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Authors
Kristensen, Louise J.
Taylor, Mark P.
Odigie, Kingsley O.
et al.

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Louise J. Kristensen, Mark Patrick Taylor, Kingsley O. Odigie, Sharon A. Hibdon, A. Russell Flegal

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

1. Introduction

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

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

Consequently, events that remobilize historic lead depositions are an environmental and human health concern. These include fires, which pose potential health risks due to smoke and particulate emissions (Weinhold, 2011) along with their role in redistributing elements such as mercury (Finley et al., 2009) and lead (Nriagu, 1989). Given that fluctuations in atmospheric lead emissions have been linked to changes in blood lead levels (Annest et al., 1983) and that there is still no established safe level for lead (NHMRC, 2009; WHO, 2010), the likelihood that bushfires mobilise historic lead depositions (Odigie and Flegal, 2011) warrants investigation. Previous studies have shown that heavy metals can become enriched in the residues formed from the burning of biomass (Nzihou and Stanmore, 2013). Up to 11.7% of the lead stored in the original biomass may remain as bottom (in situ) ash,
with the remainder forming airborne component (fly-ashes and dust) that can be widely dispersed (Narodoslawsky and Obernberger, 1996).

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

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

### 2. Methods

#### 2.1. Sample collection sites

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

Soil samples were collected from depths of 0–2 cm (surface) and 40–50 cm (deepest), using comparable trace metal clean procedures (Taylor et al., 2010). Additional soil and rock samples were collected from Kelmscott and Red Hill in 2012. The deeper soil samples were used to determine local natural background soil lead concentrations and isotopic composition as no natural lead isotopic compositions had been reported in the literature for the study sites. This assumption was based on previous studies using a similar approach to determine successfully both local natural background lead concentrations and isotopic compositions. Subsurface sampling of soils at depths >30 cm has been demonstrated previously to be a robust technique for characterizing the natural lead signature of a location (Gulson and Mizon, 1979; Gulson et al., 1981; Mackay et al., 2013; Taylor et al., 2010). Soil and rock samples were collected close to, but outside of, the bushfire areas with the footprint of the samples enveloping the ash sample areas.
Locations of the three fires studied, along with those of the Broken Hill and Mount Isa lead mines and sites referenced in the report are shown in Fig. 1. Therefore in order to establish the lead isotopic compositions and concentrations of ash sourced from Australian bushfires, this study analyses 56 ash samples, 8 surface soils, 7 subsurface soils and 6 local rocks, giving a total dataset of 77 environmental samples (Supporting information Table S1).

2.2. Sample preparation

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

2.3. Analytical methods

Sample processing at UCSC was undertaken in a HEPA (Class 100) filtered air hood, within a trace metal clean laboratory. Approximately 0.5 g of each ash and soil sample was oven dried at 65 °C. Ash samples were digested by refluxing twice in concentrated, trace metal grade HNO₃ as per the methods detailed in Flegal et al. (2010). Soil samples were processed using the digestion procedure detailed in Soto-Jimenez et al. (2006), and were refluxed once using trace metal grade aqua regia (HCl:HNO₃ 3:1 v/v). Both ash and soil solutions were analysed for lead concentrations using a Thermo Scientific XSeries 2 Quadrupole ICP-MS. Rhodium was used as an internal standard to correct for instrumental drift, which was also monitored by multiple analyses of a 1 ppb lead consistency standard. The consistency standard returned a mean concentration 0.90 ppb ± 0.77 RSD. Concentrations were calculated using the natural abundance of the calibration standards. The calibration accuracy was ascertained with multiple (n = 10) analyses of National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1640a (trace elements in natural water), with a mean recovery concentration of 0.22 ppb ± 7.25 RSD. The completeness of sample digestion and re-mobilization of lead was determined by concurrent digestion and analysis of SRM 1547 (peach leaves, n = 3) and SRM 1633b (coal fly ash, n = 4). Recovery for SRM 1547 was 91% (RSD 3%) while for SRM 1633b, recovery was 47% (RSD 8.5%). The former (SRM 1547) provided the best estimate of lead recoveries in ash samples because they are derived predominantly from vegetation and organic soil material, as observed previously (Odieg and Flegal, 2011). The soil samples were digested concurrently with NIST SRM 2704 (Buffalo River Sediment) and National Research Council Canada (NRCC) PACS-1 (British Columbia Harbor Sediment), which had recoveries of 43% (RSD 4%) and 76% (RSD 7.4%), respectively. The instrument detection limit, 3 x the standard deviation of blanks (n = 3) was 0.005 mg/L. The use of a concentrated HCl/HNO₃ digestion method in this study measures the acid-leachable (labile) levels of lead in the samples. The derived values are conservative relative to those achieved via a concentrated HF digestion, which would also extract natural lead within re-fractory aluminosilicates (Odieg and Flegal, 2011).

