

METALS AND METALLOIDS IN ATMOSPHERIC DUST: USE OF LEAD ISOTOPIC ANALYSIS FOR SOURCE APPORTIONMENT

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Introduction

Metal- and metalloid-laden dust and aerosol particles are produced during mining operations in a wide range of sizes. Coarse particles ($> 1 \mu\text{m}$ aerodynamic diameter) are produced mainly by mechanical action like grinding and wind erosion (Csavina et al. 2011) while fine particles ($< 1 \mu\text{m}$) are the result of molten ore processing and smelting, being produced by condensation and coagulation of vapors (Jacob, 1999; Banic et al., 2006). The impact of airborne particles on human health depends on particle diameter and composition. Particles larger than $10 \mu\text{m}$ are generally filtered out by the upper respiratory tract while particles smaller than $10 \mu\text{m}$ (PM_{10}) are inhaled and may be transported to the lungs where they are phagocytized by alveolar macrophages and transported to the blood stream (Zheng et al., 2004). The composition of the particles also plays a key role in health effects. Of particular concern is the presence of lead and other contaminants (e.g., arsenic) in atmospheric dust and aerosol that result from mining activities (Csavina et al., 2011, 2012; Mackay et al., 2013).

The atmosphere is the major initial recipient of lead among all environmental compartments. Global anthropogenic sources of lead are at least one order of magnitude higher than natural sources (Komárek et al., 2008). The determination of potential sources of atmospheric lead is important since its production can be controlled in advance, minimizing unwanted exposures to this toxic metal. However, it is difficult to discriminate between sources of lead and other metal and metalloid contaminants by only knowing their total concentration (Hopper et al., 1991). For this reason, lead isotopic analysis has been introduced as a “fingerprinting” technique for lead contamination. Each source of lead may have a specific isotopic composition and the differences in this composition may be used to discriminate between possible sources (Komárek et al., 2008).

The use of lead isotopes to determine possible sources has been widely reported (e.g., Munksgaard and Parry, 1998; Zheng et al., 2004; Chen et al., 2005; Grousset et al., 1994; Veysseyre et al., 2001; Kurkjian et al., 2002). Lead has four stable isotopes (average molar abundances in parenthesis): ^{204}Pb (1.4 %), ^{206}Pb (24.1 %), ^{207}Pb (22.1 %) and ^{208}Pb (52.4 %). ^{204}Pb is the only non-radiogenic isotope and its abundance has remained constant over time (Russell and Farquhar, 1960). The abundances of ^{206}Pb , ^{207}Pb and ^{208}Pb in minerals vary because they are derived from the decay of ^{238}U , ^{235}U and ^{232}Th , respectively (Adgate et al., 1998). Isotopic composition of the radiogenic isotopes varies in different ores, depending on the age of their geological formation (Faure, 1986). An advantage of the use of lead isotopes for source apportionment is the fact that isotopic fractionation does not happen in industrial or environmental processes (Ault et al., 1970), owing mainly to the high atomic mass of lead. Lead isotopic composition is often expressed in terms of the concentration ratios $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ (Chen et al., 2008; Zheng et al. 2004).

Methodology

Study Site

The Hayden site is located approximately 80 km northeast of Tucson, Arizona. It is comprised of two towns - Hayden and Winkelman - with a combined population of approximately 1200. Currently, the site includes a concentrator, a copper smelter and tailings facilities. It is located at the confluence of the Gila and San Pedro Rivers. The processed copper ore originates from various mines in the vicinity, including the Ray mine. The Ray mine consist mainly of a porphyry copper deposit hosted in Pinal schist and Pioneer shale. In 2005, soil analysis showed that arsenic, lead and copper levels exceeded their respective residential soil remediation levels (EPA 2012). The Environmental protection agency has reported elevated concentrations of arsenic, lead, copper, chromium and cadmium in atmospheric air and soil samples in Hayden and Winkelman, (EPA 20012).

