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

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ABSTRACT

Mining activities generate aerosol in a wide range of sizes. Smelting activities produce mainly fine particles (<1 µm). On the other hand, milling, crushing and refining processes, as well tailings management, are significant sources of coarse particles (> 1 µm). The adverse effects of aerosols on human health depend mainly on two key characteristics: size and chemical composition. One of the main objectives of this research is to analyze the size distribution of contaminants in aerosol produced by mining operations. For this purpose, a Micro-Orifice Uniform Deposit Impactor (MOUDI) was utilized. Results from the MOUDI samples show higher concentrations of the toxic elements like lead and arsenic in the fine fraction (<1 µm). Fine particles are more likely to be deposited in the deeper zones of the respiratory system; therefore, they are more dangerous than coarse particles that can be filtered out in the upper respiratory system. Unfortunately, knowing the total concentration of contaminants does not give us enough information to identify the source of contamination. For this reason, lead isotopes have been introduced as fingerprints for source apportionment. Each source of lead has specific isotopic ratios; by knowing these ratios sources can be identified. During this research, lead isotopic ratios were analyzed at different sites and for different aerosol sizes. From these analyses it can be concluded that lead isotopes are a powerful tool to identify sources of lead. Mitigation strategies could be developed if the source of contamination is well defined.

Environmental conditions as wind speed, wind direction, relative humidity and precipitation have an important role in the concentration of atmospheric dust. Dry environments with low relative humidity are ideal for the transport of aerosols. Results
obtained from this research show the relationship between dust concentrations and meteorological parameters. Dust concentrations are highly correlated with relative humidity and wind speed. With all the data collected on site and the analysis of the meteorological parameters, models can be develop to predict the transport of particles as well as the concentration of contaminants at a specific point. These models were developed and are part of the results shown in this dissertation.
CHAPTER 1: Introduction

Mining is considered one of the most important economical activities in the United States. In 2010, this sector had a contribution of $225 billion to the gross domestic product (GDP) (NMA, 2010). Arizona is one of the most important producers of copper. In 2006, around 65 percent of the nation’s copper was produced in the State (AZGS, 2013). Despite the importance of this economical activity, the adverse effects that it has on the environment have to be considered. Metal and metalloid containing particles are produced during mining operations in a wide range of sizes. Coarse particles (>1 µm) are produced mainly by mechanical action like grinding and mine tailings erosion (Csavina et al. 2011). Fine particles are mainly produced during smelting by condensation, diffusion and coagulation processes (Jacob, 1999; Banic et al. 2006; Wong et al., 2006). Chemical composition of these particles depends on the origin of the ore, as well as physical and chemical processes that the ore has been exposed to. There are several studies that found elevated concentrations of toxic metals like Pb and As in particles produced by mining operations (Csavina et al., 2014, 2012, 2011; Taylor et al., 2010; Monna et al., 2006).

The effects of airborne particles on human health depend on particle size and composition. Particles larger than 10 µm are generally filtered out by the upper respiratory tract and particles smaller than 10 µm (PM\textsubscript{10}) are inhaled and transported to the lungs where they are phagocytized by alveolar macrophages and transported to blood stream (Zheng et al. 2004). Particle composition also plays a key role in health effects; for example, lead causes multiple adverse effects on human health affecting peripheral and central nervous system, kidneys and blood pressure (Needleman, 2004). In children it causes irreversibly effects on the cognitive performance (Lanphear et al., 2000). On the
other hand, As is associated with an increased risk of cancer of skin and lungs (Bates et al., 1992; Chiou et al., 1995). In order to have a complete risk assessment, it is important to correlate the concentrations of contaminants with the size of the particles. For this reason, one of the main objectives of this work is to characterize the size distribution of the contaminants at different sampling sites.

The knowledge of total concentrations of lead or arsenic does not give any information about the source of contamination. Total concentrations only allow us to identify the extent of the problem. For this reason, lead isotopes have been introduced as a “fingerprinting” method: each source of lead has a specific isotopic signature. Isotopic composition between the radiogenic isotopes varies in different ores, depending on the age of their geological formation (Faure, 1986). Therefore, each ore has specific isotopic composition, which will be characteristic of the source of contamination. By knowing these differences in isotopic signatures, it is possible to identify/discriminate between possible sources. Lead is an excellent tracer of contamination because isotopic fractionation does not happen in industrial or environmental processes and it will retain the specific isotopic composition of the ore after being released into the environment (Ault, et al. 1970). The use of lead isotopes to determine possible sources has been widely reported (e.g., Zheng et al., 2004; Chen et al., 2005; Grousset et al., 1994; Veysseyre et al., 2001; Kurkjian et al., 2002).

In addition to lead isotopes, some other techniques have been widely used to identify sources of contaminants. One of these techniques is the use of strontium isotopes (Widorey, et al, 2010; Kanamaya et al. 2002; Xu and Han, 2009). Another important technique that has been used to discriminate between anthropogenic and natural sources
is the enrichment factor (EF). The enrichment factor (EF) is based on the standardization of the concentration of the element under study with respect to that of a different element used as reference (Meza - Figueroa et al., 2009).

Another important topic covered in this dissertation is the transport of particles. Particle size is a key characteristic that influences the mechanisms of transport. Coarse particles settle out of the atmosphere in a relatively short time (seconds to hours). On the other hand, fine particles have an average residence time up to ten days; therefore, they can be transported further in the environment (Seinfeld and Pandis, 2006). In addition to particle size, environmental factors such as topography, relative humidity, precipitation and wind speed/velocity should be considered when analyzing dust transport mechanisms (Csavina et al., 2014). According to the International Panel for Climate Change (IPCC, 2007) it is predicted that drought will increase during the next decades in arid and semi-arid regions, as a consequence, the potential for dust emissions could increase significantly.

This dissertation is organized in three main sections: chapter 1: introduction which gives a general idea about the research performed; chapters 2 – 5 contain published articles and work intended to be published in which the author had a major contribution; the final section of this dissertation is the appendix which contains published articles and work intended to be published in which the author had a minor contribution. In the appendix section, supplemental material is provided. Finally, Chapter 6 presents the main conclusions from the research developed during the Ph D program.

For general information purposes, a brief description of each of the chapters as well as the author’s contribution is provided below:
Chapter 2: Use of Lead Isotopes to Identify Sources of Metal and Metalloid Contaminants in Atmospheric Aerosol from Mining Operations

This study basically describes the value of using lead isotopes as a fingerprinting technique to track metal and metalloid pollutants. The study was performed in Hayden-Winkelman, AZ. This site is characterized by the presence of contaminated mine tailings and smelting activities. Lead isotopes where determined for fine and coarse particles in atmospheric aerosol in order to know if they were produced or not by different sources. Besides atmospheric aerosols, soil samples were also analyzed for lead isotopes to determine the possible deposition of particles in the surroundings of the mining activities.

The author of this dissertation performed the sample preparation, data analysis and led the writing for the publication.

Chapter 3: Laboratory Dust Generation and Size-Dependent Characterization of Metal and Metalloid-Contaminated Mine Tailings Deposits

This study was performed at the Iron King Superfund site. Samples of mine tailings as well as soil at different distances from the mine tailings were collected. The samples were separated in three different sizes by using a laboratory dust generator. Results show that metal and metalloid contaminants are more concentrated in fine particles with aerodynamic diameters less than ten micrometers. In order to perform toxicological assays a large mass of sample is required, which cannot be easily obtained from total suspended particulate (TSP) samplers. In addition, TSP samples do not provide size distribution of the contaminants. The main advantage of the method proposed in this study is the generation of a large mass of sample with a specific size distribution.
The author of the dissertation prepared the sampling plan and performed the chemical analysis as well as the interpretation of the lead and strontium isotopic data.

Chapter 4: Effect of Wind Speed and Relative Humidity on Atmospheric Dust Concentrations in Semi-Arid Climates

This study was performed in two sites: Green Valley, Arizona, USA, and Juarez City, Chihuahua, Mexico. The main objective of this study was to analyze the aerosols concentrations obtained during dust events. Sampling was performed during high wind speed events in order to correlate concentrations and wind speed. Another important parameter to consider was relative humidity, it was demonstrated that both parameters play an important role in the concentration of resuspended dust.

The author of the dissertation designed the sampling plan followed in Juarez, Chihuahua, Mexico and also analyzed all the data obtained at this site.

Chapter 5: Size-Resolved Dust and Aerosol Contaminants Associated With Copper and Lead Smelting Emission: Implications for Emission Management and Human Health

This study was conducted at three different sites: Hayden-Winkelman, Arizona; Mount Isa, Australia; Port Pirie, Australia. One of the objectives of this study was to compare the size resolved contaminant concentrations in atmospheric aerosol among the three sites. The three sites yielded results in which metal and metalloid concentrations followed a bimodal distribution with the majority of the contaminants in the fine particles (< 1 μm). This bimodal distribution might indicate the presence of two different sources of contaminants. Coarse particles might be generated by resuspension of dust while fine particles are most probable being generated by high temperature process like smelting
activities. In addition to total concentrations of metals and metalloids, lead isotopic analysis was considered in order to have a better understanding of the possible sources of lead.

The author of the dissertation performed all the chemical analysis of the samples obtained and the data analysis for the lead isotopes.

Chapter 6: Conclusions

In this chapter the author presents the main findings and conclusions obtained from the research developed during the doctorate program.

Appendix A: Simulation of Windblown Dust Transport from a Mine Tailings Impoundment Using a Computational Fluid Dynamics Model

The site selected for this study was the Iron King Superfund site. The study was focused on the elaboration of a computational fluid dynamics model in order to have information about the transport of particles from the tailings to the surrounding regions. Topographical characteristics of the site were included in the model to have more representative results; also meteorological variables were associated with the transport of particles.

The main contribution of the author in this study was the installation and maintenance of the field equipment required for the study such as Dusttraks and meteorological stations.

Appendix B: Development of a dust deposition forecasting model for a mine tailing impoundment using in situ observations and idealized particle simulations

This study was focused on the Iron King Superfund site. A model that can be used to forecast transport and deposition of windblown dust was developed during the study. In
situ observations from the tailings as well as theoretical simulations were used to build up
the model.

The main contribution of the author in this study was the installation and maintenance of
the field equipment required for the study such as Dusttraks and meteorological stations.
Also the author worked on the analysis of the data obtained from the Iron King
remediation report and used to develop the model.

Appendix C: Verification of windblown dust deposition forecasting model using
inverted-disc samplers

This study was focused at the Iron King Superfund Site and the main objective was to use
inverted-disc depositions samplers to verify the accuracy of the deposition model created
by Stovern et al (2014). Depositions patterns were compared to real data taken from the
site. The data included gravimetric analysis, chemical composition and lead isotopic
analysis.