Lead isotopic compositions were measured with a Finnigan Element 2 High-Resolution ICP-MS, after optimizing sample volumes based on their lead concentrations. Analyses were conducted with concurrent measurement of 1 ppb SRM 981 (common lead), which was used to correct for isotopic fractionation. To determine the lead isotopic composition of each sample, two replicate analyses of one ash and two soil samples were digested in triplicate. Three separate measures of the same sample were weighed into separate Teflon vials for triplicate analysis. The analytical precisions (RSD) for 206Pb/204Pb, 207Pb/206Pb and 208Pb/206Pb were 0.23%, 0.25% and 0.31%, respectively. Lead isotopic composition analysis of additional soil and rock samples was carried out in 2013 at the National Measurement Institute, Sydney, using comparable digestion and analysis methods (Evans, 2013). Each sample was bracketed by concentration matched SRM 981 (common lead) and also run on a Finnigan Element 2 High-Resolution ICP-MS. The analytical precisions (RSD) for 206Pb/204Pb, 207Pb/206Pb and 208Pb/206Pb were 0.35%, 0.31% and 0.53%, respectively.

3. Results

3.1. Lead concentration and isotope composition

Lead concentrations and isotopic compositions of the ash and soil samples from the three bushfires are listed in Table S1. Supporting information. Lead concentrations of the soils, which ranged from 4 mg/kg to 23 mg/kg (dry weight), were bracketed by those of the ash samples, which ranged from 1 to 36 mg/kg. However, the isotopic composition of 506Pb/204Pb, 507Pb/206Pb and 508Pb/206Pb for most of the ash samples and many of the surface soils differed measurably from those of the deepest (40–50 cm) soil samples and rock samples, which were assumed to represent the natural or baseline values for the three study sites. For comparison, the lead isotopic composition of Broken Hill and Mount Isa ore bodies and Australian leaded petrol are provided in Table S2, Supporting information.

3.2. Tostaree, Victoria

Fig. 2 shows that the lead isotopic composition of 80% of ash samples from Tostaree are less than 2% different with respect to the local background soils (t-test p = >0.05 for both 206Pb/204Pb and 208Pb/206Pb), indicating influence from leaded petrol depositions in the forest is minimal. Given that Tostaree, a rural location with a population of <1000, is ~340 km east of the state of Victoria’s major city Melbourne (population ~ 4 million), it is not surprising that local lead is dominant in the ash samples. However, some of the Tostaree ash samples (in particular TS_2A, TS_4A, TS_13A, Table S1) have lead isotopic compositions that are comparable to those used in Australian leaded petrol (Table S2, Supporting information), particularly petrol used in the 1990s (Gulson, 2003). The isotopic composition of ash sample TS_2A plots closer to the lead isotopic composition of aerosols recorded in Victoria in the 1990s (Bollhöfer and Rosman, 2000) than the local lead signature (Fig. 2). Although the total lead concentration is low (1.6 mg/kg) in ash sample TS_2A, its lead isotopic composition indicates that Australian leaded petrol was the predominant lead source in this ash, even though the relatively pristine site is ~340 km from the nearest city. Local surface soil samples (0–2 cm) collected immediately adjacent to the burnt bushland also have an isotopic composition distinct from that of background soil. The soil surfaces and majority of the ash samples fit a simple two end-member mixing model between the local lead of the area and the lead isotopic compositions of leaded petrol used in Australia (Table S1; Fig. 2). Isotopic compositions of ash samples that do not fit within the two end-member mixing model may reflect either a wider range of natural lead isotopic compositions in the area or another, as yet unidentified, source of industrial lead.