Sampling

The sampling site was located on the roof of a single-story High School building, approximately 2 km E of the mine tailings impoundment and 1 km SSE of the smelter (Figure 1). A weather station and data logger (CR800, Campbell Scientific) providing information about temperature, relative humidity, wind speed and wind direction, was also present at the site. Wind speed and wind direction were analyzed with WindRose Pro (Enviroware) software. In Tucson, AZ, the sampling site was located on the roof of the five-story Physics and Atmospheric Sciences building at the University of Arizona.

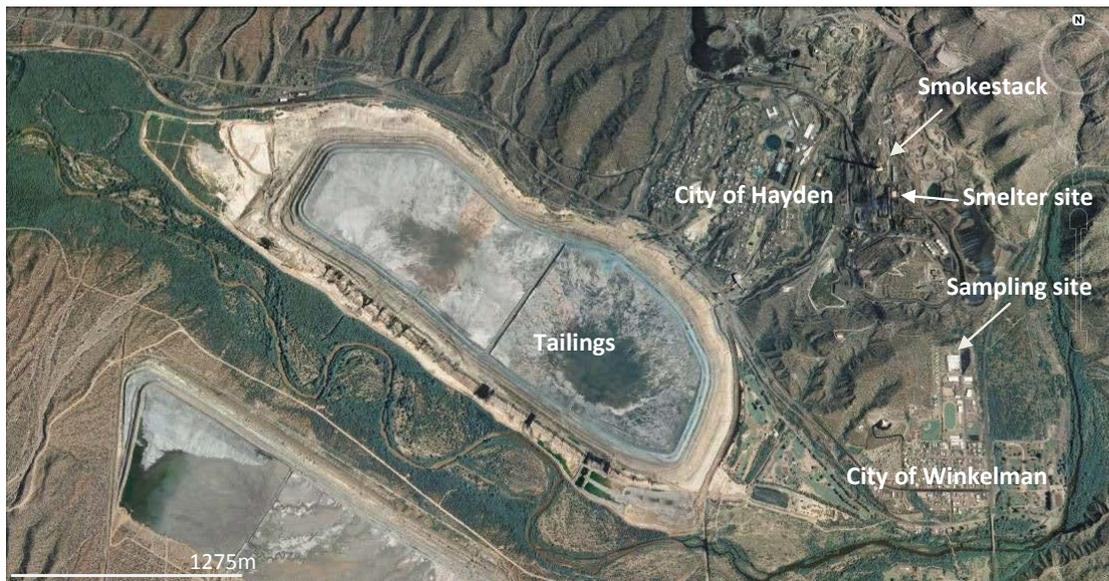


Figure 1. Satellite picture of the sampling site in Hayden, AZ, with locations of mining and sampling operations. Source: Google Earth

A ten-stage micro-orifice uniform deposit impactor (MOUDI; M110-R, MSP Corporation) (Marple et al. 1991) was used to collect atmospheric dust and aerosol. The MOUDI was operated at a flow rate of 30 L min^{-1} for 96-h sampling periods. The calibrated cut points (d_{50} -values) for the MOUDI sampler are 18, 9.9, 6.2, 3.1, 1.8, 1.0, 0.55, 0.32, 0.18, 0.10 and $0.054 \mu\text{m}$ equivalent aerodynamic diameters. Teflon substrates (PTFE membrane, $2\text{-}\mu\text{m}$ pore size, 46.2 mm diameter, Whatman) were used for sample collection.

Sample Preparation and Analysis

Exposed Teflon substrates were transferred to glass vials and extracted with 15 mL of *aqua regia* (1.03 M HNO_3 /2.23 M HCl, trace-metal grade) in a sonicator at $80 \text{ }^\circ\text{C}$ for 60 minutes (Harper et al., 1983). Aliquots of 1.2 mL were diluted to 4 mL with deionized water before analysis. Prior to lead isotope analysis, samples were concentrated on a hot plate.