The main contribution of the author in this study was the treatment and data analysis of
the samples to determine the chemical composition of the dust collected, as well as the
lead isotopic composition.
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CHAPTER 2: Use of Lead Isotopes to Identify Sources of Metal and Metalloid Contaminants in Atmospheric Aerosol from Mining Operations

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Abstract

Mining operations are a potential source of metal and metalloid contamination by atmospheric particulate generated from smelting activities, as well as from erosion of mine tailings. In this work, we show how lead isotopes can be used for source apportionment of metal and metalloid contaminants from the site of an active copper mine. Analysis of atmospheric aerosol shows two distinct isotopic signatures: one prevalent in fine particles (< 1 µm aerodynamic diameter) while the other corresponds to coarse particles as well as particles in all size ranges from a nearby urban environment. The lead isotopic ratios found in the fine particles are equal to those of the mine that provides the ore to the smelter. Topsoil samples at the mining site show concentrations of Pb and As decreasing with distance from the smelter. Isotopic ratios for the sample closest to the smelter (650 m) and from topsoil at all sample locations, extending to more than 1 km from the smelter, were similar to those found in fine particles in atmospheric dust. The results validate the use of lead isotope signatures for source apportionment of metal and metalloid contaminants transported by atmospheric particulate.

Keywords: Lead isotopes; Dust and aerosol; MOUDI; Smelting; Metal and metalloid contamination.
2.1 Introduction

Metal- and metalloid-laden dust and aerosol particles are produced during mining operations in a wide range of sizes. Coarse particles (> 1 µm aerodynamic diameter) are produced mainly by mechanical action like grinding and wind erosion (Csavina et al. 2011) while fine particles (< 1 µm) 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 µm are generally filtered out by the upper respiratory tract while particles smaller than 10 µm (PM\textsubscript{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 $^{208}$Pb/$^{206}$Pb and $^{207}$Pb/$^{206}$Pb (Chen et al., 2008; Zheng et al. 2004).

Cumming and Richards (1975) observed that a plot of the concentration ratios $^{208}$Pb/$^{206}$Pb vs. $^{207}$Pb/$^{206}$Pb led to approximately a single monotonically increasing curve for all mineral samples analyzed. The radioactive decay of $^{238}$U, $^{235}$U and $^{232}$Th in terms of their relative abundances and half-lives has led to an increase in the concentration of $^{206}$Pb over time. As a consequence, the ratios $^{207}$Pb/$^{206}$Pb and $^{208}$Pb/$^{206}$Pb have decreased over time (Mukai et al., 2001). Figure 1 shows the plot devised by Cumming and Richards, often called “growth curve”, and the distribution along the curve of three different ores:
The Iron King mine (Arizona, USA) is the oldest ore of those shown with an age of 1800 million years (Anderson and Guilbert, 1979), the Mount Isa ore (Queensland, Australia) has an age of approximately 1600 million years (Cumming and Richards, 1975) and the Ray Mine ore (Arizona, USA) has an age of 70 million years (Bouse et al., 1999).

![Figure 1](image)

**Figure 1.** The Cumming and Richards growth curve (solid line) for lead isotope concentration ratios (adapted from Chen et al. 2008), showing three mineral ores. The dashed region includes data from extensive sources (86 different sites in 35 countries) reported by Bollhöfer and Rosman (2001).

In this work, we sampled atmospheric dust and aerosol at two different sites in Arizona: The first site is located in the towns of Hayden and Winkelman, where a copper mine and smelter currently operate; while the second site is located in Tucson, representing a local urban environment. The main objectives of this work were:

1. To assess if lead isotopic analysis can be used for source apportionment of airborne particular matter associated with mining operations.
2. To investigate the extent of soil contamination in the vicinity of the smelting complex.

2.2 Materials and Methods

2.2.1 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 (w.mindat.org/loc-3377.html). 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 samples in Hayden and Winkelman (EPA 20012).

2.2.2 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 2). 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.

![Satellite picture of the sampling site in Hayden, AZ, with locations of mining and sampling operations. Source: Google Earth.](image)

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\textsuperscript{-1} for 96-h sampling periods. Sampling was performed in two modes: regular sampling was done by operating the MOUDI continuously for 96 h, while programmed sampling was performed by operating the MOUDI only for specified wind speeds and directions until total operating time reached 96 h. The calibrated cut points (d\textsubscript{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 µm equivalent aerodynamic diameters. Teflon substrates (PTFE membrane, 2-µm pore size, 46.2 mm diameter, Whatman) were used for sample collection. The substrates were cleaned sequentially by DI water and methanol before use. They were transported to and from the field site in enclosed impactor holders (MSP Corporation). Substrates were weighed before and after sampling using EPA class
I equivalent methods on an ultra-microbalance (Mettler Toledo XP2U). Aluminum substrates (47 mm, MSP Corporation) were occasionally used for electron microscope analysis samples.

Soil samples were taken at Hayden at four different distances from the smelting complex in a straight line transect NE of the smelter, a prevailing wind direction (Figure 3). Samples were collected at different depths to obtain a vertical profile of the contamination: 0 - 3 mm, 3 - 6 mm, 6 - 9 mm, at 50 mm, and finally at 100 mm below the surface. Final samples at each site and depth were obtained by mixing three different samples. The composite samples were dried for 10 hours at a temperature of 110 °C and then sieved (ASTM, 2010) through a 0.84 mm sieve to discard coarser fractions.
2.2.3 Sample Preparation

Exposed Teflon substrates were transferred to glass vials and extracted with 15 mL of *aqua regia* (1.03 M HNO₃/2.23 M HCl, trace-metal grade) in a sonicator at 80 °C for 60 minutes (Harper et al., 1983). Aliquots of 1.2 mL were diluted to 4 mL with deionized water before analysis. Soil samples were extracted in the same way, using 5 mg of soil in each sample. Prior to lead isotope analysis, samples were concentrated on a hot plate. The extraction method was verified by comparing it with the use of concentrated HNO₃, or a combination of concentrated HNO₃/H₂O₂ solutions in conjunction with microwave digestion, all of which yielded similar concentrations for representative samples (Gonzales et al., 2014), which suggests that element measures represent total acid extractable concentrations.
2.2.4 Sample Analysis

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%. Certified calibration standards from Accustandard were prepared with MiliQ water, 0.669 M HCl (Fisher, trace-metal grade) and 0.309 M HNO₃ (EMD, Omnistrace). National Institute of Standards and Technology (NIST) standard reference material (SRM 1643e trace elements in water) was analyzed with each set of samples. NIST SRM 981 (lead isotopic standard) was used for calibration of lead isotope measurements. The analytical precision of lead isotopic ratios was under 0.5 % for the concentration ratios Pb²⁰⁷/Pb²⁰⁶ and Pb²⁰⁸/Pb²⁰⁶.

Morphologic and elemental analyses were done at University Spectroscopy and Imaging Facilities of the University of Arizona using a field emission scanning electron microscope (Hitachi S-4800 Type II SEM) coupled to energy dispersive spectroscopy (ThermoNORAN NSS EDS). Aluminum substrates were used in the MOUDI when collecting samples for this purpose to improve resolution.

2.3 Results and Discussion

Figure 4a 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 µm. 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.

Lead and arsenic concentrations of the mine tailings impoundment in Hayden are $14.0 \pm 6.8$ and $46.4 \pm 33.7$ ppm (EPA, 2012), respectively, which suggests that the main source of atmospheric contamination at this site is smelting activity and not the erosion of mine tailings, given the high contaminant concentrations in atmospheric particulate ($100 – 1000$ ppm, Figure 4a).
Figure 4. (a) 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). Arsenic and cadmium were below detection limits in the Tucson samples. (b) Mass concentration of total particles as a function of particle size for the sample in (a).

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 5 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 5a), which suggests the existence of two different atmospheric lead sources. The isotopic ratios of the fine particles coincide with those of the Ray Mine (Figure 1) 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 (see below). It is interesting to note that the two sampling periods shown in Figure 5 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 5. (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 (300-360°). Results obtained from these samples, as well as a representative wind rose of the sampling periods are presented in Figure 6. Figure 6a
shows that both coarse and fine particles exhibit only one isotopic signature with high ratios similar to the results shown on Figure 5a for fine particles. This indicates that for the programmed samples the smelter was the predominant source. Note that the isotopic ratios for all the sampling periods are within experimental error, which suggests that smelter emissions have a consistent signature, that is, the ore processed in the smelter seems to have the same origin or, at least, the same lead isotopic composition. This does not mean dust and aerosol from other sources were absent. However, since the lead concentration is appreciably higher for samples coming from the smelter area, their lead isotopic signature predominates. We also note that due to the complex topography of the Hayden site, there is no certainty that winds followed the general line of sight (300-360°).
Figure 6. (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 programmed samples were analyzed by scanning electron microscopy (SEM). Sample of images obtained are shown in Figure 7. Deposition of fine particles onto coarse particles is clearly observed in Figure 7a. Energy dispersive spectroscopy (EDS)
was used to determine the content of lead in the fine particles attached; it was found that these particles contain lead in concentrations as high as 14.85 ± 1.88 % by weight. Figure 7b shows coarse particles in which the attachment of fine particles is absent. The lead content of these particles was negligible, as determined by EDS. This confirms that the second lead signature seen in the MOUDI samples collected without discriminating for wind direction (coarse particles in Figure 5a) is, in this case, masked by the prevalence of lead-enriched aerosol in both fine and coarse particles.
Figure 7. Scanning electron microscope images from MOUDI samples from period 3: (a) Some coarse particles show fine particles attached to them, while (b) other coarse particles are free of fine particles.

The coarse particle lead ratios (Figure 5a) were similar to those found in samples taken at the Tucson site, which is free of mining activity (Figure 8). 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: \( \frac{^{208}\text{Pb}}{^{206}\text{Pb}} = 2.07 \), \( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} = 0.84 \) (Sutherland et al., 2003; Bollhöfer and Rosman, 2001).

![Figure 8](image-url)

**Figure 8.** 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. We investigated how this contamination affects the soil in the vicinity of the smelter. Soil samples were analyzed for Pb, As and Cd at various distances from the smelter and various depths. Contaminant
concentrations are shown in Figures 9 and 10. As expected, contaminant concentrations in topsoil decreased monotonically with distance from the smelter (Figure 10).
Figure 9. Total lead, cadmium and arsenic in Hayden site soil samples; Distance from the smelter: (a) 650 m; (b) 900 m; (c) 1300 m; (d) 4000 m. Horizontal axis values represents range of depth of samples in mm.
Figure 10. Lead and arsenic concentrations in topsoil (0-3 mm depth) at the Hayden site as a function of distance from the smelter.

