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Size-resolved dust and aerosol contaminants associated with copper and lead smelting emissions: Implications for emission management and human health

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HIGHLIGHTS

- Lead and copper smelting produce significant atmospheric concentrations of lead and arsenic.
- Atmospheric lead and arsenic concentrations depend on particle size.
- Lead isotopic analysis can be used to assess source of atmospheric contamination from smelters.

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ABSTRACT

Mining operations, including crushing, grinding, smelting, refining, and tailings management, are a significant source of airborne metal and metalloid contaminants such as As, Pb and other potentially toxic elements. In this work, we show that size-resolved concentrations of As and Pb generally follow a bimodal distribution with the majority of contaminants in the fine size fraction (<1 μm) around mining activities that include smelting operations at various sites in Australia and Arizona. This evidence suggests that contaminated fine particles (<1 μm) are the result of vapor condensation and coagulation from smelting operations while coarse particles are most likely the result of windblown dust from contaminated mine tailings and fugitive emissions from crushing and grinding activities. These results on the size distribution of contaminants around mining operations are reported to demonstrate the ubiquitous nature of this phenomenon so that more effective emission management and practices that minimize health risks associated with metal extraction and processing can be developed.

1. Introduction

The role of mining activities in the fate and transport of environmental contaminants is an important yet under investigated field of study (Csavina et al., 2012). Dust and aerosol produced by mining operations often contain elevated levels of metal and metalloid contaminants, including the toxic elements Pb and As (Benin et al., 1999; Bellinger, 2008; Taylor et al., 2010; Csavina et al., 2011; Mackay et al., 2013). Both Pb and As are known to have contributed to negative ecological and human health effects in surrounding communities, including elevated blood Pb levels in children (Queensland Health, 2008; Munksgaard et al., 2010; Simon and Lewis, 2010). However, the specific physiochemical nature of these exposures remains poorly understood. With dust emissions predicted to increase as climate change intensifies drought in arid and semi-arid regions and human land use increases, contaminant transport from mining operations is likely to become increasingly important in the coming decades (Breshears et al., 2012).

Two Australian mining communities of Mount Isa, Queensland, and Port Pirie, South Australia, are examples of significant contaminant emissions from smelting and mining activities. At Mount Isa, Cu, Zn, Pb and Ag mining and smelting result in the emission of significant quantities of airborne contaminants, with As and Pb emissions for 2009/2010 being 20,000 kg and 120,000 kg, respectively (Department of Sustainability et al., 2011). With a population of 21,000, Mount Isa's most recent study reported that children aged 1–4 years had mean blood Pb levels (BLL) of 5 μg/dL, with 37% having levels >6 μg/dL and 11.3% having levels >10 μg/dL (Queensland Health, 2008). Pb and Zn smelting in Port Pirie is also associated with significant atmospheric pollution, with As and Pb total suspended particulate (TSP) measurements

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in 2009 as high as 0.25 $\mu g/m^3$ and 19.7 $\mu g/m^3$, respectively, taken 0.4 km from smelting activities (South Australia Environmental Protection Agency, 2012). In 2005, 56.5% of children in Port Pirie had BLL >10 μg/dL (Simon and Lewis, 2010). Epidemiological and environmental studies have revealed that dust generation associated with mining and smelting activities largely contributes to the extensive childhood Pb poisoning within the Australian mining communities of Port Pirie and Mount Isa (Mackay et al., 2013; Taylor et al., 2010; Simon et al., 2007).

The towns of Hayden and Winkelman in Arizona have a combined population of approximately 1200. The site includes a concentrator, a smelter and tailings facilities, and it is currently administered through an Administrative Settlement Agreement and Order on Consent between EPA, ASARCO (the plant proprietor) and the Arizona Department of Environmental Quality. In 2005, soil analysis showed that arsenic, lead and copper levels exceeded their respective residential soil remediation levels (US Environmental Protection Agency, 2008). In addition, elevated concentrations of arsenic, lead, copper, chromium and cadmium have been measured in atmospheric air samples.

Many studies have explored the neurotoxic nature of Pb, especially in children who are more adversely impacted due to their early stage in neurological development and their higher relative contaminant dosage at the same concentration when compared to adults (Baghurst et al., 1992; Jusko et al., 2008; Soto-Jimenez and Flegal, 2011). Additionally, higher Pb exposures have been shown to lower academic performance and contribute to negative social outcomes related to antisocial behavior and criminality (Wright et al., 2008). Similarly to Pb, As has also shown impaired cognitive development in children and may have a synergistic toxic effect with Pb (Hwang et al., 1997; Calderón et al., 2001; Wright et al., 2006). Arsenic is also a known carcinogen and, even though the World Health Organization (World Health Organisation (WHO), 2000) has not set a safe level of atmospheric concentrations, a value of 6.6 ng/m^3 has been identified as a lifetime risk level of 1:100,000. Due to the known effects of these pollutants, human Pb and As exposure should be minimized.