An ICP-MS (Agilent 7700X with Octopole reaction system) was used for the determination of lead, arsenic and cadmium, as well as lead isotopes. The equipment was tuned for robust plasma conditions to reduce the formation of oxides to less than 2%. The analytical precision of lead isotopic ratios was under 0.5 % for the concentration ratios $\text{Pb}^{207}/\text{Pb}^{206}$ and $\text{Pb}^{208}/\text{Pb}^{206}$.

Results and Discussion

Figure 2 shows a comparison of concentrations in atmospheric particulate at the two field sites for a representative sampling period. Contaminant concentrations follow a bimodal distribution at the Hayden site with maxima around 0.18 and $9.9 \mu\text{m}$. This trend was consistently seen over sampling periods spanning several years of sampling (Csavina et al., 2011). The highest concentration of contaminants is

present in the accumulation mode (particles between 0.1 and 1 μm) (Seinfeld and Pandis, 2006). Smelting and high-temperature processes release submicron particles formed by condensation of vapors, which coalesce to enrich the accumulation mode. Note that both contaminant concentration and particle mass concentration follow a bimodal distribution at the Hayden site.

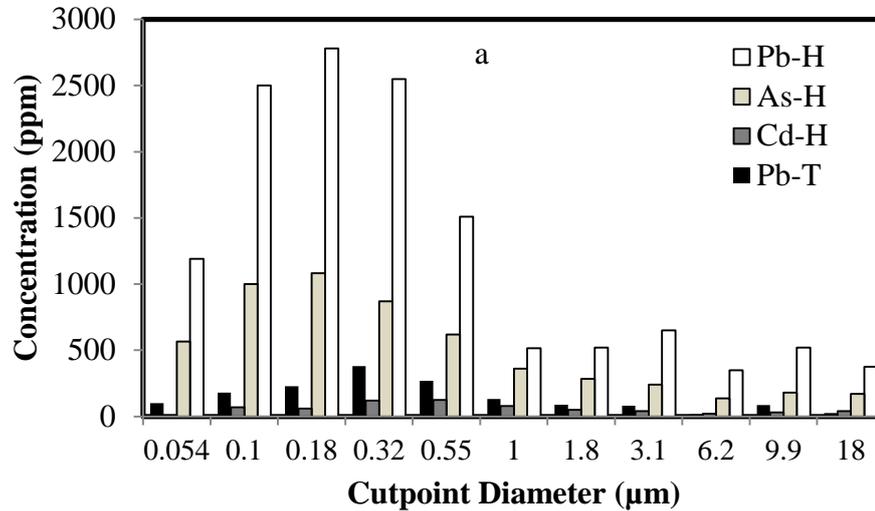


Figure 2. Concentrations (wt/wt) of As, Cd and Pb as a function of particle size from representative (consecutive 96-hour operation) MOUDI samples of dust and aerosol in atmospheric air taken at the two sites (H – Hayden site, T – Tucson site).

Lead isotope analysis was performed at the two sites of study. Particles in the range of 0.32 - 0.55 μm (denoted as fine particles here) and 3.1 - 6.2 μm (coarse particles) were analyzed to obtain the lead isotopic composition. Figure 3 shows the lead isotope ratios associated with two sampling periods at Hayden, along with the corresponding wind roses. Two different isotopic signatures for coarse and fine particles are evident (Figure 3a), which suggests the existence of two different atmospheric lead sources. The isotopic ratios of the fine particles coincide with those of the Ray Mine which is the main ore source for the smelter. This is evidence that the lead found in the fine particles is associated with condensation of high-temperature vapors produced at the smelting site. The different isotopic signature of the coarse particles suggests a different origin, possibly related to the background lead present in the area. It is interesting to note that the two sampling periods shown in Figure 3 corresponded to completely different average wind directions. In fact, the concentration of lead in the fine particles during period 1 (12.5 ng/m^3 , wind from WSW) was around twice the concentration for period 2 (6.2 ng/m^3 , wind from NE). Note that during period 1, wind patterns favor the direction from the smelter to the sampling site.