Lead isotopic analyses were performed on soil samples A, B and C (Figure 3) to determine the source of contamination and possible effect of the deposition of smelter fine particles on the soil. Sample D was not analyzed for lead isotopes due to the low concentration of lead present. For each of the samples analyzed, only the top and the bottom layers were considered. Figure 11 shows the isotopic ratios obtained for the different soil samples. Isotopic ratios obtained in the sample closest to the smelter (sample A) are similar to the ratios obtained for the airborne fine particles in the atmosphere at Hayden (Figure 5). Similar ratios were observed in the 100 mm deep sample, which indicates a similar source of lead throughout the soil profile analyzed. Sampling point A is located only 650 m from the smelter. These results indicate that, despite weathering and rain runoff, lead and arsenic accumulate in the soil, and the contamination extends uniformly through at least 10 cm of depth (Figure 9a). Lead
Isotope results provide strong evidence that the contamination originates in atmospheric transport of smelter emissions.

**Figure 11.** Isotopic ratios for soil samples in Hayden. Distance from the smelter specified in Figure 3. Numbers in parentheses represent the depth of the sample.

Isotopic ratios for the topsoil of sample B (Figure 11) are again close to the smelter emissions. However, the ratios for the deepest sample (100 mm) definitely indicate the presence of a different source mixed with the emissions source. This trend becomes more evident for sample C (1300 m), for which the topsoil layer still exhibits the smelter isotopic ratios, but the 100 mm depth sample shows significantly lower ratios, which trend in the direction of the presumed background measured in the coarse atmospheric particles (compare with Figure 5a).
2.4 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. Topsoil samples near the smelting site show concentrations of Pb and As decreasing with distance from the smelter but lead isotope ratios similar to those found in fine particles in atmospheric dust, which are characteristic of smelting emissions. On the other hand, isotope ratios at a soil depth of 100 mm decrease with distance from the smelter. These results are consistent with a contaminant deposition pattern from windblown particles from the smelter site to surrounding soils. These results validate the use of lead isotope signatures for source apportionment of metal and metalloid contaminants transported by atmospheric particulate.

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2.5 References


CHAPTER 3: Laboratory Dust Generation and Size-Dependent Characterization of Metal and Metalloid-Contaminated Mine Tailings Deposits

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Highlights:

- A laboratory dust fractionator was developed for the production of respirable dust.
- The size-dependent distribution of arsenic and lead in mine tailings dust is reported.
- Metal and metalloid contaminants are enriched in particles smaller than 10 µm.
- Lead isotope signatures show spread of mine tailings particles onto surrounding soils.
Abstract

The particle size distribution of mine tailings material has a major impact on the atmospheric transport of metal and metalloid contaminants by dust. Implications to human health should be assessed through a holistic size-resolved characterization involving multidisciplinary research, which requires large uniform samples of dust that are difficult to collect using conventional atmospheric sampling instruments. To address this limitation, we designed a laboratory dust generation and fractionation system capable of producing several grams of dust from bulk materials. The equipment was utilized in the characterization of tailings deposits from the arsenic and lead-contaminated Iron King Superfund site in Dewey-Humboldt, Arizona. Results show that metal and metalloid contaminants are more concentrated in particles of < 10 µm aerodynamic diameter, which are likely to affect surrounding communities and ecosystems. In addition, we traced the transport of contaminated particles from the tailings to surrounding soils by identifying Pb and Sr isotopic signatures in soil samples. The equipment and methods developed for this assessment ensure uniform samples for further multidisciplinary studies, thus providing a tool for comprehensive representation of emission sources and associated risks of exposure.

Keywords: Dust generator; Respirable dust; Mine tailings; Arsenic; Lead
3.1 Introduction

Current air pollution standards are based on concentrations of particulate matter (PM) without regard to the specific nature of such particles and thus under simplify the complexity of potential impacts to human health and the environment. While several studies have correlated PM exposures to adverse health effects, considerable uncertainties remain with regard to the mechanisms and particle characteristics that are responsible for such outcomes [1,2]. In recent years, the National Research Council (NRC) has described research priorities for airborne PM, focusing broadly on bridging the gap between sources and observed health outcomes [3]. These recommendations emerge along with increased concerns of dust emissions resulting from intensified land use and climate change [4]. Semiarid regions such as the United States Southwest are particularly vulnerable to wind erosion and dust emissions due to the lack of vegetative cover and low humidity [5]. The greatest risk to human health associated with these environments is attributed to mining operations and tailings deposits [6,7]. Exposed mine tailings are not only abundant in the US Southwest, but also generate relatively large amounts of airborne contaminated particles [7,8]. Atmospheric dust originating from these sources represents an important air quality concern that should be systematically characterized to provide an accurate assessment of the potential risks to surrounding communities and the environment.

The level of risk associated with dust particles depends on chemical composition and particle size. Depending on the specific nature of the mining site, tailings may contain toxic contaminants, such as arsenic and lead [6,7]. The size of the particles associated with these contaminants may determine the extent of contaminant dispersion, as fine
particles (e.g. PM$_{2.5}$) are susceptible to long-range transport over local, regional, or even global scales [9]. Furthermore, finer particles are more reactive due to their high specific surface area, which makes associated contaminants more likely to become solubilized and bioavailable [10]. Current regulations target atmospheric particles < 10 µm (PM$_{10}$) and < 2.5 µm (PM$_{2.5}$), which are representative of the inhalable fraction that is able to penetrate the thoracic region and the pulmonary gas-exchange region, respectively [11]. The inherent hazards associated with the size-distribution of atmospheric particles highlights the importance of implementing size-dependent characterization methods rather than relying on bulk samples when assessing contaminated PM emission sources.

Finding correlations between dust emission source characteristics and adverse health effects, especially when considering size-dependence, can help guide regulations and remediation strategies for dust sources. A major limitation is the difficulty of producing uniform samples in the respirable size range. Current field sampling technologies are commonly limited to PM collection on the order of a few hundred milligrams.

Furthermore, ambient dust samples are comprised of mixtures of particles from multiple sources, which make the characteristics of the collected material highly variable depending on meteorological conditions [12]. This presents a challenge when trying to integrate results from different studies. Physicochemical and bioavailability studies have been reported for the size-dependent characterization of contaminated sources [10,13-15]. However, exposure studies for toxicological characterization are limited by the relatively large amount of material needed in comparison to physicochemical studies [16]. Innovative methods are required for generating larger quantities of size-fractionated samples that can be used in multidisciplinary PM research.
Different approaches have been taken to generate dust from mineral materials in a laboratory setting [17]. A common method with the capacity to produce large quantities of dust is the use of a rotating drum in which the sample is mechanically dispersed, resulting in fluidization of particles into a stream of air. Previous studies using this type of device report coupling the flow of entrained dust to either an analysis or a separation module to provide particle size characterization [17]. Variations of this system have been reported in dust generation testing for agricultural operations [18-20]. However, only a few of these systems were developed for dust generation and research specifically related to atmospheric particulate matter emissions [17]. To our knowledge, no previous studies have utilized this kind of device for the characterization of dust emissions from mine tailings.

The present study focuses on the Iron King and Humboldt Smelter Superfund (IKHSS) site in Dewey-Humboldt, AZ. The overall objective was to characterize the contaminated tailings at this site and their potential impact on the surrounding community. For this purpose, current work includes: (1) the development of a dust generator for the collection of several grams of size-fractionated dust representative of contaminated sources; (2) initial characterization of the size-dependent chemical composition of the tailings and surrounding soils; and (3) analysis of the extent of contamination as a function of particle size based on enrichment factors and multi-isotope source apportionment methods.
3.2 Materials and Methods

3.2.1 Site description and sampling

The IKHSS site in Dewey-Humboldt, AZ, was added to the U.S. EPA National Priorities List in 2008. The site was periodically mined for gold, silver, copper, lead, and zinc from the late 1800s until 1969 [21], processing approximately 1,000 metric tons of ore daily during peak operation [22]. The resulting tailings were deposited in large piles adjoining the mine property boundaries. The tailings contain high concentrations of several hazardous materials, of which As and Pb have been identified as primary contaminants [23]. The IKHSS site comprises 153 acres of land adjacent to commercial, industrial, and residential areas. Topsoil near the mine and smelter have been found to contain significant As and Pb levels [23].

We collected bulk tailings samples from the Iron King Superfund Site as well as soil samples at different distances from the tailings for an assessment of the extent of dispersion of contaminants in the area. Soil samples were collected from three locations in the direction of prevailing winds (approximately NNE): site C at 130 m from the tailings, site H at 1150 m, and a background sample at site L at 5032 m (Figure 1). All samples were composited from the top 5 cm of soil (20-30 kg per sample). Samples were sieved in the field using a standard #10 mesh (< 2.0 mm) and placed in plastic buckets for transport.
Figure 1: Location of the four sites sampled in this study. The sites were selected following approximately a NNE transect, which is the prevailing wind direction. From Google maps.

### 3.2.2 Laboratory dust generation and fractionation

The dust generation and fractionation system depicted in Figure 2 is a three-step process comprised of dust generation chamber, fractionation module, and collection chamber. The dust generation chamber is a 208-L steel drum (58 cm in diameter and 86 cm in length) that rotates horizontally on top of four 4-inch rubber wheels driven by a single-speed motor. A rectangular (25.5 cm × 30.5 cm) plexiglas window on the side of the drum allows for material addition and removal. The window adjusts to the curvature of the drum and is held in place by two belts tightened around the circumference of the
drum. Four steel baffles bolted perpendicularly to the interior surface of the drum facilitate mixing and re-suspension of the bulk material (Figure 3b).

**Figure 2:** Schematic of the laboratory dust generation and fractionation apparatus. A 3.2-cm diameter PVC pipe is threaded through the center of the drum and remains fixed while the drum rotates (Figure 3a). The pipe extends out on both ends of the drum through orifices that are sealed by rings of insulating foam. On one end of the drum, clean atmospheric air is introduced to the PVC pipe. The air used is provided by a compressor followed by a coalescing filter, a pressure regulator, a flow regulator, and an orifice flow meter. Inside the drum, the pipe is blocked in the middle by a ball valve. The first half of the pipe has holes facing down, which allow the air to enter the rotating chamber. Another set of holes in the second half of the pipe allows the air containing entrained particles to leave the chamber.
After exiting the generation chamber, air enters tangentially into a cyclone separator for size fractionation (Model URG-2000-30EA, URG Corp. Chapel Hill, NC). The cyclone has a design cut-point diameter of 10 μm for a flow rate of 28.3 LPM. Two size fractions were collected using this system: (1) a coarse fraction, consisting of particles that get resuspended but are discharged to the bottom of the cyclone, and (2) a fine fraction of particles that are small enough to get carried with the outlet flow of air towards the collection chamber (Figure 2). This chamber is made of sheet with a horizontal projected area of 1.5 m by 1.5 m and a tapered bottom. The size of the settling chamber was designed to allow particles as small as 2.5 μm to settle by gravity at the specified flow rate of 28.3 LPM. Two HEPA filters, 26.5 cm by 30.5 cm each, are attached to the top wall on the far side of the chamber to remove up to 99.97% of particles as small as 0.3
μm. While this design proved to be effective for the collection of dust samples, the large size of the chamber made it difficult to clean and thus introduced a potential source of cross-contamination. Therefore, soil samples were collected by an alternative method in which a disposable high-efficiency vacuum bag (model VF3501, Ridge Tool Co. Elyra, OH) was directly coupled to the outlet of the cyclone.

