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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