana*	Terrey Hills	141	162	5	0.06	1.3	0.10	9	5
1989	*C. cervicornis*	Hazelbrook, Blue Mtns	433	427	8	0.39	1.9	0.50	18	7
1990	*C. ochrochlora*	Bradleys Head	305	597	16	0.39	3.0	2.59	15	41
1991	*C. praetermissa*	Macquarie University	1267	1411	59	1.65	7.1	1.51	62	106
1992	*C. ochrochlora*	Lane Cove National Park	272	269	9	0.30	1.4	0.35	13	30
1993	*C. praetermissa*	Macquarie University	2304	3055	24	2.50	3.2	1.62	12	38
1995	*C. cerricornis*	Dyarrabin Nature Reserve	307	292	10	0.30	1.4	0.21	10	12
1996	*C. furcata*	Smith Park, East Hills	559	763	12	0.83	3.3	0.62	27	30
1997	*C. praetermissa*	Terrys Creek	308	462	13	0.54	8.5	1.24	85	43
1998	*C. floerkeana*	West Pennant Hills, Palm Gully	343	491	18	0.34	2.0	0.36	8	19
1999	*C. floerkeana*	Pennant Hills Park, Cheltenham	134	139	3	0.07	1.5	0.11	10	3
2000	*C. furcata*	Lyrebird Gully track, Mt Kuring-gai	227	413	6	0.41	1.7	0.48	12	5
2001	*C. praetermissa*	Near Maroubra Beach	440	1577	9	2.09	8.1	0.81	27	570
2002	*C. corniculata*	Rickards Road, SW of Richmond	272	346	11	0.39	1.4	0.26	13	4
2003	*C. celata*	Oatley West	1968	2118	114	1.03	5.6	1.28	17	22
2009*	*C. chlorophaea*	East of Pitt Town	1981	5791	55	4.70	6.6	2.50	56	3

Sample marked with (*) was processed eight times.

[a] Pb concentrations are taken from Wu et al. (2016b).

bdl = below detection limit

Supplementary Table S2. Trace metal concentrations of *Usnea* lichens collected from the Greater Sydney area between 1902 and 2010.

Year	Species	Locations	Al	Fe	Ti	Cr	Cu	Ni	Zn	Pb[a]
1902	*Usnea*	Pine Ridge, Liverpool	652	666	12	1.20	1.5	0.69	4	6
1903	*U.baileyi*	Toongabbie	343	272	10	0.90	1.7	0.24	6	10
1906	*Usnea*	Nepean and Warragamba Rivers	286	707	4	0.80	1.6	0.83	13	9
1907	*Usnea*	Nepean and Warragamba Rivers	286	411	4	0.80	5.0	0.93	23	30
1908	*Usnea*	Parramatta	332	364	11	1.00	3.1	0.46	20	16
1910	*Usnea*	Ermington	289	585	13	1.40	10.3	1.27	69	88
1917	*Usnea*	Castle Hill	114	182	2	0.40	0.9	0.17	4	20
1951	*U. angulata*	Blue Mtns	193	94	11	0.90	1.1	0.24	8	7
1963	*U. molliuscula*	Royal National Parks near Port Hacking	280	350	9	0.60	1.6	0.60	21	24
1965	*Usnea*	37 km S of Milbrodale	241	793	9	0.80	1.1	2.00	29	48
1972	*Usnea*	Mount Irvine	127	191	4	0.80	4.9	0.45	27	28
1977	*Usnea*	Jamieson Valley, below Katoomba Falls	189	300	8	1.00	1.7	0.58	17	28
1978	*Usnea*	Mount Bouddi, Bouddi National Park	182	265	7	1.10	1.2	0.69	23	45
1984Nov	*Usnea*	25 km NNE of Katoomba	191	113	9	1.00	1.4	0.22	11	31
1984Nov	*Usnea*	Zig-Zag Road, Mount Wilson	103	165	8	1.40	1.2	0.36	15	181
1988	*Usnea*	Mount Wilson, Blue Mtns	120	86	9	1.00	1.6	0.18	12	8
1989	*Usnea*	Ku Ring Gai Chase National Park	240	211	6	1.10	1.8	0.20	8	18
1990	*Usnea*	Brooklyn, Long Island Nature Reserve	151	286	6	0.90	6.6	0.59	26	42
1991	*U. inermis*	12 km E of Cullen Bullen	83	81	3	0.60	0.8	0.22	8	6
1996	*Usnea*	Wentworth Falls	190	246	4	0.80	2.0	0.50	15	18
1997	*U. sp*	North Rocks, Lomatia Creek	95	189	2	0.80	2.6	1.05	31	22
2000	*Usnea*	Centennial Glen, Blackheath	172	194	4	0.70	1.1	0.43	6	1
2002	*U. undulata*	Grand Canyon track, Blackheath	281	160	2	0.60	1.8	0.21	15	3
2009	*Usnea*	Blue Mountains National Park	122	115	5	0.80	1.2	0.22	8	2
2010	*Usnea*	Mitchell Park, Cattai National Park	354	267	12	1.50	1.9	0.13	6	1

[a] Pb concentrations are taken from Wu et al. (2016b).

Supplementary Table S3. Trace metal concentrations of *Trametes* fungi collected from the Greater Sydney area between 1924 and 1988.

Year	Species	Locations	Al	Fe	Ti	Cr	Cu	Ni	Zn	Pb[a]
1924	*T. versicolor*	Fairfield, Canley Vale	122	192	7	0.32	3.7	0.19	51	2
1926	*Trametes*	Mount Wilson	27	40	5	0.17	1.8	0.08	7	2
1939	*T. versicolor*	Hazelbrook and Bullaburra Glen, Blue Mtns	61	43	4	0.22	2.5	0.17	8	3
1951	*T. lactinea*	Royal Botanic Gardens, Sydney	104	106	9	0.48	9.9	0.60	29	7
1953	*T. lactinea*	North Ryde, Sydney	353	189	10	3.04	75	1.37	68	17
1955	*T. lactinea*	Royal Botanic Gardens, Sydney	20	56	3	0.19	1.7	0.61	12	1
1956	*T. ochracea*	Beaconsfield, Alexandria	91	105	8	0.23	4.2	0.36	17	1
1982	*T. versicolor*	Mount Tomah, Blue Mtns	43	67	7	0.13	5.9	0.11	27	1
1983	*T. hirsuta*	10.4 km NNW of Yarramalong Public School	97	41	10	0.12	2.8	0.11	21	4
1988	*T. versicolor*	Mount Wilson, 17 km NE of Mount Victoria	54	26	6	0.06	2.6	0.04	10	0.5

[a] Pb concentrations are taken from Wu et al. (2016b).

Supplementary Table S4. Trace metal concentrations of *Cladonia* lichens collected from central and southern Victoria between 1885 and 2006.