3.2.3 Dust generation and fractionation

Previous studies utilizing rotating drums to generate dust highlight the importance of speed of rotation, duration of sampling, air flow rate, and characteristics of the initial material to determine system performance [19,24]. Here, all bulk material was oven dried at 105 °C for 24 hours as recommended by standard methods [25] prior to fractionation to avoid biases in the resuspension potential due to sample moisture [26,27]. The dried material is introduced into the drum and rotation and airflow are set for a continuous operation period of approximately 5 h. The speed of rotation of the drum was 17 rpm, comparable to the typical range used in previous studies [19]. As fractionation at the cyclone is highly dependent on the flow rate of air, the system was calibrated to provide a continuous flow of 28.3 LPM for all samples, consistent with the cyclone manufacturer’s recommendation for PM$_{10}$ fractionation. At this rotation speed and flow rate, an initial mass of 5 to 7 kg of material was selected due to the capacity to produce several grams of fractionated material without overloading the cyclone during operation. Once the operation stops, samples are allowed to settle for several hours before collecting the fractionated material. The equipment was disassembled, thoroughly cleaned with a vacuum cleaner and wiped down between runs of different samples.
3.2.4 **Particle size analysis**

Generated dust samples were introduced into a Fluidized Bed Aerosol Generator (FBAG model 3400A, TSI Inc. Shoreview, MN) to resuspend the particles. The output was coupled to a Scanning Mobility Particle Sizer spectrometer (SMPS model 3936, TSI Inc. Shoreview, MN) and an Aerodynamic Particle Sizer spectrometer (APS model 3321, TSI Inc. Shoreview, MN) to obtain size distributions in the ranges 0.056-0.750 µm and 0.523-20 µm, respectively. Data from both instruments were merged using TSI software (model 390069, TSI Inc. Shoreview, MN) to generate a continuous size distribution curve.

The instruments described are limited to the analysis of particles smaller than 20 µm. For confirmation of both fine and coarse particle sizes separated by the cyclone, samples were additionally inspected using a field emission scanning electron microscope (Hitachi S-4800 Type II SEM) coupled to electron dispersive spectroscopy (ThermoNORAN NSS EDS). Samples were coated with a thin layer of platinum using a Hummer 6 Sputtering Device to enhance SEM examination and micrographs were compiled from each sample. Particle size was measured using NIH ImageJ v1.47 to generate image-based particle size distributions. The optical projected area reported by ImageJ was converted to aerodynamic diameter by estimating a specific gravity of 2.6 for tailings and 1.0 for soils. No corrections were made for non-sphericity.

3.2.5 **Chemical composition analysis**

The elemental composition of fractionated samples was characterized by acid digestion followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis to determine total contaminant concentrations, as well as Pb and Sr isotopic ratios.
Digestions were performed by adding 15 mL of *aqua regia* solution (2.23 M HCl/1.03 M HNO₃ trace-metal grade) to 10 mg samples of dust and placing the mixture in a sonicator at 80 °C for 60 minutes [27]. This was shown to be a high-yielding extraction method for tailings materials, comparable to the use of concentrated HNO₃, or a combination of concentrated HNO₃/H₂O₂ solutions in conjunction with microwave digestion (Figure 4). Extracted samples were analyzed by ICP-MS (Agilent 7700X with and Octopole reaction System). The certified standard reference materials NIST 1643e (trace elements in water) and NIST 981 (lead isotopic standard) were analyzed for every data set. Calibration standards were made from Accustandard with MiliQ water, 0.669 HCl (Fisher, trace-metal grade) and 0.309 M HNO₃ (EMD, Omnitrace). The analytical precision of this method was under 0.5% for isotopic ratios.
Figure 4: Comparison of (a) As and (b) Pb yield using three different extraction methods: concentrated nitric acid and hydrogen peroxide followed by microwave digestion, concentrated nitric acid followed by microwave digestion, and *aqua regia* followed by sonication. Error bars show standard deviation of duplicate samples. Particle size range: bulk < 2 mm, coarse dust < 50 µm, fine dust < 10 µm.

3.2.6 Enrichment factors

Contaminants may be present in soils to a certain extent as a result of natural processes. Enrichment factors (EF) can be used to discriminate between anthropogenic and natural sources of metal contamination. Pb EFs were calculated using aluminum as a reference from [28]:

where $C$ represents mass concentration. Samples from site L (5032 m from the tailings) were used to determine background concentrations and EFs were calculated for the tailings and soil samples from sites C (130 m) and H (1150 m). EF values close to one indicate crustal origin, while values higher than 10 point to anthropogenic enrichment [8].

3.2.7 Lead (Pb) and Strontium (Sr) isotopic ratios

Pb isotopic ratios are useful fingerprints for the evaluation of contamination sources. Four main isotopes of Pb occur in the environment: $^{204}$Pb, $^{206}$Pb, $^{207}$Pb and $^{208}$Pb. While $^{204}$Pb is a stable isotope with constant abundance over time, $^{206}$Pb, $^{207}$Pb and $^{208}$Pb are of radiogenic origin, derived from the radioactive decay of $^{238}$U, $^{235}$U and $^{232}$Th, respectively [30]. Given that the abundance of the radiogenic Pb isotopes is strictly related to their parent isotopes and respective rates of decay, relative concentrations can be associated with distinct sources. Furthermore, Pb emitted into the environment will retain the same isotopic composition of its source [31]. We present results in terms of $^{208}$Pb/$^{206}$Pb vs. $^{207}$Pb/$^{206}$Pb as suggested by Cumming and Richards [32] to determine age-dependent isotopic signatures. This method relies on the higher abundance of $^{238}$U relative to $^{235}$U and $^{232}$Th, which leads to increasing concentrations of $^{206}$Pb over time. As a result, $^{208}$Pb/$^{206}$Pb and $^{207}$Pb/$^{206}$Pb ratios are high for samples originating from older ores, and low for newer sources. In addition, we quantified Sr isotopes, in particular the $^{87}$Sr/$^{86}$Sr
ratio, which is another soil constituent that has been used for apportionment of airborne particle emissions [33-36].

3.3 Results and Discussion

3.3.1 Dust generation efficiency

The dust generation and fractionation system consistently produced relatively large amounts of fractionated dust. An initial load of 5 to 7 kg produced 4 to 10 g of fine particles from the tailings (here, we are calling “fine” to the fraction produced at the top of the PM$_{10}$ cyclone and “coarse” the bottom fraction – see below for particle size characterization), and 15 to 30 g of fine particles from soils at an air flow rate of 28.3 LPM and operation time of 5 hours. In contrast, a standard high-volume sampler in the field would require about a month of operation to collect a sample of 2 to 3 g of particulates [16]. To our knowledge, no previous studies have been able to produce and collect gram-size samples of mineral dust in the respirable size range.

The fine dust produced in this study is effectively comprised of particles smaller than 10 µm, with the majority of particles by number in the range of 0.5 to 5 µm. Fine dust generated from all samples has a size distribution with a count median diameter around 1.2 µm and a geometric standard deviation of approximately 3 µm as determined by spectrometric size distribution analysis (Figure 5).
Figure 5: Particle size distributions of fine dust from mine tailings and background soil (sample L). The y-axis is expressed as the fractional count of particles of a given size, normalized by the log of the aerodynamic diameter.

In comparison to the fine dust, the coarse dust also displays a size distribution that includes a sizable number of sub-10 µm particles, but with a wider range between 0.5 - 50 µm (Figure 6). The largest particle size collected by the cyclone also represents the upper limit of particles resuspended by the equipment.
Figure 6: Size-based mass distributions of the fine and coarse dust separated from tailings material. The y-axis is expressed as the fractional mass of particles of a given size, normalized by the log of the aerodynamic diameter.

The size distribution of the fine fraction differs from the cyclone’s design cut-point diameter of 10 µm at the specified flow rate of 28.3 LPM. The design cut-point diameter represents the mean of the particle size distribution [37]. The fact that the mean of the distribution found in this work is below the design cut off can be attributed to the high dust mass loadings produced by the rotating drum, which affect the separation dynamics inside the cyclone. Based on the total amount of dust produced during each run, we estimate the airflow going into the cyclone carries dust concentrations in the order of 10 g/m³. This number is about five orders of magnitude higher than what is generally observed in the atmosphere in an urban environment [38]. In this range of inlet loadings, our results are consistent with previous studies that show an increase in collection efficiency at the bottom of the cyclone with increasing particle loadings [39,40]. Mathematical models and computational simulations explain this phenomenon as the
result of multiple effects including particle-particle interactions (mainly collisions and their effect on air flow modification), suppression of fluid turbulence, and decrease in gas swirl inside the cyclone [41,42]. The interplay between these effects hinders the free flow of fine particles that would normally be able to follow the outlet flow of air. As a result our system favors fractionation of smaller particles, where instead of a well-defined cut-point diameter we obtain high removal of submicron particles, effective separation (50-70%) of particles in the range 1-5 µm, and increasing removal with particle size for particles larger than 5 µm, with complete removal of particles larger than 10 µm (Figure 7). Regardless of the complex effects of inlet dust loadings, the consistency in size distributions of generated dust fractions (e.g. Figure 5) shows that the use of uniform operating conditions (initial mass, drum rotation, flow rate, and operation time) allows us to produce reproducible results, and sufficient mass of fine dust for extensive characterization as described above.