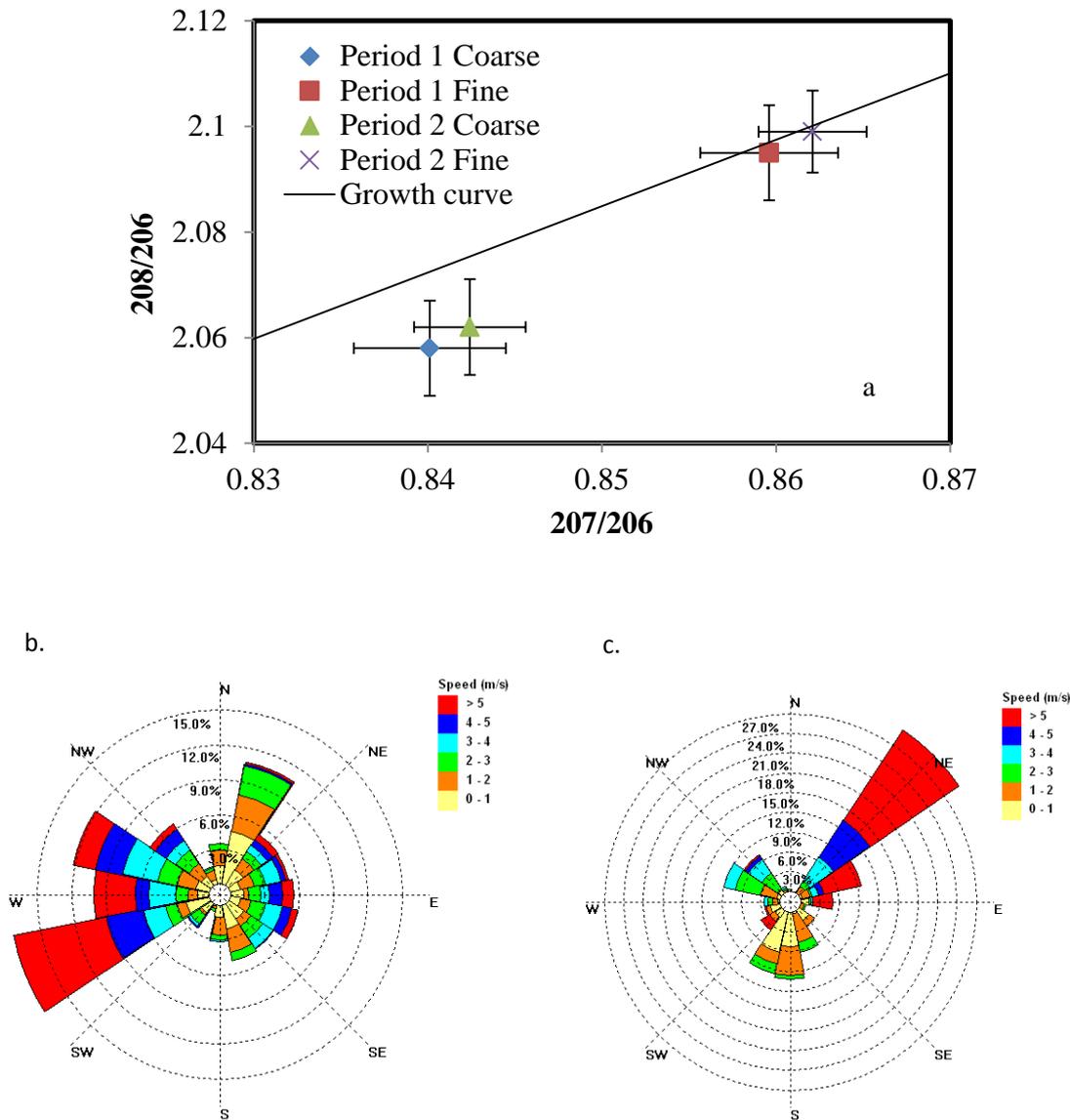


Figure 3. (a) Lead isotope concentration ratios obtained during MOUDI sampling for two 96-hour sampling periods at the Hayden site. Error bars show standard deviations of triplicate measurements by ICP-MS; (b) Wind rose for period 1; (c) Wind rose for period 2.