Year	Species	Locations	Al	Fe	Ti	Cr	Cu	Ni	Zn	Pb[b]
1885	*C. sulcata*	Mount Macedon	1914	1429	54	0.96	6.3	0.45	33	439
1886	*C. capitellata*	Mount Macedon	215	201	6	0.67	1.4	0.19	201	216
1889	*C. squamosa*	Mount Macedon	424	303	9	1.06	3.2	0.53	6	3
1934	*C. sp*	Cardinia Creek, near Clematis	2318	2046	39	2.51	2.4	1.38	15	4
1940	*C. fimbriata*	Hardy's Gully, Kallista	1859	1497	46	2.26	7.6	1.23	21	11
1953	*C. squamosa*	Sherbrooke Forest, Kallista. Below Coles Ridge	247	197	6	0.69	1.5	0.24	8	3
1954	*C. fimbriata*	Lilydale	987	1018	16	1.40	2.7	0.88	125	25
1955	*Cladonia*	Brisbane Ranges, Reilly's Creek Gorge	448	392	7	1.62	1.5	1.15	12	3
1957	*C. macilenta*	North Ringwood	489	426	8	0.94	12	0.42	73	7
1959	*C. fimbriata*	On the lower slopes of Mount Vinegar	286	228	6	0.62	1.9	0.20	12	5
1960	*C. sp*	Blackwood Ranges	212	212	5	0.61	1.6	0.34	6	3
1961	*C. gracilis*	Brisbane Ranges	61	61	3	0.47	1.1	0.24	7	1
1963	*Cladonia*	Moorabool River 3 km SW Eggerton	170	125	6	0.56	4.5	0.52	8	2
1964	*C. pleurota*	Lerderderg River	440	421	6	0.83	1.6	0.43	13	8
1965	*Cladonia*	Moorabool Reservoir	1700	1707	45	2.77	3.0	1.58	20	6
1967	*C. staufferi*	Spion Kopje 0.8 km W of Mount Nelse North	1303	988	22	1.20	1.9	0.48	11	3
1968	*Cladonia*	Brisbane Ranges, Little River	1960	2074	27	2.50	2.6	1.28	11	6
1969	*Cladonia*	Lauriston Reservoir, Macedon Ranges	331	266	5	0.65	0.8	0.25	4	2
1970	*C. pertricosa*	Camels Hump, Mount Macedon	144	96	3	0.50	1.3	0.19	9	7
1971	*Cladonia*	24 km SW of Bacchus Marsh, Brisbane Ranges	319	252	6	0.63	0.8	0.16	7	2
1972	*C. sp*	Victoria, You Yangs	460	301	17	0.67	1.0	0.24	7	11
1974	*Cladonia*	Near Mount Blackwood	399	220	7	0.77	0.9	0.24	6	4
1976	*C. sp*	You Yangs. N and NE of Branding Yard Hill	182	129	7	0.68	0.9	0.26	7	7
1978	*Cladonia*	Brisbane Ranges	2177	1991	30	2.29	1.8	1.75	9	14
1981	*C. fimbriata*	Mount Macedon - Wooden Road	403	390	13	0.67	1.1	0.45	6	5
1982	*C. sp*	Jumping Creek National Park, Warrandyte	232	242	6	0.62	2.4	0.64	13	13
1985	*C. floerkeana*	Antonio Park, Ringwood, 23 km W of Melbourne	832	788	23	1.60	25	0.66	28	70
1986	*Cladonia*	Brisbane Ranges National Park	139	144	5	0.49	1.2	0.17	12	2
1993	*C. enantia*	Ironbark Gorge, Bambra Rd, Aireys Inlet, Anglesea	1080	802	15	1.72	2.0	0.57	7	4
1994	*C. ramulosa*	3 km SSW of Buxton, Buxton Silver Gum Reserve	88	65	3	0.44	1.3	0.39	22	3
1995*	*C. ochrochlora*	South of Blackwood, Trentham	761	655	17	1.15	1.5	0.51	11	5
1996	*C. fimbriata*	One Tree Hill (Mount Donna Buang excursion)	645	613	19	1.15	1.9	0.78	8	18
1997	*C. humilis*	Wombat State Forest, Babbington Hill	235	188	7	0.62	1.8	0.21	12	0.8
1998	*C. furcata*	Brock Monument	224	197	7	0.61	0.8	0.19	7	2
2000	*C. humilis*	Parwan Valley, White Elephant Reserve	339	276	5	0.71	2.7	0.44	14	0.5
2001	*Cladonia*	Parwan Valley, White Elephant Reserve	326	213	8	0.69	1.2	0.49	11	0.7
2002	*C. rigida*	Black Range, 5 km W of Romsey	190	160	5	0.55	1.0	0.20	11	0.8
2005	*C. scabriuscula*	Wombat State Forest, New Sultan Mine Track	359	320	8	0.65	1.3	0.29	7	0.4
2006	*C. confusa*	Bryces Flat picnic ground and carpark	287	216	5	0.57	0.9	0.29	81	0.2

Sample marked with (*) was processed eight times.

[b] Pb concentrations are taken from Wu et al. (2016a).

Supplementary Table S5. Trace metal concentrations of *Usnea* lichens collected from central and southern Victoria between 1900 and 2008.

Year	Species	Locations	Al	Fe	Ti	Cr	Cu	Ni	Zn	Pb[b]
1900	*U. scabrida*	Mount Macedon	194	201	6	0.77	1.1	0.23	15	36
1940	*U. scabrida*	Ferntree Gully	1058	969	22	1.71	1.9	0.91	21	15
1944	*U. scabrida*	Daylesford	943	968	45	1.75	2.0	1.06	13	16
1961	*U. scabrida*	Bullengarook	321	275	12	1.11	2.7	0.73	13	11
1963	*U. meridionalis*	Moorabool River	186	145	4	0.85	1.2	0.37	77	5
1966	*U. scabrida*	Mount Macedon	686	719	21	1.60	2.4	0.92	17	24
1967	*Usnea*	Camels Hump, Mount Macedon	120	125	3	0.58	0.7	0.12	8	17
1975	*U. baileyi*	Eastern foothills of Pine Mountain	242	166	5	2.69	0.8	0.77	4	10
1977	*Usnea*	Daylesford Caravan Park	509	570	28	1.33	1.2	0.44	7	21
1980	*U. scabrida*	Coranderrk Bushland Reserve	170	185	6	1.00	1.6	0.48	14	42
1981	*Usnea*	Mount Macedon	292	335	9	1.37	1.8	0.36	24	58
1983	*Usnea*	Two Mile Creek	526	717	15	1.88	1.9	0.52	18	18
1984	*Usnea*	Daylesford-Trentham via Domino Road	708	734	23	2.59	2.6	0.49	12	86
1986	*Usnea*	Mount Donna Buang	551	461	14	1.35	1.6	0.37	15	20
1993	*Usnea*	E side of Mount Gisborne Road	203	300	10	0.86	1.8	0.52	19	26
1994	*U. molliuscula*	Lake Mountain Alpine Reserve	112	97	3	0.71	0.6	0.21	4	7
1996	*U. subalpina*	Observation Road, O'shannessy	57	53	3	0.61	0.7	0.32	14	2
1997	*U. molliuscula*	Summit of Mount Alexander, Castlemaine	446	413	15	1.12	1.8	0.37	16	3
1999	*U. dasaea*	SW of Hepburn, Tipperary Track	75	67	3	0.56	0.9	0.34	6	2
2001	*Usnea*	Yarra Ranges National Park	112	131	3	0.67	0.7	0.17	4	0.7
2006	*U. scabrida*	Long Forest Nature Conservation Reserve	157	141	4	0.79	1.2	0.45	6	1
2008	*U. subeciliata*	Yarra Ranges National Park	202	150	6	0.76	1.1	0.51	10	0.4

[b] Pb concentrations are taken from Wu et al. (2016a).

Supplementary Table S6. Trace metal concentrations of *Trametes* fungi collected from central and southern Victoria between 1852 and 2006.