![Figure 7: Cyclone separation efficiency. Markers show data obtained from size distributions of the fine and coarse dust fractions.](image-url)
3.3.2 Size-dependent As and Pb concentrations

Even though the tailings and soils sampled in this study are inherently heterogeneous material, the present results show clear indications that contaminants are consistently enriched in the smaller particles. We examined three size fractions, each subsequently comprised of a wider size range and inclusive of the previous fraction: fine dust, coarse dust, and original bulk material. Figure 8 shows that for all sampling sites, the Pb and As concentrations are highest in the fine fraction, and lowest in the bulk fraction, with the coarse fraction somewhere in between. This trend is also observed for Fe, Sb, Cd, Cu, K, Al, and Mn (results not shown). These results point to preferential concentration of metals and metalloids in particles <10 µm, whereas larger particles appear to be less contaminated and thus produce a dilution effect of mass-based concentrations in the bulk and coarse dust samples. Tailings samples present the highest As and Pb concentrations, reaching over 2000 mg/kg with coarse and fine dust concentrations of 11,000 and 13,000 mg/kg respectively. It is noteworthy that the highest contaminant levels are associated with particles that are also more likely to become airborne, may be dispersed over longer distances, and pose higher inhalation risks than their coarser counterparts.
Figure 8: As and Pb concentrations in the three fractions collected from each sample location as a function of particle size. Error bars show +/- one standard deviation of duplicate samples. Particle size range: bulk < 2 mm, coarse dust < 50 µm, fine dust < 10 µm.

Consistent with our findings, previous field studies have reported an inverse relationship between particle size and metal and metalloid contaminant concentrations in particulate matter near tailings deposits [7,14,15], attributed to mineralogical factors and the different mechanisms of formation of the particles. Tailings deposits at the Iron King site contain materials that have been subjected to ore processing, including excavating, crushing, grinding, separation, and smelting. All of these activities, as well as subsequent wind erosion, may produce large quantities of dust particles. Kim et al. [14] suggest that the size-dependence of elemental composition could be due to the occurrence of the elements of interest in highly insoluble phases, which persist through chemical weathering and the physical breakdown of material, especially if these element-bearing phases have low mineralogical hardness and progressively break into finer particles.
Alternatively, if the contaminants were associated with soluble phases, contaminated fine particles may be a result of the dissolution of sulfide minerals during rain events and subsequent evapotranspiration and formation of efflorescent deposits. This phenomenon has been commonly reported in arid and semi-arid environments including the surficial tailings at Iron King and can form metal-enriched crystals with concentrations significantly higher than those found in bulk tailings [8]. A third relevant process is the sorption of soluble species onto particle surfaces from liquid ponded on the tailings surface, which would result in preferential enrichment of smaller particles due to their higher specific surface area [14].

Based on the geology of the Iron King mine site, the speciation of toxic metals and metalloids at this site is likely controlled by the geochemistry of Fe and S, both of which form redox-sensitive phases that could become solubilized under the prevailing acidic conditions following rain events. Hayes et al. [43] performed sequential extractions of the top 25 cm of bulk Iron King mine tailings to determine the metal and metalloid content associated with Fe-bearing phases and soluble salts. They report on the mineralogy and elemental composition of the tailings material and observed that iron and sulfur were present at relatively high concentrations (130-140 mg/g and 100-120 mg/g, respectively.) In terms of mineralogy of the samples, minerals present at concentrations higher than 1 wt% were: SiO₂ 49 %, Fe₂O₃ 18 %, Al₂O₃ 5 %, CaO 3 %, MgO 2 %. Considerable amounts of As and Pb were associated with poorly crystalline Fe(III) and Al-bearing phases. Most of the remaining As was found in the more crystalline Fe(III) secondary phases. No steps were used to target sulfide minerals in the method by Hayes et al., which suggests that the remaining unextractable fraction of Pb (87%) and As (30%) may
be associated with such phases. This previous study hints to sorption and co-precipitation of soluble species onto secondary minerals as the primary mechanism controlling Pb and As fate in bulk tailings at Iron King. Such behavior has been previously associated with size-selective enrichment of contaminants in a study of the Randsburg Historic Mining District, California, explained by the increasing reactive surface area with decreasing particle size [13]. Overall, the inverse relationship between contaminant concentrations and particle size is likely a combination of all three processes described above (physical breakdown of insoluble phases, efflorescent deposits, and preferential sorption of soluble species). Further size-resolved geochemical characterization, such as that performed by Kim et al. [13], is required to confirm the prevalence of these and other potential mechanisms.

### 3.3.3 Source apportionment of contaminated soils

As and Pb concentrations are highest in the tailings, and consistently decrease in the soil samples when comparing all size fractions at increasing distance from the tailings (Figure 9). The elevated contaminant concentrations in samples closer to the tailings are indicators of anthropogenic enrichment above background levels. We hypothesize that contamination of the soils from sites C (130 m) and H (1150 m) resulted from deposition of airborne particles originating from the tailings, while site L (5032 m) represents background contamination. The transport and deposition of contaminated dust is more likely to affect smaller particles that are more easily resuspended and is consistent with the size-dependent concentrations of As and Pb previously described.
Figure 9: (a) As and (b) Pb concentrations in the three fractions collected for each sample location as a function of distance from the tailings. Solid lines are straight lines joining data points to visualize trends. Particle size range: bulk < 2 mm, coarse dust < 50 µm, fine dust < 10 µm.

Enrichment factors (Table 1) emphasize that the Pb content of mine tailings is significantly higher than the levels attributable to crustal sources in the region (EF > 100). Soil samples at 130 m from the tailings are also clearly affected by Pb enrichment (EF > 30), while samples at 1150 m are closer to background levels (EF between 3 and 5). It is also worth noting that the ratios of enrichment between the different size fractions decrease with distance from the tailings. These observations are consistent with the predicted deposition scenario.
Table 1. Pb/Al enrichment factors for the three size fractions collected from each sample location. Numbers in parentheses indicate distance of sampling site from tailings. Site L is used as the base point. Fine and coarse dust refer to fractions separated in the PM$_{10}$ cyclone.

<table>
<thead>
<tr>
<th>Location</th>
<th>Fine dust</th>
<th>Coarse dust</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tailings</td>
<td>643</td>
<td>194</td>
<td>192</td>
</tr>
<tr>
<td>C (130 m)</td>
<td>93</td>
<td>42</td>
<td>35</td>
</tr>
<tr>
<td>H (1150 m)</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>L (5032 m)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

While enrichment factors provide a qualitative indication of non-crustal contamination, they are subject to uncertainties due to the high variability of elemental composition in geological materials [44]. A more definitive alternative is the examination of stable isotopes, as each source has distinct isotopic ratios that can be used to trace environmental emissions. Figure 10 shows Pb isotopic ratios for each of the size fractions analyzed (fine, coarse, and bulk) for the four sample locations (tailings, 130 m, 1150 m, and 5032 m) in this study. Three different isotopic signatures can be distinguished in this plot: (1) high $^{208}\text{Pb} / ^{206}\text{Pb}$ and high $^{207}\text{Pb} / ^{206}\text{Pb}$ associated with ore from the Iron King mine tailings, (2) low $^{208}\text{Pb} / ^{206}\text{Pb}$ and low $^{207}\text{Pb} / ^{206}\text{Pb}$ associated with background levels, and (3) an intermediate region with mixed contributions from tailings and background soil. The isotopic signatures progress with distance from the tailings towards the background values. Note that the lead in site C (130 m from the tailings) seems to originate mostly from the tailings, whereas in site H, an intermediate signature is clearly observed. It is interesting to note that in all the sites, the separated fractions (coarse and fine) have signatures closer to the tailings than the bulk samples. This is consistent with the fact that the smaller particles that compose the separated fractions have been transported from the tailings as windblown dust. Similarly, Figure 11 shows that Sr
isotopic ratios agree with these trends and further support the prevalence of distinctive signatures that progressively diverge with distance from the tailings. It is clear that all size fractions from site C (130 m from the tailings) have very similar $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to those found in the tailings, while all size fractions from site L (5032 m) show considerably different isotopic ratios.

**Figure 10:** Pb isotope ratios for the three size fractions collected for each of the sample locations. Three different signatures are identified. Error bars show +/- one standard deviation of duplicate samples. Distance from the tailings is specified. Squares: bulk, triangles: coarse, rhombs: fine. Particle size range: bulk < 2 mm, coarse dust < 50 µm, fine dust < 10 µm.
**Figure 11:** Sr vs Pb isotope ratios for all size fractions generated from each of the sample locations. Distance from the tailings is specified. Squares: bulk, triangles: coarse, rhombs: fine. Particle size range: bulk < 2 mm, coarse dust < 50 µm, fine dust < 10 µm.

### 3.4 Conclusions

The dust generation and fractionation system used in this work proved to be effective in the production of multi-gram samples of fine dust. The elemental composition results indicate that As and Pb are significantly enriched in particles < 10 µm diameter compared to particles < 50 µm, and to < 2 mm bulk samples. We attribute this relationship to the co-precipitation and preferential sorption of soluble species onto the higher available surface area of smaller particles. An assessment of stable isotope fingerprints traces the deposition of contaminated tailings particles on surrounding soils in the direction of prevailing wind, correlated to the higher metal(loid) content of the more easily transported particle sizes. Particle size and chemical composition are clear indicators of exposure risks. The fact that contaminants are considerably enriched in the
respirable size range suggests that assessments based on bulk concentrations do not accurately represent exposure levels.

**Acknowledgements**

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3.5 References


CHAPTER 4: Effect of Wind Speed and Relative Humidity on Atmospheric Dust Concentrations in Semi-Arid Climates

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Abstract

Atmospheric particulate have deleterious impacts on human health. Predicting dust and aerosol emission and transport would be helpful to reduce harmful impacts but, despite numerous studies, prediction of dust events and contaminant transport in dust remains challenging. In this work, we show that relative humidity and wind speed are both determinants in atmospheric dust concentration. Observations of atmospheric dust concentrations in Green Valley, AZ, USA, and Juárez, Chihuahua, México, show that PM$_{10}$ concentrations are not directly correlated with wind speed or relative humidity separately. However, selecting the data for high wind speeds (> 4 m/s at 10 m elevation), a definite trend is observed between dust concentration and relative humidity: dust concentration increases with relative humidity, reaching a maximum around 25% and it subsequently decreases with relative humidity. Models for dust storm forecasting may be improved by utilizing atmospheric humidity and wind speed as main drivers for dust generation and transport.

Keywords: Dust emission, Relative humidity, Wind speed, Semi-arid, PM$_{10}$
4.1 Introduction

Dust storms have been shown to have deleterious impacts to human health. When near-zero visibility occurs during these events, serious traffic accidents have claimed numerous lives and shut down entire highways for extended periods of time (Novlan et al., 2007). The mere presence of dust in breathed air can have negative impacts on the human respiratory and cardiovascular systems (Schwartz, 1993; Pope et al., 1995; Peters et al., 1997; Donaldson et al., 2001; Ghio and Devlin, 2001). Additionally, spores and contaminants associated with dust and aerosol can adversely impact human health, causing a range of issues from respiratory infections to toxic exposure (Low et al., 2006; Quintero et al., 2010; Csavina et al., 2011; Degobbi et al., 2011). In particular, the transport of metals and metalloids in atmospheric dust around mining operations may lead to increased human exposure to toxic contaminants such as arsenic, lead and cadmium (Csavina et al., 2011, 2012).