Three different programmed sets of samples were taken with the MOUDI at the Hayden site (periods 3 to 5). The MOUDI was programmed to sample only when the wind was coming from the smelting area ($300\text{-}360^\circ$). Results obtained from these samples, as well as a representative wind rose of the sampling periods are presented in Figure 4. Figure 4a shows that both coarse and fine particles exhibit only one isotopic signature with high ratios similar to the results shown on Figure 3a for fine particles. This indicates that for the programmed samples the smelter was the predominant source.

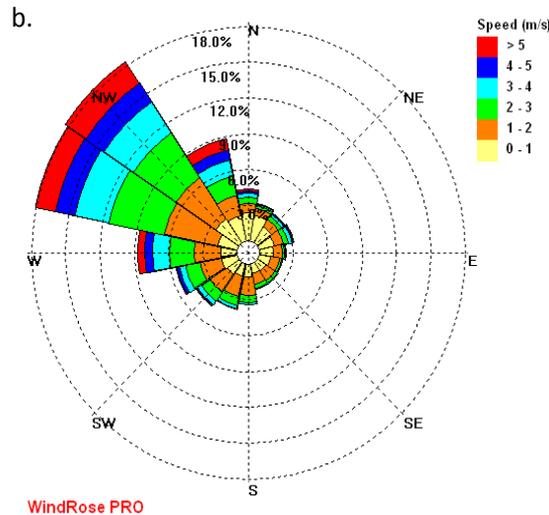
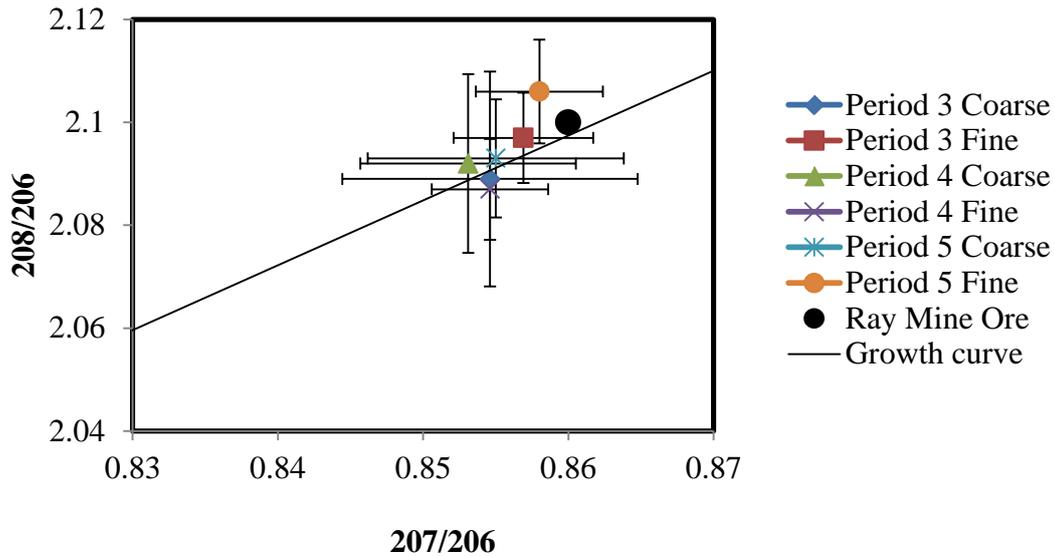


Figure 4. (a) Lead isotopic ratios obtained from MOUDI samples during programmed sampling when wind direction was from the smelter to the sampling site (300-360°) at the Hayden site; (b) Representative wind rose of the programmed sampling periods.