Year	Species	Locations	Al	Fe	Ti	Cr	Cu	Ni	Zn	Pb[b]
1852	*T. versicolor*	Port Phillip	93	85	5	0.48	8	1.50	12	14
1932	*T. ochracea*	Belgrave	76	115	11	0.42	6	0.34	22	3
1939	*T. versicolor*	Pole Yard, Fishermans Bend	189	418	18	1.02	21	0.92	68	15
1947Aug	*T. velutina*	Acheron Way	110	100	7	0.34	3	0.20	9	2
1949	*T. ochracea*	Cement Creek	120	158	9	0.64	5	0.47	32	8
1951	*T. ochracea*	Blackwood	40	74	7	0.59	6	0.20	16	2
1953May	*T. ochracea*	Kilsyth	72	187	25	0.50	31	0.54	56	2
1953Aug	*T. velutina*	Royal Park, Melbourne	64	172	9	0.36	8	2.50	14	5
1954	*T. ochracea*	Emerald Lake	33	51	5	0.26	9	0.27	28	3
1957	*T. velutina*	Glenferrie	384	1046	22	1.32	18	2.46	76	24
1958	*T. versicolor*	Clayton	439	495	23	0.84	29	0.94	28	9
1959	*T. ochracea*	Box Hill	298	473	14	0.97	9	0.76	36	7
1960	*T. ochracea*	Caulfield	37	229	9	0.89	6	0.21	24	18
1962Jun	*T. ochracea*	Powelltown, Mackley's Road	68	170	4	0.37	3	0.32	21	0.7
1962Jul	*T. lactinea*	Woori Yallock	54	55	5	0.19	9	0.07	10	4
1963	*T. ochracea*	Ingles St store, South Melbourne	758	1284	20	1.60	39	2.22	139	23
1964	*T. versicolor*	Melbourne, Royal Botanic Gardens	299	494	25	0.72	13	1.35	55	8
1967	*T. velutina*	Flinders ln, Melbourne city	143	272	12	0.37	9	0.65	26	19
1969	*T. versicolor*	Sherbrooke Forest, Kallista	217	213	5	0.32	2	0.49	6	2
1974	*T. ochracea*	East Brighton	22	39	12	0.08	3	0.13	10	5
1975	*T. versicolor*	Acheron Way	206	218	16	0.39	9	0.30	25	2
1976Jun	*T. versicolor*	Ferntree Gully National Park	16	38	6	0.09	4	0.33	12	0.5
1976Nov	*T. hirsuta*	Sir Colin MacKenzie Wildlife Sanctuary	43	50	11	0.12	4	0.13	19	1
1980	*T. hirsuta*	Melbourne, Port Phillip Bay	54	140	5	0.27	1	0.31	9	3
1994	*T. versicolor*	Melbourne, Yarra Bend	151	212	8	0.42	4	0.60	14	3
1995	*Trametes*	Wattle Park	26	49	5	0.16	4	0.37	26	2
1996Jul	*T. versicolor*	Melbourne, Royal Botanic Gardens	29	84	17	0.13	11	0.22	17	2
1996Jul	*T. versicolor*	Melbourne, outer suburb of Eltham	57	99	13	0.22	3	0.37	41	5
1999	*T. versicolor*	Kinglake National Park	36	40	4	0.15	2	0.29	5	0.2
2006	*T. hirsuta*	Beaumaris, foreshore reserve	46	100	7	0.23	6	0.19	15	0.7

[b] Pb concentrations are taken from Wu et al. (2016a).

Supplementary Table S7. Enrichment Factors (EFs) for *Cladonia* lichens collected from the Greater Sydney area between 1885 and 2009.

Year	Species	Locations	Fe	Ti	Cr	Cu	Ni	Zn	Pb
1885	*C. furcata*	Ross Cave, Mt Victoria	2	1.0	5	29	7	415	176
1894	*C. cervicornis*	Eastern Creek, near Blacktown	3	0.5	3	10	3	33	23
1897	*C. fimbriata*	Lithgow	2	0.7	3	1370	8	79	576
1898	*C. floerkeana*	Penshurst	3	0.5	2	10	2	24	19
1899	*C. floerkeana*	Sydney	4	1.3	4	25	3	60	190
1900	*C. floerkeana*	Randwick	3	1.8	2	31	2	37	190
1902	*C. floerkeana*	Hurstville	2	1.3	2	17	2	31	69
1903	*C. fimbriata*	Oatley	2	1.4	2	30	3	47	134
1906	*C. pertricosa*	Gladesville	2	1.4	2	18	3	38	61
1907	*C. humilis*	Gladesville	3	1.5	3	17	4	34	64
1908	*C. fimbriata*	Wahroonga, near Sydney	2	0.6	2	10	2	16	62
1909	*C. furcata*	Near Manly, Sydney	4	1.0	4	16	3	46	72
1910	*C. fimbriata*	Penshurst.	4	1.3	3	13	2	11	195
1911	*C. sulcata*	Gladesville	3	0.6	3	12	3	73	6
1914	*C. pertricosa*	Balmoral, Sydney	3	1.6	3	22	4	24	78
1971	*C. P.Browne*	23 km N of Sydney	2	1.2	2	13	4	49	174
1974	*C. sp*	Bradley's Head, Sydney	3	1.9	1	49	8	123	502
1977	*C. ramulosa*	Jamieson Valley, Blue Mtns	1	1.0	10	18	3	98	96
1978	*C. cervicornis*	Old Great Northern Rd	5	0.6	3	15	5	39	401
1980	*C. kuringaiensis*	Grosvenor Track	4	1.0	4	32	8	114	470
1981	*C. floerkeana*	Near McCarrs Creek	2	0.9	1	22	2	36	136
1982	*C. furcata*	Epping, near Devlins Creek	3	1.4	6	33	8	69	561
1983	*C. praetermissa*	Towler Bay. 30 km N of Sydney	2	0.4	2	14	4	35	218
1984	*C. sulcata*	Mona Vale Rd, 18 km N of Sydney	2	1.8	2	19	5	116	191
1985Feb	*C. kuringaiensis*	Glaston Gorge near Sydney	2	1.4	2	20	5	54	492
1985Mar	*C. floerkeana*	Yeoman's Bay	2	1.2	2	9	1	12	95
1985July	*C. pertricosa*	Erskine Creek, Blue Mtns	2	1.3	N/A	33	6	79	569
1986	*C. fruticulosa*	Toby`s Glen, Blue Mtns	2	0.4	3	4	2	7	51
1987Mar	*C. floerkeana*	Jenolan Caves, Blue Mtns	2	0.7	2	10	2	19	10
1987Sep	*C. sulcata*	Hazelbrook, Blue Mtns	4	0.9	1	32	3	105	134
1988	*C. floerkeana*	Terrey Hills	3	0.9	1	30	3	70	148
1989	*C. cervicornis*	Hazelbrook, Blue Mtns	2	0.5	2	14	5	48	64
1990	*C. ochrochlora*	Bradleys Head	5	1.4	3	31	34	55	547
1991	*C. praetermissa*	Macquarie University	3	1.2	3	18	5	56	336
1992	*C. ochrochlora*	Lane Cove National Park	2	0.9	3	17	5	56	442
1993	*C. praetermissa*	Macquarie University	3	0.3	2	4	3	6	65
1995	*C. cerricornis*	Dyarrabin Nature Reserve	2	0.8	2	15	3	39	161
1996	*C. furcata*	Smith Park, East Hills	3	0.6	3	19	4	55	215
1997	*C. praetermissa*	Terrys Creek	3	1.2	4	89	16	311	565
1998	*C. floerkeana*	West Pennant Hills, Palm Gully	3	1.4	2	19	4	28	224
1999	*C. floerkeana*	Pennant Hills Park, Cheltenham	2	0.6	1	36	3	83	99
2000	*C. furcata*	Lyrebird Gully track, Mt Kuring-gai	4	0.7	4	25	8	61	85
2001	*C. praetermissa*	Near Maroubra Beach	8	0.5	11	59	7	68	5211
2002	*C. corniculata*	Rickards Road, SW of Richmond	3	1.1	3	17	4	54	59
2003	*C. celata*	Oatley West	2	1.6	1	9	3	10	46
2009	*C. chlorophaea*	East of Pitt Town	7	0.7	5	11	5	32	5

EFs: Trace metals normalized to Al and to upper crust values from Taylor and McLennan (1995); standard error (SE) for each EF values: Fe: 0.2, Ti: 0.1, Cr: 0.3, Cu: 29, Ni: 0.7, Zn: 11, Pb: 112.