In arid and semi-arid climates, dust storms are common. In El Paso, TX, alone, Novlan et al. (2007) reported that an average of 14.5 significant dust events (i.e. blowing dust leading to visibility reductions of 6 miles or less for duration of 2 hours or more) have occurred annually since 1932. These dust events are predicted to increase in occurrence in the US Southwest due to warmer and drier conditions from climate change and therefore are becoming an increasingly studied phenomenon (IPCC - International Pannel for Climate Change 2007; Breshears et al. 2012).

Dust events are caused by local and regional aeolian erosion. Wind speed is a primary factor in dust generation with vegetation cover and soil structure also playing significant roles (Zobeck and Fryrear, 1986; Zobeck, 1991; Yin et al., 2007). Wind tunnel studies
have shown that threshold velocity for aeolian erosion is dependent on atmospheric humidity due to its impact on soil surface moisture content which, in turn, affects interparticle cohesion (Ravi et al., 2004; Ravi et al., 2006; Neuman and Sanderson, 2008). Temperature has also been found to correlate with dust concentrations (Hussein et al., 2006). Yet, despite the many studies on the wind erosion of soils, prediction of dust events is still a significant challenge (Desouza et al., 2010).

A growing body of research is showing the importance of relative humidity on dust emissions and, consequently, atmospheric dust levels (Ravi et al., 2004; Ravi and D'Odorico, 2005; Karar and Gupta, 2006; Ravi et al., 2006; Shah et al., 2006; Vassilakos et al., 2007; Giri et al., 2008; Neuman and Sanderson, 2008). Ravi et al. (2004) found that the threshold friction velocity for dust emissions was positively correlated with relative humidity. However, later studies found opposite trends at high relative humidity (>40%) when temperature was relatively constant (Ravi and D'Odorico, 2005; Ravi et al., 2006).

At low air relative humidity (RH<40%), water content in soil particles at equilibrium with atmospheric air occurs as single-layer adsorption (Neuman and Sanderson, 2008). This water layer interferes with interparticle forces: in some cases, the threshold friction velocity decreases with an increase in water content, since the adsorbed water layer decreases particle cohesion. This effect was found to be the controlling factor in emission experiments performed with various types of sand in a wind tunnel set up by Ravi et al. (2004). However, in the same range of relative humidity, the water layer might increase cohesion in which case an increase in threshold velocity with relative humidity is observed. This type of effect was reported by Neuman and Sanderson (2008) in wind tunnel experiments with simulated soils made up of approximately monodisperse sand
and glass beads. The opposite effects of an adsorbed single water layer and a multilayer liquid film suggest that dust emission is not completely determined by ambient humidity and wind speeds, but other factors that affect particle cohesion, such as surface roughness and chemical composition, might play an important role in low humidity environments. At high relative humidity (RH>40%), multiple adsorbed water layers exist and eventually liquid films and bridges (RH>60%) form, which invariably increase soil particle cohesion. In this regime, an increase in relative humidity leads to an increase in threshold friction velocity. Changes in the threshold velocity lead to changes in dust emission fluxes and, consequently, atmospheric particulate concentrations.

In this study, we examine dust events in two semi-arid sites: Green Valley, AZ, USA (average annual precipitation 11.3 in), and Juárez, Chihuahua, Mexico (average annual precipitation 10.5 in). During the spring months of March – May, dust storms are a common occurrence in these locations. Dust was sampled at six field locations, ranging in soil and vegetation cover, in the region of Green Valley and two locations in Juárez. In addition, PMx and meteorological data from the Pima Department of Environmental Quality (PDEQ) in Arizona were analyzed for longer term trends. We hypothesize that both wind speed and relative humidity may play an important role in observed atmospheric dust concentrations. In particular, the effect of relative humidity on dust emission rates should have a bearing on atmospheric dust.

4.2 Materials and Methods

4.2.1. Green Valley Study

Green Valley (lat. 31° 52’ 16’’, long. –110° 59’ 24’’) is a unique location because it is impacted by regional dust sources from mining operations, including ore extraction and
mine tailings, and it is proximate to the Santa Rita Experimental Range (a long-term ecological research station for semi-arid grasslands.) Green Valley is predominantly a retirement community so that the region has a large population of elderly people who may be especially sensitive to particulate inhalation health effects (Donaldson et al., 2001). Figure 1 shows six sampling locations chosen for the study of wind events in the period March – May, 2011. The southernmost mine tailings seen on the map are inactive and contain negligible concentrations of toxic species, such as As, Pb and Cd. The other three mining areas contain active mining operations, including ore extraction and mine tailings impoundment. The sampling sites were chosen to give a regional perspective on dust concentrations. The five sites represent a spectrum of vegetation and soil cover in the region. Wind events chosen for this study were selected for prevailing westerly winds, as defined by having 95 % or more of the wind vector from the directions between 200 and 340°. Because of this selection, the sampling sites are all downwind of the local mine tailing impoundments. Seasonally, April and May are generally the windiest months while in July and August, the months in which the North American Monsoon affects the region, winds are mostly the result of thunderstorm outflows. Prevailing winds are usually westerly, with a more southerly component during the winter months.
Figure 1. Field locations for dust monitoring in Green Valley, AZ, USA. Pecan North and Pecan South are located on the edge of a pecan tree grove and beside a dry river bed; Wastewater is located beside the same river bed; PDEQ represents an urban sample; 10 Mile is approximately 10 miles (16 km) from mining activities; HQ (Santa Rita Experimental Range) represents a natural background site chosen for the region. Annual data were taken from Green Valley Fire. Mining activities for the region are labeled in blue.

Two of the sites, Pecan North and Pecan South, are located on the edge of a pecan tree grove (which is upwind of the events) and beside a dry river bed (downwind). The site named Wastewater is near the Green Valley wastewater treatment plant, and is also located along the dry river bed (which is downwind of the events). The PDEQ (Pima Department of Environmental Quality) site is in a commercial/residential area in Green Valley and was co-located with monitoring equipment from PDEQ, including PM$_{2.5}$ and PM$_{10}$ samplers. This site had the closest proximity to the mine tailings. The 10-Mile site was chosen to be approximately 10 miles (16 km) from a mining area. The Green Valley Fire location was not a part of the dust monitoring for this study, but 2011 annual data
from the PDEQ PM$_{10}$ monitor and meteorological data at this station were utilized for data validation.

The mine tailings and active mining areas around Green Valley (Figure 1) may contribute to local dust emissions, given their relatively large surface area. However, it is important to point out that the mine operators have implemented dust mitigation measures, such as moistening the surface of mine tailings impoundments.

Forecasts from the Arizona Regional WRF model with a horizontal resolution of 1.8 km (Leuthold, 2013)) were used to select sampling events: six windy events (wind speed $\geq 10$ m/s at 10 m above ground level) and three calm events (wind speed $\leq 5$ m/s at 10 m) were considered. Previous work (Tai et al., 2012) has shown that PM$_{2.5}$ correlations with temperature and relative humidity are not a result of direct dependence but from covariation with synoptic transport that may be a consequence of, for example, the passage of a cold front. In this work, sampling events were selected when prevailing winds were from a southwesterly direction, which is the prevailing wind direction previous to cold front passage in the region. Event time periods took place between 11:00 and 18:00 Mountain Standard Time. Dust collection equipment was operated at each site for 4 hours during the forecast event period. The equipment consisted of a Dusttrak Aerosol Monitor (TSI Inc. DRX 8532), a Kestrel Weather Meter (Nielsen Kellerman 4500), and a Total Suspended Particulate (TSP) collector (F&J Specialty Products DF-AB-75L-Li). Dusttrak flow rate was 3.0 L/min and TSP flow rate was 60 L/min. Dusttrak measurements were taken with five-minute resolution and provide simultaneous real-time mass readings (mg/m$^3$) for PM$_1$, PM$_{2.5}$, PM$_4$, PM$_{10}$, and TSP (<37 µm) (Wang et al. 2009). The Dusttrak was housed in an Environmental Enclosure (TSI Inc. 8535)
with omni-directional inlet resulting in a cut-point diameter of 37 µm. Meteorological data, including wind speed and direction, relative humidity and temperature were also taken at a five minute resolution on all field instruments, which were synchronized before monitoring began. Glass fiber filters (F&J Specialty Products 206447) were used as TSP collection substrates. Filter substrates were transported to and from the field site in sealed petri dishes. Gravimetric analysis of the filters were performed using EPA class I equivalent methods on an ultra-microbalance (Mettler Toledo XP2U). The sample inlet for the Dusttrak and TSP and the weather vane for the Kestrel were set at a height of 1 m above ground level.

4.2.2. Juárez Study

PM$_{10}$ was monitored at two sites in Juárez, Mexico (lat. 31° 38’ 33”, long. –106° 25’ 48”), during the summer of 2008 (May – September). Both locations were in an urban setting, with Location A situated in the middle of a residential/commercial area surrounded by paved roads and Location B situated close to the city outskirts and surrounded by unpaved roads (Figure 2). Meteorological stations were co-located at Site A and within 2.5 km of Site B and managed by the Department of Civil and Environmental Engineering at Universidad Autónoma de Ciudad Juárez. Duplicate dust samples at each site were collected on standard filters (Partisol® 2000-FRM, Thermo Scientific) with a PM$_{10}$ inlet. The sampler was operated at a flow rate of 16.7 L min$^{-1}$ for 24-hour sampling periods. Glass fiber filters were used as substrates (1.5 µm pore, 47 mm diameter, Whatman) for collection of particulate matter.
Figure 2. Field locations for monitoring in Juárez, Chihuahua, Mexico. PM$_{10}$ monitoring was performed at the two locations show: Location A is surrounded by paved roads and Location B is surrounded by unpaved roads.

4.2.3. Dust sampler comparison

While all samplers utilized for this study are proven technologies for measuring windblown dust, it is important to note the differences in the variety of samplers. The samplers have varying flow rates, which will affect the cut-point of particle sizes sampled. Additionally, the PM$_{10}$ TEOM operated by PDEQ and the Dusttrak have omni-directional inlets while PM$_{10}$ and TSP filter samplers are directional inlets. Further, the TEOM and Dusttrak are optical samplers having errors associated with resolution and flow accuracy while filter samples’ accuracies largely depend on weighing and handling practices. The samplers are not intended to be compared directly between measurements due these varying biases, but rather to show trends of the magnitude of windblown dust with correlating conditions. All calibrations for instruments were maintained by
University of Arizona, PDEQ, and Universidad Autónoma de Ciudad Juárez for the respective samplers.