3.3. Red Hill, Western Australia

Isotopic compositions of ash and surface soils (0–2 cm) differ from those of background soil (40–50 cm) and rock from the Red Hill Fire (Fig. 3, Table S1). Analysis of the isotopic composition of the ash samples shows that 80% of ash samples are >2% different compared to local background soil and rock, with the two samples groups being statistical different for only 206Pb/207Pb (t-test, t(17) = 3.912 p = 0.001). These differences are partially attributed to leaded petrol emissions from the Perth region, which was Australia’s third largest consumer of petrol in 1976 (Farrington and Boyd, 1981) and the fourth largest in 1985 (Farrington, 1988). The isotopic compositions of those legacy inputs are characterized by aerosols in the region during that period (Fig. 3) (Bollhöfer and Rosman, 2000).

However, isotopic compositions of the ash and surface soil samples indicate they do not fall within a simple two end-member mixing model of natural lead and petrol lead (Fig. 3), evidencing other sources of lead in the ash and surface soils. These could include atmospheric depositions from the Red Hill Quarry, operating since 1963, and the Red Hill Waste Management Facility, operating since 1981. The quarry produces granite and diorite/dolerite aggregate (EPA, 2011) while the waste management facility accepts Class 1 to IV waste, which can include contaminated soils (EPA, 1997). The isotopic composition of the Red Hill ash lead does not reflect lead recoveries at the former Freemantle Smelting Works (closed 1920), located 6 km south east of Perth city (Fig. 1). Red Hill is ~40 km downwind of Freemantle, in the track of one of the most energetic sea breeze systems in the world (Masselink,
The Fremantle Smelting Works sourced lead from the Western Australian Eastern Goldfields (206Pb/207Pb: 0.933; 208Pb/207Pb: 2.289, Cumming and Richards, 1975) and Northampton Complex ~500 km north from Perth (206Pb/207Pb: 1.145; 208Pb/207Pb: 2.465, Richards et al., 1985). In both cases, the smelted lead has isotopic compositions distinct from the environmental samples analysed in this study (Fig. 3).

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

3.4. **Kelmscott, Western Australia**

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

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

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

3.5. **Significance of findings**

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

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**Fig. 4.** Lead isotopic composition of ash and soil samples collected at the Kelmscott, Perth, Western Australia. Australian leaded petrol lead isotopic composition is indicated by the dotted and dashed lines. Lead isotopic signature of 1990s Perth aerosols (Bollhöfer and Rosman, 2000) and soils (Bollhöfer et al., 1999) indicated by shaded regions. The standard error inset represents $^{206}\text{Pb}/^{207}\text{Pb}$: 0.018 and $^{208}\text{Pb}/^{207}\text{Pb}$: 0.015.
Hill (Gulson et al., 1995) and Mount Isa (Taylor et al., 2010), it is worth noting that environmental samples analysed in this study were collected from what are considered to be relatively pristine environments of national and regional parks, in a large, sparsely populated continent. However, because this study measured in situ ash (akin to bottom ash sensu Narodoslawsky and Obernberger, 1996), it is likely to be a conservative estimate of the effect of wildfires on the re-release of lead to the environment because most of the lead is mobilised in an aerosol-ash component. Therefore, given the pervasive effect of industrial lead emissions on the environment (Bollhöfer and Rosman, 2000, 2001; Nriagu, 1996), and the fact that wildfire events are likely to increase in frequency, intensity and magnitude due to global temperature rises (Hennessey et al., 2006; IPCC, 2007; Liu et al., 2010), we contend that historic industrial lead depositions will be concomitantly re-released during such events. Of particular concern are fires occurring near urban centres or industrial towns where lead and other anthropogenic metal loadings in the environment are higher (Chiaradia et al., 1997; Farrington and Boyd, 1981; Farrington, 1988; Gulson et al., 1981; Laidlaw and Taylor, 2011) and because a greater proportion of the industrial emissions from leaded petrol occurred in these locations. Given the paradigm that there still is no established safe level for lead (NHMRC, 2009; WHO, 2010), it is feasible that young children could be at risk of additional lead exposures from wildfires, especially when they are close to large urban centres.

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Appendix A. Supplementary data

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

References


References