Supplementary Table S8. Enrichment Factors (EFs) for *Usnea* lichens collected from the Greater Sydney area between 1902 and 2010.

Year	Species	Locations	Fe	Ti	Cr	Cu	Ni	Zn	Pb
1902	*Usnea*	Pine Ridge, Liverpool	2	0.5	4	7	4	6	34
1903	*U. baileyi*	Toongabbie	2	0.8	6	16	3	20	113
1906	*Usnea*	Nepean and Warragamba Rivers	6	0.3	6	18	12	52	131
1907	*Usnea*	Nepean and Warragamba Rivers	3	0.3	6	56	13	92	421
1908	*Usnea*	Parramatta	3	0.9	7	30	6	67	196
1910	*Usnea*	Ermington	5	1.2	11	115	18	270	1219
1917	*Usnea*	Castle Hill	4	0.5	7	25	6	35	701
1951	*U. angulata*	Blue Mtns	1	1.5	11	19	5	44	143
1963	*U. molliuscula*	Royal National Parks near Port Hacking	3	1	5	18	9	85	345
1965	*Usnea*	37 km S of Milbrodale	8	1.0	8	14	33	137	800
1972	*Usnea*	Mount Irvine	3	0.9	14	125	14	245	892
1977	*Usnea*	Jamieson Valley, below Katoomba Falls	4	1.2	13	29	12	100	587
1978	*Usnea*	Mount Bouddi, Bouddi National Park	3	1.0	14	21	15	146	984
1984Nov	*Usnea*	25 km NNE of Katoomba	1	1.3	12	23	5	67	645
1984Nov	*Usnea*	Zig-Zag Road, Mount Wilson	4	2.1	31	36	14	162	7042
1988	*Usnea*	Mount Wilson, Blue Mtns	2	2.1	19	42	6	114	271
1989	*Usnea*	Ku Ring Gai Chase National Park	2	0.7	10	25	3	37	303
1990	*Usnea*	Brooklyn, Long Island Nature Reserve	4	1.1	14	141	16	192	1113
1991	*U. inermis*	12 km E of Cullen Bullen	2	1.1	18	32	11	107	273
1996	*Usnea*	Wentworth Falls	3	0.6	10	34	11	88	378
1997	*Usnea sp*	North Rocks, Lomatia Creek	5	0.7	18	87	44	367	908
2000	*Usnea*	Centennial Glen, Blackheath	3	0.6	9	21	10	40	34
2002	*U. undulata*	Grand Canyon track, Blackheath	1	0.2	5	21	3	61	37
2009	*Usnea*	Blue Mountains National Park	2	1.1	16	30	7	70	57
2010	*Usnea*	Mitchell Park, Cattai National Park	2	0.9	10	17	2	20	11

EFs: Trace metals normalized to Al and to upper crust values from Taylor and McLennan (1995); standard error (SE) for each EF values: Fe: 0.3, Ti: 0.1, Cr: 1, Cu: 7, Ni: 2, Zn: 18, Pb: 280.

Supplementary Table S9. Enrichment Factors (EFs) for *Trametes* fungi collected from the Greater Sydney area between 1924 and 1988.

Year	Species	Locations	Fe	Ti	Cr	Cu	Ni	Zn	Pb
1924	*T. versicolor*	Fairfield, Canley Vale	4	1	6	98	6	471	63
1926	*Trametes*	Mount Wilson	3	5	14	210	12	296	265
1939	*T. versicolor*	Hazelbrook and Bullaburra Glen, Blue Mtns	2	2	8	130	11	141	212
1951	*T. lactinea*	Royal Botanic Gardens, Sydney	2	2	11	306	23	315	252
1953	*T. lactinea*	North Ryde, Sydney	1	1	20	682	16	219	189
1955	*T. lactinea*	Royal Botanic Gardens, Sydney	6	4	22	278	123	713	223
1956	*T. ochracea*	Beaconsfield, Alexandria	3	2	6	147	16	210	40
1982	*T. versicolor*	Mount Tomah, Blue Mtns	4	4	7	445	10	712	113
1983	*T. hirsuta*	10.4 km NNW of Yarramalong Public School	1	3	3	93	5	244	183
1988	*T. versicolor*	Mount Wilson, 17 km NE of Mount Victoria	1	3	3	154	3	207	37

EFs: Trace metals normalized to Al and to upper crust values from Taylor and McLennan (1995); standard error (SE) for each EF values: Fe: 1, Ti: 0.4, Cr: 2, Cu: 59, Ni: 14, Zn: 66, Pb: 28.

Supplementary Table S10. Enrichment Factors (EFs) for *Cladonia* lichens collected from central and southern Victoria between 1885 and 2006.

Year	Species	Locations	Fe	Ti	Cr	Cu	Ni	Zn	Pb
1885	*C. sulcata*	Mount Macedon	2	0.8	1	11	1	20	922
1886	*C. capitellata*	Mount Macedon	2	0.8	7	21	3	1058	4046
1889	*C. squamosa*	Mount Macedon	2	0.6	6	24	5	15	31
1934	*C. sp*	Cardinia Creek, near Clematis	2	0.4	2	3	2	7	7
1940	*C. fimbriata*	Hardy's Gully, Kallista	2	0.7	3	13	3	13	24
1953	*C. squamosa*	Sherbrooke Forest, Kallista. Below Coles Ridge	2	0.7	6	20	4	37	44
1954	*C. fimbriata*	Lilydale	2	0.4	3	9	4	144	102
1955	*C. P. Browne*	Brisbane Ranges, Reilly's Creek Gorge	2	0.4	8	11	10	29	23
1957	*C. macilenta*	North Ringwood	2	0.4	4	78	3	168	59
1959	*C. fimbriata*	On the lower slopes of Mount Vinegar	2	0.6	5	21	3	47	68
1960	*C. sp*	Blackwood Ranges	2	0.6	7	24	6	30	49
1961	*C. gracilis*	Brisbane Ranges	2	1.5	18	58	16	136	82
1963	*C. P. Browne*	Moorabool River 3 km SW Eggerton	2	0.9	8	86	12	56	42
1964	*C. pleurota*	Lerderderg River	2	0.4	4	12	4	34	69
1965	*C. P. Browne*	Moorabool Reservoir	2	0.7	4	6	4	13	15
1967	*C. staufferi*	Spion Kopje 0.8 km W of Mount Nelse North	2	0.4	2	5	1	9	8
1968	*C. P. Browne*	Brisbane Ranges, Little River	2	0.4	3	4	3	6	12
1969	*C. P. Browne*	Lauriston Reservoir, Macedon Ranges	2	0.4	5	8	3	13	24
1970	*C. pertricosa*	Camels Hump, Mount Macedon	2	0.5	8	29	5	67	187
1971	*C. P. Browne*	24 km SW of Bacchus Marsh, Brisbane Ranges	2	0.5	5	9	2	23	18
1972	*C. sp*	Victoria, You Yangs	2	1.0	3	7	2	18	94
1974	*C. P. Browne*	Near Mount Blackwood	1	0.4	4	7	2	18	37
1976	*C. sp*	You Yangs. N and NE of Branding Yard Hill	2	1.0	9	15	6	41	161
1978	*C. P. Browne*	Brisbane Ranges	2	0.4	2	3	3	4	25
1981	*C. fimbriata*	Mount Macedon - Wooden Road	2	0.9	4	9	4	16	50
1982	*C. sp*	Jumping Creek National Park, Warrandyte	2	0.7	6	34	11	64	219
1985	*C. floerkeana*	Antonio Park, Ringwood, 23 km W of Melbourne	2	0.7	4	98	3	37	337
1986	*C. P. Browne*	Brisbane Ranges National Park	2	0.9	8	28	5	95	55
1993	*C. enantia*	Ironbark Gorge, Bambra Rd, Aireys Inlet, Anglesea	2	0.4	4	6	2	7	13
1994	*C. ramulosa*	3 km SSW of Buxton, Buxton Silver Gum Reserve	2	1.0	12	47	18	280	140
1995	*C. ochrochlora*	South of Blackwood, Trentham	2	0.6	3	6	3	17	25
1996	*C. fimbriata*	One Tree Hill (Mount Donna Buang excursion)	2	0.8	4	9	5	14	110
1997	*C. humilis*	Wombat State Forest, Babbington Hill	2	0.8	6	24	4	56	14
1998	*C. furcata*	Brock Monument	2	0.8	6	11	3	37	35
2000	*C. humilis*	Parwan Valley, White Elephant Reserve	2	0.4	5	26	5	48	5
2001	*C. P. Browne*	Parwan Valley, White Elephant Reserve	2	0.6	5	12	6	38	9
2002	*C. rigida*	Black Range, 5 km W of Romsey	2	0.8	7	18	4	66	17
2005	*C. scabriuscula*	Wombat State Forest, New Sultan Mine Track	2	0.6	4	12	3	23	5
2006	*C. confusa*	Bryces Flat picnic ground and carpark	2	0.5	5	11	4	321	3