4.3 Results and Discussion

4.3.1. Green Valley site comparison

Average concentrations of PM fractions for the nine wind events during which sampling took place are presented in Figure 3, and the corresponding average wind rose is shown in Figure 4, which shows a generally southwesterly wind direction for the sampling events, consistent with the experimental design procedure. Without tracers, it is difficult to link the observed dust concentrations with specific sources, but it is worthwhile pointing out that the Pecan North site is exposed to a larger area of desert and mine tailings than any of the other sites, which might explain the substantially higher dust concentrations observed and the higher proportion of TSP with respect to smaller particle sizes. On the other hand, partly vegetated terrain and mountain foothills are located southwest of the Headquarters site, which is consistent with the relatively low amounts of dust measured. It is interesting to note the relatively high variability of the average dust concentrations among the sites, which are all contained within an area of about 100 km². The overall change in concentration between any two sites generally extends to all particle size ranges; that is, if the total concentration decreases from one site to the next, the concentration of all particle size ranges also decreases. The proportional drop is always higher for the large particle size range (TSP), which exhibits the highest fractional variation among the sites.
Figure 3. Overall average of PM$_x$ for the 9 events during March – May 2011 captured from TSP and Dusttrak observations at the Green Valley sites. The inset shows an expanded version of the plot without the TSP data.

Figure 4. Overall average wind rose for the nine sampling events during March – May 2011 at the Green Valley site.
4.3.2. *Green Valley wind event comparison*

We term three of the nine events corresponding to average wind speeds lower than 5 m/s as “calm” events. The other six events corresponded to average wind speed higher than 10 m/s (Figure 4). Three of these events, termed “windy” events, resulted in significantly lower dust concentrations than the other three events, which we term “windy dusty” events (Figure 5), despite the fact that both the wind speed and gustiness (high wind frequencies >5 m/s) of the “windy” events were higher than those of the “windy dusty” events. On those windy but non-dusty days, the humidity was found to be higher than on windy, dusty days (Figure 5). Wind speed and relative humidity data were acquired from the PDEQ site while frequency of wind speed > 5 m/s was measured by the co-located Kestrel weather stations at each site. The frequency of high winds gives a sense of gustiness (with a consequent greater potential for particle entrainment) for the field locations while wind speed gives a sense for the event’s dust generation potential (Zeng et al., 2010; Cheng et al., 2012). Because relative humidity before and during the event is an important factor for soil moisture content, 24-hour average and event average relative humidity are compared in Figure 5. Since all the events occurred in the same season, the temperature variation was minimal between and during events, averaging 23.2 ± 2.6 °C. Differences in relative humidity were related to synoptic weather patterns. The corresponding summary wind roses (PDEQ site) for calm, windy, and windy dusty events can be seen in Figure 6. The data for the wind rose were also taken from the PDEQ weather station. These show that wind direction was fairly consistent for all the events, especially among the six windy events.
Figure 5. Wind speed, relative humidity and dust concentration for measurements separated into “Calm”, “Windy”, and “Windy Dusty” events, each containing average of three different measurements, for the Green Valley events. Error bars represent standard deviations of repeat measurements of the same sample.
Figure 6. Wind roses for “Calm”, “Windy”, and “Windy Dusty” events, each corresponding to three different measurements.
To determine the possible roles that relative humidity and wind speed have on PM$_{10}$ concentrations, we analyzed correlations among these parameters using the Spearman correlation coefficient, which measures the strength of association between two variables. Relative humidity and wind speed data were used from the Kestrel weather station co-located with the Dusttrak measuring the PM$_{10}$ concentrations. Results are presented in Table 1. Independently, PM$_{10}$ vs. wind speed and PM$_{10}$ vs. relative humidity show very little correlation. However, when correlation factors are calculated for specific ranges of wind speed above a cut-off value, the strength of the correlation increases with wind cut-off wind speed and negative correlation coefficients are obtained, which indicates an overall decreasing trend of PM$_{10}$ with increase in relative humidity.

**Table 1.** Spearman correlation coefficients between PM$_{10}$ (µg/m$^3$), and wind speed (WS, m/s) and relative humidity (RH, %), using data from all nine events and six sites at Green Valley locations. Correlation factors with relative humidity are shown for all data, and data that include only measurements for wind speed exceeding the value noted (m/s) and RH>10%.

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>Spearman correlation factor (y vs. x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS</td>
<td>PM$_{10}$</td>
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</tr>
<tr>
<td>RH</td>
<td>PM$_{10}$</td>
<td>0.10</td>
</tr>
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</tr>
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</tr>
<tr>
<td>RH (WS &gt; 7)</td>
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<td>-0.88</td>
</tr>
</tbody>
</table>
4.3.3. Green Valley annual analysis

Annual (2011) PM$_{10}$ data from the Green Valley Fire Station (Figure 1) were analyzed to examine long term interdependent correlations between PM$_{10}$, wind speed, relative humidity and temperature. As discussed below, temperature did not have a significant effect on PM$_{10}$ concentrations and the best correlation was obtained with relative humidity at high wind speed. The relation between these two variables is shown in Figure 7, where all data at wind speeds greater than 4 m/s are shown. In the range 0≤RH≤25%, the PM$_{10}$ concentration increases with relative humidity. This could be due to increased dust emissions due to weakening interparticle cohesion as water starts adsorbing on dry particles, which would increase friction velocity. This observation is consistent with the results of Ravi et al. (2004) discussed above. However, the trend is reversed at RH>25%. The attenuation of PM$_{10}$ by increasing relative humidity in this range may be a consequence of increasing interparticle cohesion forces due to presence of liquid water films on the particles.
Spearman correlation coefficients for data at RH>25% are shown in Table 2. A weak correlation is seen between PM$_{10}$ and wind speed and relative humidity when analyzed independently, similar to results presented in the previous section. A stronger correlation between PM$_{10}$ and RH is seen when data were parsed out for high wind speeds, but no dependence on temperature is observed independently. This correlation indicates a monotonically decreasing trend in PM$_{10}$ concentrations with RH at RH>25%.

**Figure 7.** PM$_{10}$ vs. relative humidity (WS>4 m/s) at the Green Valley Fire Station for 2011.
Table 2. Spearman correlation coefficients between PM10 (µg/m³), wind speed (WS, m/s), temperature (°C) and relative humidity (RH, %), using 2011 annual data from Green Valley Fire. Data analyzed include only RH>25%.

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>Spearman correlation factor (y vs. x)</th>
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<tbody>
<tr>
<td>WS</td>
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<tr>
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<td>-0.0003</td>
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</tbody>
</table>

The combined effects of wind speed and relative humidity on PM₁₀ concentrations can be more clearly seen in Figure 8. At wind speeds less than 6 m/s, PM₁₀ concentrations are low and insensitive to either wind speed or relative humidity. However, at high wind speeds, the maximum in PM₁₀ concentration with relative humidity is clearly seen. An absolute maximum close to 80 µg/m³ is obtained at 40% relative humidity and 11 m/s wind speed.
The World Health Organization and US EPA PM$_{10}$ 24-hour guideline are 50 $\mu$g/m$^3$ and 150 $\mu$g/m$^3$, respectively (WHO, 1995; EPA, 2012). The minimum wind speed necessary to create these concentrations according to Figure 8 is approximately 7 m/s at a relative humidity of 35%. If relative humidity were to increase to 50% then the minimum wind speed would rise to 9 m/s. These values hold consistent with a field scale study by Ravi and D’Odorico (2005) in which wind erosion threshold velocities were found to peak at RH 35% with an increasing trend with air humidity (RH<35%) and subsequent decreasing trend with humidity (RH>35%).
4.3.4. Juárez PM$_{10}$ study

The interdependence of PM$_{10}$ concentration on wind speed and relative humidity was also observed in Juárez, Chihuahua, Mexico. Similar to Green Valley, Juárez is situated in a semi-arid region that experiences frequent dust storms. Figure 9 shows PM$_{10}$ concentrations contours as a function of relative humidity and wind speed, using data from a field campaign to study the difference between PM$_{10}$ concentration of paved (A) and unpaved roads (B). As would be expected, higher concentrations of PM$_{10}$ are seen for unpaved roads. Both contour plots show a comparable trend of low relative humidity and high wind speeds yielding high PM$_{10}$ concentrations.
Figure 9. PM$_{10}$ concentration ($\mu g/m^3$) contours compared to relative humidity (%) versus and speed (km/h) from a study in Juárez, Chihuahua Mexico. Location A monitored PM$_{10}$ near paved roads (top) and Location B monitored near unpaved roads (bottom).
As in the Green Valley study (Figure 8), an absolute maximum in PM$_{10}$ concentration is observed. The wind speeds and relative humidities at which the maxima occur (11 m/s WS and 23% RH for paved roads and 16 m/s WS and 23% RH for unpaved roads) are of the same order of magnitude as those observed in Green Valley, although the maxima of PM$_{10}$ concentrations are noticeably higher, especially for the case of unpaved roads, where the PM$_{10}$ concentration reaches a maximum of 350 µg/m$^3$. The higher concentration values may be a result of surfaces with higher propensity to wind erosion, but it is interesting to note that similar conditions at both sites in terms of wind speed and relative humidity are necessary to obtain relatively high PM$_{10}$ concentrations. García et al. (2004) used chemical fingerprinting to assess dust sources in the neighboring city of El Paso, TX, and concluded that anthropogenic dust sources (e.g. fugitive dust from a smelter and quarry) had significant impact on atmospheric dust concentrations of pollutants. It is not known if these results translate to the Juárez area directly, but, if so, it would imply that both anthropogenic and natural sources follow the same trends with variations in wind speed and relative humidity.

4.4 Concluding Remarks

The study of dust generation in Green Valley has implications to dust event predictions. While dust storm forecasts factor drought conditions in models, wind speed is considered the main driver in dust concentration predictions (Lu and Shao, 2001; Yin et al., 2005). Here, we show that both relative humidity and wind speed are determinants of dust generation. Results from annual PM$_{10}$ data confirm there is no seasonal reliance on relative humidity or wind speed being a factor in dust concentration. Additionally, results
from a study in Juárez, Chihuahua, Mexico, confirm the interdependent importance of relative humidity and wind speed in PM$_{10}$ concentration in semi-arid regions.

The underappreciated role of relative humidity on atmospheric dust concentrations should be considered in the prediction of atmospheric dust concentrations. Our results show a complex, nonlinear dependence of PM$_{10}$ on wind speed and relative humidity in which water sorption seems to control friction velocities at low relative humidity (< 25%) while interparticle cohesion forces due to liquid bridges predominate at high relative humidity (> 25%), which needs to be considered in regional dust event forecasts, as well as in future effects of climate change on dust events in the US Southwest. The wide scatter of the data suggests that wind speed and relative humidity are not the only factors determining dust concentrations. Effects of variability of wind direction and speed (e.g. in terms of wind gusts) should also be considered. However, our limited data set did not allow us to look into these additional variables.