Dust and aerosol generated from mining operations vary in size, which is critical for physical interactions in the environment and human exposure. An important route of human exposure is the inhalation of the airborne contaminated particulate. A knowledge of the physical and chemical properties and size distribution of inhaled aerosols is necessary to completely assess risks associated with contaminant exposure (Spear et al., 1998). The size of the particle can predict the efficiency and region of deposition in the respiratory tract (Park and Wexlerm, 2008). Coarse particles (>3 μm), such as those resulting from crushing and grinding of ore, deposit in the upper respiratory system and are swallowed and eliminated through the digestive system (Hinds, 1999). In contrast, fine particles (<1 μm), such as those originating from smelting operations, are respired deep into the lungs where they may be transported directly to the blood stream and have a higher bioavailability due to their higher surface to volume ratios (Krombach et al., 1997; Park and Wexlerm, 2008; Valiulis et al., 2008). Particle size is also a critical characteristic for transport distance and building penetration within the adjoining environment: fine particles can travel further in the environment with residence times in the atmosphere that may reach days (Hinds, 1999). Therefore, determining the chemical composition of dust and aerosol from mining operations as a function of particle size is crucial in quantifying the potential deleterious effects on human health and the environment.

This study reports on the size-resolved As and Pb concentrations found in dust and aerosol in the Australian communities of Mount Isa and Port Pirie mentioned earlier, as well as in Hayden, Arizona. These multi-sire measurements, performed with common sampling and analysis techniques, allowed us to perform general observations on the size-fractionated contaminant concentration in the atmosphere around mining operations. In addition, we report on the use of lead isotope analysis to asses sources of contamination in the studied sites.

2. Materials and methods

Ambient dust and aerosol sampling was carried out in the communities of Port Pirie (South Australia), Mount Isa (Queensland), and Hayden (Arizona), which are impacted by smelting activities. Samples were also collected in urban settings of Tucson (Arizona) and Sydney (New South Wales), and where mine tailings with no smelting operations are the primary source of dust and aerosol in the communities of Green Valley (Arizona) and Iron King (Arizona), for comparison purposes. An overview map of these sites can be seen in Fig. 1.

According to US Environmental Protection Agency (2008), the Hayden smelter processes 27,400 tons of ore per day from pre mining operations in nearby Green Valley and Ray, Arizona. Copper sulfide ore is crushed and milled at the Hayden facility and concentrated by froth flotation using sulfuric acid. The waste from the flotation is sent as slurry to tailing impoundments while the concentrate is sent to the smelting facilities, which include an oxygen flash furnace, converters, anode casting, oxygen plant and acid plant. Electrostatic precipitators are used to reduce particulate matter in the air emissions from bed driers and flash furnace. The matte from the flash furnace is sent to a converter furnace to remove impurities and blister the copper. Slag waste from the smelting process is dumped in open waste stockpiles. A bag house is used to capture the converter's secondary particulates. Final refining occurs off-site and emissions from the smelter are released through a 330-m tall stack.

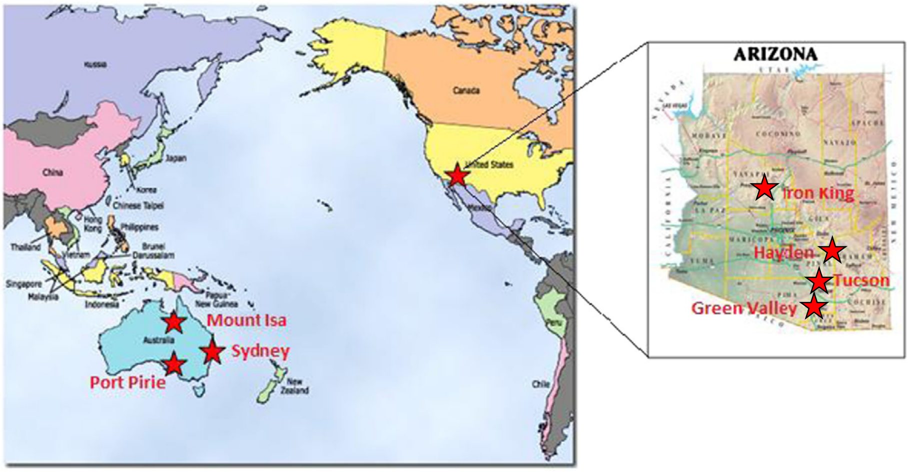

Fig. 1. Field sites for size fractioned aerosol sampling: Mount Isa, Port Pirie and Hayden mining sources include smelting activities; Tucson and Sydney represent urban settings.