EFs: Trace metals normalized to Al and to upper crust values from Taylor and McLennan (1995); standard error (SE) for each EF values: Fe: 0.03, Ti: 0.04, Cr: 0.5, Cu: 4, Ni: 1, Zn: 28, Pb: 105.

Supplementary Table S11. Enrichment Factors (EFs) for *Usnea* lichens collected from central and southern Victoria between 1900 and 2008.

Year	Species	Locations	Fe	Ti	Cr	Cu	Ni	Zn	Pb
1900	*U. scabrida*	Mount Macedon	2	0.8	9	18	5	85	751
1940	*U. scabrida*	Ferntree Gully	2	0.6	4	6	3	22	55
1944	*U. scabrida*	Daylesford	2	1.3	4	7	5	15	69
1961	*U. scabrida*	Bullengarook	2	1.0	8	27	9	46	136
1963	*U. meridionalis*	Moorabool River	2	0.6	10	20	8	467	108
1966	*U. scabrida*	Mount Macedon	2	0.8	5	11	5	28	142
1967	*Usnea*	Camels Hump, Mount Macedon	2	0.8	11	19	4	78	564
1975	*U. baileyi*	Eastern foothills of Pine Mountain	2	0.6	26	11	13	20	162
1977	*Usnea*	Daylesford Caravan Park	3	1.5	6	7	4	16	162
1980	*U. scabrida*	Coranderrk Bushland Reserve	2	0.9	13	30	11	91	992
1981	*Usnea*	Mount Macedon	3	0.9	11	19	5	91	806
1983	*Usnea*	Two Mile Creek	3	0.8	8	12	4	38	135
1984	*Usnea*	Daylesford-Trentham via Domino Road	2	0.9	8	12	3	19	488
1986	*Usnea*	Mount Donna Buang	2	0.7	6	9	3	30	144
1993	*Usnea*	E side of Mount Gisborne Road	3	1.3	10	28	10	105	512
1994	*U. molliuscula*	Lake Mountain Alpine Reserve	2	0.7	14	16	8	41	255
1996	*U. subalpina*	Observation Road, O'shannessy	2	1.4	25	41	23	269	101
1997	*U. molliuscula*	Summit of Mount Alexander, Castlemaine	2	0.9	6	13	3	41	27
1999	*U. dasaea*	SW of Hepburn, Tipperary Track	2	1.1	17	40	18	92	100
2001	*Usnea*	Yarra Ranges National Park	3	0.8	14	20	6	39	26
2006	*U. scabrida*	Long Forest Nature Conservation Reserve	2	0.7	12	25	11	41	34
2008	*U. subeciliata*	Yarra Ranges National Park	2	0.7	9	17	10	57	7

EFs: Trace metals normalized to Al and to upper crust values from Taylor and McLennan (1995); standard error (SE) for each EF values: Fe: 0.1, Ti: 0.1, Cr: 1, Cu: 2, Ni: 1, Zn: 22, Pb: 61.

Supplementary Table S12. Enrichment Factors (EFs) for *Trametes* lichens collected from central and southern Victoria between 1852 and 2006.

Year	Species	Locations	Fe	Ti	Cr	Cu	Ni	Zn	Pb
1852	*T. versicolor*	Port Phillip	2	2	12	281	65	149	596
1932	*T. ochracea*	Belgrave	3	4	13	235	18	335	170
1939	*T. versicolor*	Pole Yard, Fishermans Bend	5	3	12	360	20	406	315
1947Aug	*T. velutina*	Acheron Way	2	2	7	101	7	92	70
1949	*T. ochracea*	Cement Creek	3	2	12	139	16	299	258
1951	*T. ochracea*	Blackwood	4	5	33	464	20	438	229
1953May	*T. ochracea*	Kilsyth	6	9	16	1380	30	883	129
1953Aug	*T. velutina*	Royal Park, Melbourne	6	4	13	389	156	238	325
1954	*T. ochracea*	Emerald Lake	4	4	18	855	33	983	405
1957	*T. velutina*	Glenferrie	6	2	8	150	26	224	250
1958	*T. versicolor*	Clayton	3	1	4	209	9	71	81
1959	*T. ochracea*	Box Hill	4	1	7	95	10	137	97
1960	*T. ochracea*	Caulfield	14	7	55	489	22	728	1929
1962Jun	*T. ochracea*	Powelltown, Mackley's Road	6	2	12	128	19	348	39
1962Jul	*T. lactinea*	Woori Yallock	2	2	8	535	5	204	310
1963	*T. ochracea*	Ingles St store, South Melbourne	4	1	5	167	12	208	120
1964	*T. versicolor*	Melbourne, Royal Botanic Gardens	4	2	6	135	18	209	108
1967	*T. velutina*	Flinders ln, Melbourne city	4	2	6	192	18	205	520
1969	*T. versicolor*	Sherbrooke Forest, Kallista	2	1	3	37	9	32	37
1974	*T. ochracea*	East Brighton	4	15	9	483	24	522	904
1975	*T. versicolor*	Acheron Way	2	2	4	148	6	137	35
1976Jun	*T. versicolor*	Ferntree Gully National Park	6	11	13	859	85	886	138
1976Nov	*T. hirsuta*	Sir Colin MacKenzie Wildlife Sanctuary	3	7	7	280	12	500	121
1980	*T. hirsuta*	Melbourne, Port Phillip Bay	6	2	12	83	23	191	254
1994	*T. versicolor*	Melbourne, Yarra Bend	3	1	6	76	16	107	80
1995	*Trametes Fr.*	Wattle Park	4	5	14	509	58	1169	252
1996Jul	*T. versicolor*	Melbourne, Royal Botanic Gardens	7	15	10	1173	30	648	275
1996Jul	*T. versicolor*	Melbourne, outer suburb of Eltham	4	6	9	146	26	819	354
1999	*T. versicolor*	Kinglake National Park	3	3	10	219	32	147	24
2006	*T. hirsuta*	Beaumaris, foreshore reserve	5	4	11	445	17	376	64

EFs: Trace metals normalized to Al and to upper crust values from Taylor and McLennan (1995); standard error (SE) for each EF values: Fe: 0.4, Ti: 0.7, Cr: 2, Cu: 60, Ni: 6, Zn: 56, Pb: 67.