The coarse particle lead ratios (Figure 3a) were similar to those found in samples taken at the Tucson site, which is free of mining activity (Figure 5). Coarse particles may be associated with wind-blown soil from the site. For Tucson, coarse and fine particles had the same lead isotopic ratios. This result suggests that the Tucson lead, which coincides with the Hayden lead in coarse particles, is unaffected by smelting activities, and it might be representative of a background source of lead common to the region, presumably legacy lead from fuel sources, since this isotopic signature is similar to that of lead used as a gasoline additive, which originates from

Missouri ores: $^{208}\text{Pb}/^{206}\text{Pb} = 2.07$, $^{207}\text{Pb}/^{206}\text{Pb} = 0.84$ (Sutherland et al., 2003; Bollhöfer and Rosman, 2001).

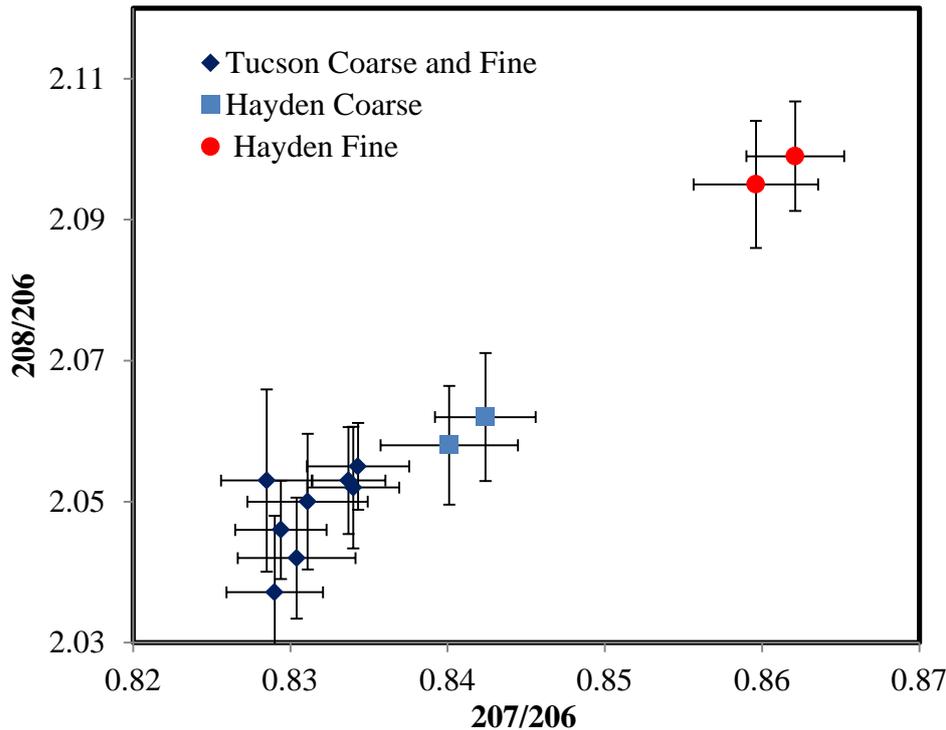


Figure 5. Comparison between lead isotopic ratios obtained in atmospheric dust and aerosol in Hayden and Tucson, AZ.

The results presented above point to a significant atmospheric contamination at the Hayden site that originates from smelting activities.

Conclusions

The results obtained in this work demonstrate that lead isotope analysis can be used for source apportionment of metal and metalloid contaminants from mining operations. At the mining site in Hayden, AZ, two different lead sources were identified: one associated with fine particles originating from condensation of high temperature vapors emitted at the smelter site, and another one associated with a regional background, which shows the same isotopic composition as legacy lead used in fuels.

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