Supplementary Table S13. Relative Standard Deviations (% RSD) for the replicate analysis (n = 8) of two lichen samples.

Samples	**n**	**Al**	**Fe**	**Ti**	**Cr**	**Cu**	**Ni**	**Zn**	**Pb**
Sydney *Cladonia* 2009	8	1.5	1.7	2.4	3.8	1.1	2.6	0.7	1.8
Victoria *Cladonia* 1995	8	3.8	2.9	2.2	1.8	1.1	0.5	0.3	3.0

Supplementary References

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Appendix D: Supplementary Information for Chapter Five

Supplementary Table S1. Lead concentrations (mg/kg) and Pb isotopic compositions for ash, soils and rocks collected from four wildfire sites, Cherryville, Adelaide, South Australia, Forcett, Hobart, Tasmania, Woy Woy and Duffys Forest, Sydney, New South Wales (see Figure 1 in the main article for a location map).

ID	Sample Type	Pb	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Cherryville					
CV01	Ash	21	17.8	1.141	2.434
CV02	Ash	17	17.5	1.126	2.416
CV03	Ash	16	17.6	1.136	2.439
CV04	Ash	17	19.3	1.224	2.539
CV05A	Ash	12	19.5	1.233	2.574
CV05B	Ash	10	20.1	1.267	2.689
CV06	Ash	13	19.3	1.218	2.536
CV07	Ash	15	17.8	1.136	2.451
CV08	Ash	10	18.7	1.189	2.523
CV09	Ash	78	19.7	1.239	2.602
CV10	Ash	65	19.4	1.227	2.587
CV11	Ash	60	18.7	1.192	2.535
CV12	Ash	33	18.0	1.146	2.449
CV13	Soil_1_0-2cm	22	19.2	1.213	2.575
CV14	Soil_2_0-2cm	53	17.3	1.110	2.441
CV15	Soil_2_40-50cm	31	19.8	1.247	2.625
CV16	Rock	12	18.4	1.163	2.469
CV17	Rock	3	18.6	1.183	2.514
Forcett					
IL01	Ash	3	17.9	1.144	2.458
IL02	Ash	2	18.1	1.165	2.497
IL03	Ash	14	16.6	1.075	2.363
IL04	Ash	2	18.2	1.164	2.493
IL05	Ash	0.6	16.8	1.094	2.421
IL06	Ash	3	17.9	1.153	2.462
IL07	Ash	2	18.2	1.166	2.480
IL08	Ash	0.7	18.0	1.172	2.507
IL09	Ash	1.4	17.7	1.140	2.443
IL10	Ash	4	18.8	1.198	2.530
IL11	Ash	24	18.3	1.179	2.455
IL12	Ash	10	17.7	1.137	2.405
IL13	Ash	7	18.3	1.171	2.456
IL14	Ash	10	18.5	1.188	2.460
IL15	Ash	2	18.9	1.208	2.505
IL16A	Ash	5	18.2	1.159	2.427
IL16B	Ash	7	17.9	1.148	2.430
IL17	Ash	6	18.3	1.170	2.453
IL18	Ash	12	18.1	1.162	2.430
IL19	Ash	7	18.2	1.166	2.441
IL20	Ash	44	18.8	1.199	2.465
IL21	Ash	11	18.1	1.167	2.452
IL22	Ash	15	18.8	1.199	2.468
IL23	Ash	2	18.0	1.153	2.483
IL24	Ash	12	18.3	1.174	2.454
IL25	Ash	12	18.2	1.169	2.451
IL26	Ash	7	18.5	1.182	2.462
IL27	Ash	80	18.5	1.188	2.462
IL28	Ash	8	18.5	1.181	2.459
IL29	Ash	10	17.6	1.132	2.412
IL30	Ash	6	17.5	1.127	2.408
IL31	Ash	1.2	17.6	1.139	2.430
IL32	Ash	1.5	18.4	1.169	2.489
IL33	Ash	3	17.9	1.144	2.459
IL34A	Ash	5	18.7	1.191	2.524
IL34B	Ash	1.7	18.3	1.166	2.488

IL35	Soil_1_0-2cm	11	18.5	1.191	2.465
IL36	Soil_2_0-2cm	14	18.3	1.175	2.458
IL37	Soil_1_30-40cm	8	18.9	1.204	2.477
IL38	Rock	8	18.8	1.204	2.470
IL39	Rock	2	18.9	1.211	2.509
Woy Woy					
PB01	Ash	6	17.2	1.109	2.406
PB02	Ash	41	17.3	1.117	2.408
PB03	Ash	8	17.4	1.119	2.415
PB04	Ash	3	18.2	1.155	2.497
PB05	Ash	3	18.5	1.163	2.527
PB06	Ash	7	17.6	1.139	2.443
PB07	Ash	7	18.0	1.153	2.476
PB08	Ash	10	17.1	1.104	2.386
PB09	Ash	3	17.4	1.126	2.436
PB10	Ash	0.5	18.4	1.161	2.519
PB11	Ash	4	18.3	1.176	2.512
PB12	Ash	5	17.8	1.151	2.457
PB13	Ash	9	17.4	1.126	2.420
PB14	Soil_1_0-2cm	3	17.3	1.114	2.435
PB15	Soil_2_0-2cm	6	17.6	1.124	2.418
PB16	Soil_3_0-2cm	25	17.2	1.110	2.400
PB17	Soil_2_30-40cm	6	18.1	1.166	2.490
PB18	Rock	8	18.1	1.160	2.487
PB19	Rock	18	18.3	1.159	2.489
PB20	Rock	11	18.0	1.159	2.451
PB21	Rock	4	18.3	1.157	2.478
PB22	Rock	4	18.0	1.152	2.458
PB23	Rock	11	18.3	1.175	2.547
Duffys Forest					
DF01	Ash	20	17.4	1.121	2.409
DF02	Ash	25	17.4	1.124	2.416
DF03	Ash	72	17.0	1.100	2.378
DF04	Ash	40	17.0	1.099	2.376
DF05	Ash	15	17.2	1.111	2.394
DF06	Ash	10	17.2	1.106	2.390
DF07	Soil_1_0-2cm	4	17.5	1.121	2.439
DF08	Soil_2_0-2cm	8	17.3	1.121	2.432
DF09	Soil_3_0-2cm	4	17.7	1.150	2.441
DF10	Soil_1_40-50cm	4	18.5	1.192	2.597

Supplementary Figure S1. Photographs of the 2012 Woy Woy wildfire burned area showing the grey-white ash that was collected for this study (photographs by Mark P. Taylor).

Supplementary Table S2. Pb isotopic compositions of potential emission sources.

Sample types	Samples	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Reference
Australian mines	Broken Hill	1.041	2.315	(Gulson, 1984)
	Broken Hill	1.039	2.316	(Gulson, 1984)
	Mount Isa	1.043	2.318	(Gulson, 1985)
Sydney air filters	1978	1.084	2.359	(Wu et al., 2016)
	1979	1.111	2.382	
	1980	1.148	2.410	
	1981	1.113	2.375	
	1983	1.074	2.346	
	1987	1.074	2.351	
	1991	1.081	2.349	
	1992	1.077	2.351	
	1993	1.067	2.341	
	1994	1.067	2.341	
	1995	1.070	2.348	
	1996	1.084	2.360	
	1997	1.098	2.366	
	1998	1.107	2.374	
	1999	1.089	2.363	
Adelaide air filters	1994	1.060	2.332	(Bollhöfer and Rosman, 2000)
	1997	1.071	2.345	(Kristensen et al., 2016)
	1998	1.086	2.351	
	1999	1.081	2.354	
	2000	1.079	2.349	
	2001	1.102	2.376	
	2002	1.111	2.383	
	2003	1.109	2.383	
	2004	1.110	2.382	
Hobart aerosols	1994	1.068	2.340	(Bollhöfer and Rosman, 2000)
	1999	1.1118	2.3750	(Bollhöfer et al., 2005)
	2000	1.0984	2.3652	(Bollhöfer et al., 2005)
Hobart leaded petrol	1999	1.110	2.365	(Bollhöfer et al., 2005)
	1999	1.108	2.362	(Bollhöfer et al., 2005)
NSW Coals	Coal 1	1.2057	2.4865	(Díaz-Somoano et al., 2009)
	Coal 2	1.2053	2.4867	(Díaz-Somoano et al., 2009)
	Fly ash	1.2107	2.4885	(Chiaradia et al., 1997)

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ORIGINAL PAPER

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

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Abstract This study examines the recent soil Lead Abatement Strategy (LAS) in Boolaroo, New South Wales, Australia, that was designed to "*achieve a reduction in human exposure to lead dust contamination in surface soils*". The abatement programme addressed legacy contamination of residential areas following closure of lead smelting operations in 2003 at the Pasminco Cockle Creek Smelter (PCCS). The principal objective of the LAS was to "cap and cover" lead-contaminated soils within the urban environment surrounding the PCCS. Soil lead concentrations of 2500–5000 mg/kg were scheduled for removal and replacement, while concentrations between 1500 and 2500 mg/kg were replaced only under limited circumstances. To date, there has been no industry, government or independent assessment of the clean-up programme that involved >2000 homes in the township of Boolaroo. Thus, by measuring post-abatement soil lead concentrations in Boolaroo, this study addresses this knowledge gap and evaluates the effectiveness of the LAS for reducing the potential for lead exposure. Soil lead concentrations above the Australian residential soil health investigation level value for residential soils (300 mg/kg) were identified at all but one of the residential properties examined ($n = 19$). Vacuum dust samples ($n = 17$) from the same homes had a mean lead concentration of 495 mg/kg (median 380 mg/kg). Bio-accessibility testing revealed that lead in household vacuum dust was readily accessible (% bio-accessible) (mean = 92 %, median = 90 %), demonstrating that the risk of exposure via this pathway remains. Assessment of a limited number of properties ($n = 8$) where pre-abatement soil lead levels were available for comparison showed they were not statistically different to post-abatement. Although the LAS did not include treatment of non-residential properties, sampling of community areas including public sports fields, playgrounds and schools ($n = 32$) was undertaken to determine the contamination legacy in these areas. Elevated mean soil lead concentrations were found across public lands: sports fields = 5130 mg/kg (median = 1275 mg/kg), playgrounds and schools = 812 mg/kg (median = 920 mg/kg) and open space = 778 mg/kg (median = 620 mg/kg). Overall, the study results show that the LAS programme that was dominated by a "cap and cover" approach to address

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widespread lead contamination was inadequate for mitigating current and future risk of lead exposures.

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

Introduction

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

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

Lead Abatement Strategy (LAS) for Pasminco Cockle Creek Smelter

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

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

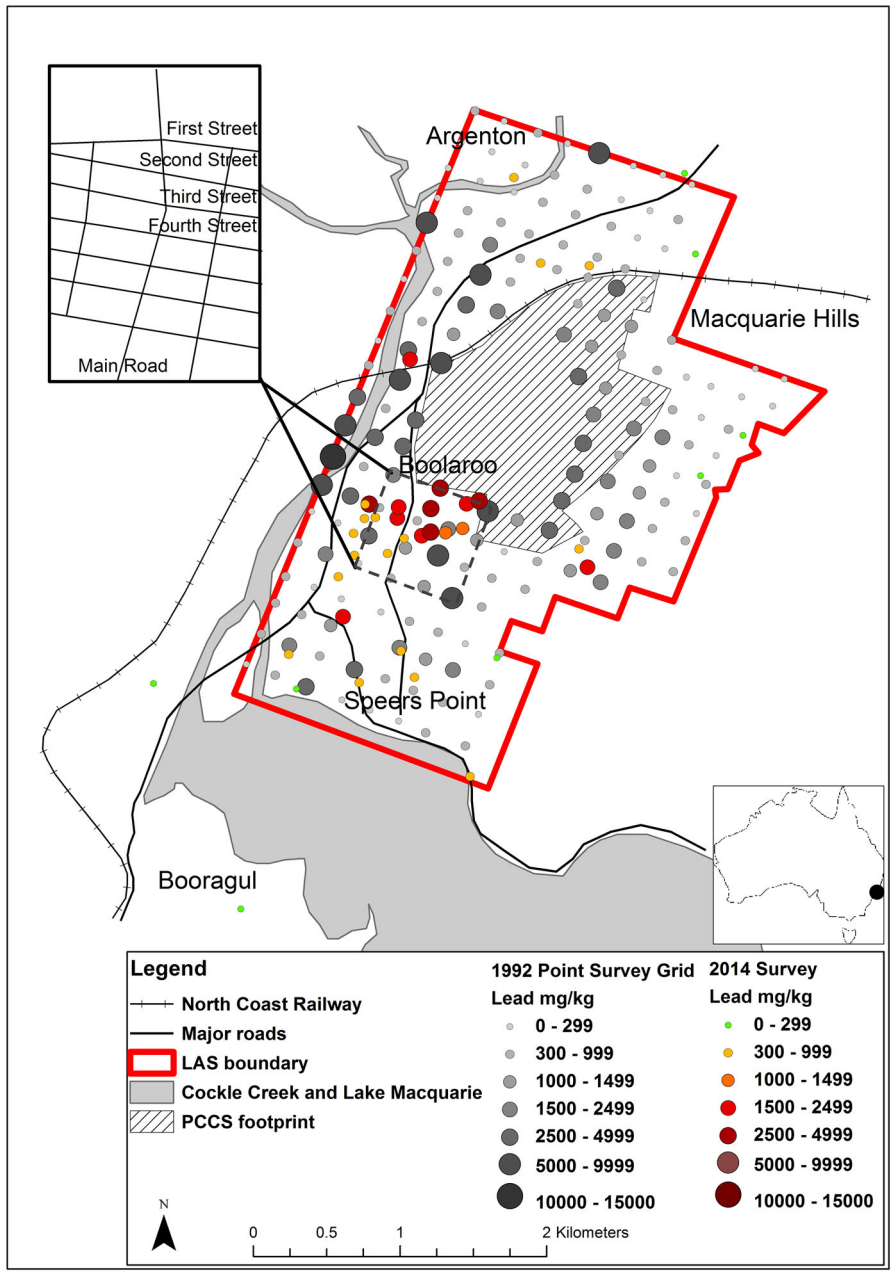

Fig. 1 Soil lead concentrations from Boolaroo, NSW, Australia, in the <180-µm fraction superimposed on the 1992 point survey grid soil lead data. Contemporary soil lead concentrations are greatest proximal to the PCCS

a significant other source of environmental lead exposure arose from the highly bio-accessible (54 % bio-accessible) smelter slag that was distributed widely as backyard fill throughout the suburbs surrounding the PCCS (Morrison and Gulson 2007). Batley (1992) concluded that "*most of the heavy metals present in the slag are in readily bio-available forms. It is likely that ingested slag reaching the gut would readily release lead, zinc, cadmium and copper, and this could have toxic consequences*" (p. 5).

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

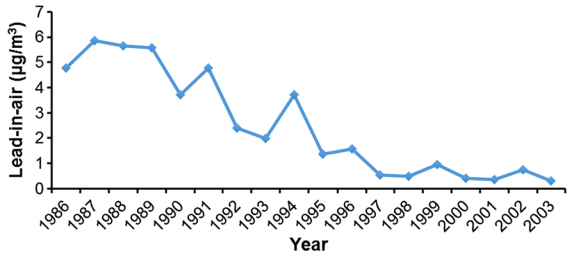

Fig. 2 Average annual atmospheric lead concentrations—First Street, Boolaroo, NSW

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

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

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

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

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

Methods and materials

Field methods

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

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

Laboratory methods

Soil samples were oven dried at 60 °C and then sieved to <180 μm. The <180-μm fraction was selected as

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

Soil ($n = 75$; front yards, back yards, open spaces, sports fields, playgrounds, schools and 2 mm fractions) and dust ($n = 17$) samples were analysed at the National Measurement Institute (NMI), Sydney. Approximately 0.5 g of dust or soil was digested in 3 mL concentrated, trace metal grade HNO_3 and 3 mL HCl. Elements commonly detected in smelting environments, antimony, arsenic, cadmium, lead and zinc concentrations were determined using a Perkin Elmer Elan DRC II Inductively Couple Plasma Mass Spectrometer (ICP-MS). Three procedural laboratory blanks returned concentrations below limit of reporting (LOR) of <0.5 mg/kg for all elements. Recovery rates of two NMI standard reference materials, AGAL-10 (river sediment) and AGAL-12 (bio-soil), for all elements were between 92 and 114 %. Duplicate analyses for the samples returned relative per cent difference (RPD) of <20 %.

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

Statistical analysis on the various sample media was performed using the Web-based statistical application developed by Stangroom (2014).

Results and discussion

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

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

Residential properties

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

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

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

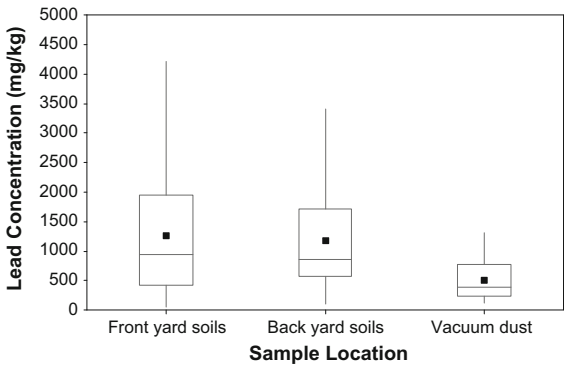

Fig. 3 Distribution of lead concentrations in soils and dust collected from front yards, back yards and household vacuum cleaner dust in Boolaroo. Mean concentrations are similar across each sampling area

Publically accessible areas

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

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

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

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

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

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

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

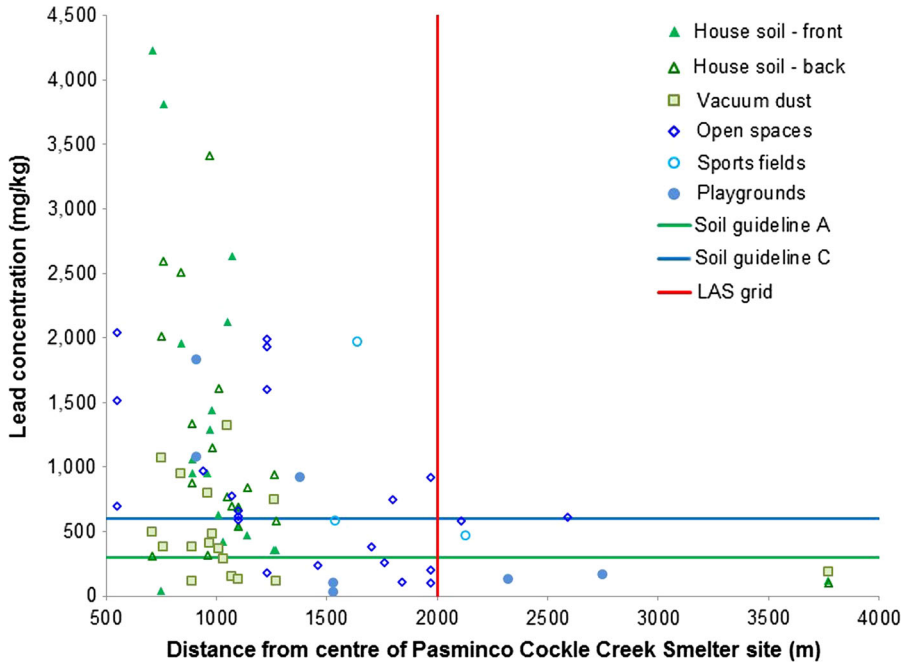

Fig. 4 Soil and dust lead concentrations from Boolaroo homes and community areas plotted against distance from the centroid of the PCCS site, illustrating a decrease in contamination with distance from the former smelter

number of community areas contain lead concentrations unacceptable for regular community use. Lead contamination of child play areas is not uncommon, particularly in industrial towns (Haugland et al. 2008; Mielke et al. 2011; Taylor et al. 2013, 2014b). Playground equipment has been identified as a pathway for lead exposure in children where dust deposited on the equipment collects on the hands of playing children (Taylor et al. 2013, 2014b). Although playing sports on grass-covered sporting fields would limit lead exposure to players, there is a reasonable risk that grass will be degraded during play or

seasonally, increasing the risk of exposure to lead-contaminated soils (Carr et al. 2008). High total lead concentrations and the well-established bio-accessibility of lead in community areas around Boolaroo (Kim et al. 2009) strongly suggest that unacceptably elevated environmental lead contamination is more prevalent than that was addressed by the LAS.

Residential vacuum dust

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

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

Assessment of effective management strategies

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

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

incident and declared lead free (Government of Western Australia 2011).

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

These abatement strategies were effective clean-up methods because either they completely removed contaminated soil or a thick physical barrier was used to limit contact between contaminated soil and the human environment, reducing the opportunity for exposure to high concentrations of lead in soil. In order to apply the same rigorous, world's best practice approach to the lead-contaminated soil clean-up in Boolaroo, i.e. total removal of the potential lead-exposure risks from children, as was conducted in Boston (15 cm of contaminated soil), it will require approximately 234,000 m^3 of soil to be removed (calculated by determining the exposed soil surface area on each property within the LAS boundary).

Evaluating the success of the LAS through monitoring blood lead concentrations

Elevated blood lead levels in mining and smelting communities are often attributed to additional environmental sources including leaded petrol and paint (Gulson et al. 1996). Prior work examining blood lead source apportionment at Boolaroo illustrates that these additional sources contribute little to blood lead levels at Boolaroo (Gulson et al. 2004). Further, the elemental correlations between concentrations of soil antimony and lead ($r = 0.86$, $p < 0.00001$) and cadmium and lead ($r = 0.87$, $p < 0.00001$) demonstrate a single smelter point source and not one derived from former lead petrol emission or old lead paint. Unsurprisingly, similar arguments have often been promulgated in lead mining and smelting towns as part of an institutional approach to downplaying risk (Taylor et al. 2011, 2015; Sullivan 2014). Regardless of the contributions of these additional sources, residential soils in Boolaroo remain a modifiable lead-exposure risk, with the quality of the soil far below that reasonably expected for a contemporary living environment.

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

Lessons from the LAS

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

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

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

Conclusion

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

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