Acknowledgements

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CHAPTER 5: Size-Resolved Dust and Aerosol Contaminants Associated with Copper and Lead Smelting Emissions: Implications for Emissions Management and Human Health

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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 emissions management and practices that minimize health risks associated with metal extraction and processing can be developed.

Keywords: Mining, Dust and Aerosol, Arsenic and Lead, Dust Transport
5.1 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, 2010; 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 results 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 (Australian Department of Sustainability, 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 in 2009 as
high as 0.25 µg/m³ and 19.7 µg/m³, respectively, taken 0.4 km from smelting activities (South Australia EPA, 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., 2013, 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 EPA 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;
Arsenic is also a known carcinogen and, even though the World Health Organization (WHO, 2000) has not set a safe level of atmospheric concentrations, a value of 6.6 ng/m³ 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 Wexler, 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 Wexler, 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 assess sources of contamination in the studied sites.

5.2 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 Figure 1.
According to US EPA (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 tailings 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 matter 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.
The Mount Isa smelter produces Pb and Cu while recovering Zn and Ag. Local underground mines provide the ore which is then crushed and refined at the surface. Ball mills grind the rock to ~ 100 μm, the product of which is concentrated by flotation. The Cu concentrate is further processed in furnaces. The Pb concentrate is fed to a blast furnace where it is recovered as 99.6 % lead bullion. Mount Isa has an electrostatic precipitator and scrubber in the copper smelter and a bag house in the lead smelter. The plant claims to only allow emissions from operations when the prevailing winds are towards the NW direction, away from the community, as part of their pollution control strategy.

The Port Pirie smelter is primarily a Pb plant that produced 158,000 tons of Pb in 2012, but also Zn, Cu, Ag, and Au are recovered as by-products. The ore concentrate is sintered before being sent to a blast furnace. Spent slag from the furnace is sent to a Zn recovery plant before being discarded as waste. The Pb bullion is further processed to remove Cu, As, Sb, Au, and Ag before the final refining stage. Emissions are controlled by bag house, electrostatic precipitator and scrubbers, as well as mist treatment for dust suppression on processes such as ore transfer.

Sampling of atmospheric air at all sites was performed with a ten-stage micro-orifice uniform deposit impactor, MOUDI (MSP Corporation) (Marple et al., 1991). The MOUDI provides separate fractions of dust and aerosol at the 50% cut off points (d_{50}-values) of 18, 9.9, 6.2, 3.1, 1.8, 1.0, 0.55, 0.32, 0.18, 0.10 and 0.054 μm equivalent aerodynamic diameter. Total sampling time at 30 L min⁻¹ varied according to distance from and strength of the source. The sampling duration for Port Pirie was the shortest at 24 hours due to relatively high Pb concentrations (the sampling location was at 0.3 km
from smelting operations). The MOUDI was run for 72 hours at Mount Isa (2.8 km from smelting operations). All other sites were sampled for 96 hours. At Australian sites, weather data were acquired from local Australian Environmental Protection Agency’s monitoring sites, whereas at the Hayden site, weather data were acquired from a collocated weather station and data logger (Campbell Scientific CR800).

Teflon filters (PTFE membrane, 2 µm pore, filter substrate 46.2 mm, Whatman) were used as impaction substrates in the MOUDI. Filters were transferred in clean petri dishes (Micro Analytix, 800100). Field blanks were used as controls. Substrates were weighed before and after sampling using an ultra-microbalance (Mettler Toledo XP2U) according to EPA Class I equivalent methods. Once gravimetric analysis was complete, filters were extracted in sealed glass vials with trace metal grade aqua regia and sonication at 80 °C for 60 min (Harper et al., 1983). Extracted aliquots were analyzed for metal and metalloid concentrations by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500ce with an Octopole Reaction System). For the analysis of total lead, the equipment was tuned for robust plasma conditions to reduce the formation of oxides to less than 2%. The plasma gas flow used was 1.5 L/min and the carrier gas flow was 1 L/min. The solutions were measured after instrument calibration, then repeatedly throughout the analytical run, after every three sample injections. Certified calibration standards from Accustandard were made with MiliQ water, 0.669 HCl (Fisher, trace-metal grade) and 0.309 M HNO₃ (EMD, Omnitrace). National Institute of Standards and Technology (NIST) standard reference material (SRM 1643e trace elements in water) was analyzed with each set of data. For the analysis of lead isotopic ratios, the operating conditions were the same as those used for elemental concentration measurements. NIST SRM 981
(lead isotopic standard) was used for validation and calibration. The analytical precision of lead isotopic ratios was under 0.5 % for Pb$^{207}$/Pb$^{206}$ and Pb$^{208}$/Pb$^{206}$.

5.3 Results and Discussion

The size-fractionated aerosol and dust collected near the Hayden mining and smelting site clearly shows a bimodal distribution for both Pb and As, with maxima located at approximately 0.32 and 9.9 μm diameter (Figure 2).

![Figure 2. Airborne lead and arsenic content by particle size (MOUDI samples) observed at Hayden, Arizona, for a 96-h sample collected 1 km south-southeast from smelting operations with sampling starting on February 5, 2011; AF denotes after filter sample. The wind rose inset is from a co-located weather station, which shows that winds from the direction of the smelting activities (NNW) account for roughly 30% of prevailing winds during the sampling period.](image-url)
Scanning electron micrographs of fine particles (< 1 μm) show that particles containing relatively high concentrations of Pb and As are spherical (Figure 3a), which suggests that the origin of these particles is condensation from the high temperature smelter emissions. Some of the fine particles also show evidence of coagulation of two or more spheres. Coarse particles tend to be of irregular shape (Figure 3b), suggesting that they consist primarily of windblown dust. Lead and arsenic laden particles in this range may originate from mine tailings, or other exposed ore or slag.

![Figure 3](image)

**Figure 3.** Representative Scanning Electron Microscope images from MOUDI stages (Hayden site samples) with cutpoint particle diameters of (a) 0.32 μm, particle depicted was identified to contain 10.88± 1.00 % Pb by weight by Electron Dispersive Spectroscopy; and (b) 6.2 μm.

Results from MOUDI samples collected in Mount Isa, also an active mining and smelting site, are shown in Figure 4. As was the case in Hayden, both Pb and As are concentrated in the submicron fraction, with maxima located at approximately 0.32 μm (As) and 0.55 μm (Pb). However, Figure 4 shows that the arsenic coarse mode maximum occurs at about 18 μm and a distinct coarse mode maximum for Pb is absent, although relatively high lead concentrations are observed in the coarse fractions.
Figure 4. Airborne lead and arsenic content by particle size (MOUDI samples) observed at Mount Isa, New South Wales, for a 72-hour sampling period beginning on February 21, 2012. The MOUDI sampler was located 2.8 km northeast from the smelter; AF denotes after filter sample. Wind rose was from a weather station located approximately 1.5 km NNE of the smelter.

Similar results for Port Pirie are shown in Figure 5. Arsenic again shows a bimodal distribution with maxima at approximately 0.55 μm and 9.9 μm diameter. The Pb size distribution is significantly different from Hayden and Mount Isa. First, the highest concentration is found in the coarse mode (9.9 μm). The maximum in the fine mode is found at about 0.32 μm diameter. It should be noted that the Pb concentrations here are an order of magnitude higher than at Hayden or Mount Isa.
Figure 5. Airborne lead and arsenic content by particle size (MOUDI samples) observed at Port Pirie, South Australia for a 24-hour sampling period 0.4 km south from the smelter on April 17, 2012; AF denotes after filter sample. The wind rose is from a weather station located approximately 2.8 km south-southeast from the smelter.

Fine particles contaminated with As and Pb are thought to arise primarily from smelting operations as a result of condensation of high temperature vapors and coagulation, leading to a sub-micron maximum of contaminant concentration in the accumulation mode (Seinfeld and Pandis, 2006). On the other hand coarse particles, which are mainly windblown dust, originate either from background sources (topsoil or crust), or mine tailings or fugitive emissions from the crushing, grinding and transportation of the ore. In particular, if the lead contained in the particles originates from different sources, the isotopic composition of lead is potentially different for each source. It is known that the concentration of $^{206}$Pb, a product of the radioactive decay of $^{238}$U, increases over time at rates that are higher than those associated with changes in $^{207}$Pb and $^{208}$Pb. As a
consequence, the concentration ratios $^{207}$Pb/$^{206}$Pb and $^{208}$Pb/$^{206}$Pb have decreased over time (Mukai et al., 2001; Komárek et al., 2008) and this type of analysis has been used widely to discriminate between anthropogenic lead sources (mined ores) and natural lead sources (derived from erosion of surface minerals) (Grousset and Quetel, 1994; Erel et al., 1997; Reuer and Weiss, 2002; among others).

Figure 6 shows a comparison of lead isotopic ratios of samples collected in this investigation. For both the Mount Isa and Hayden sites, where active smelters operate, there is a clear difference between the isotopic ratios between coarse and fine particles, which suggests a different origin. On the other hand, at the urban control site (Tucson), there is no change in the isotopic ratios with particle size. It is interesting to note that the isotopic signature of the coarse particles in Hayden is close to the signature of the Tucson particles (100 km away), which suggests that the Hayden coarse particles are heavily influenced by the regional background while the lead in fine particles corresponds to the ore processed in the smelter. This is further confirmed by the fact that the lead isotopic ratios of the Hayden fine particles (Figure 6) are identical to the ratios reported for the Ray Mine ore, the main supplier for the Hayden smelter: $207/206$: 0.86, $208/206$: 2.1 (Bouse et al., 1999).
Figure 6. Lead isotopic composition ratios of samples from various locations. Analysis samples were obtained by combining particles collected from various stages of the MOUDI sampler. Results are presented for two particle size ranges: 0.32 - 0.55 µm (fine particles) and 3.1 - 6.2 µm (coarse particles). The solid line is the growth curve, adapted from Chen et al. (2008) and developed by Cumming and Richards (1975).

The lead isotopic ratios for the Mount Isa samples also show a difference between fine and coarse particle, which suggests two different sources. The lead isotopic ratios for the Mount Isa mine ore are: 207/206: 0.96, 208/206: 2.22 (Sturges and Barrie, 1987). These ratios are appreciably different from the two particle sizes (Figure 6). However, a second source of lead in the Mount Isa region has been identified as the local crustal material, which contains relatively high concentration of lead (Mackay et al, 2013; Stacey and Kramers, 1975). The crustal lead isotope ratios are: 207/206: 0.83, 208/206: 2.05. The results in Figure 6 clearly indicate that both fine and coarse particles in the dust collected contain a mixture of crustal lead and ore lead, with the coarse fraction being closer to the
ore signature. This indicates that windblown dust (coarse fraction) from tailings and ore exposure is an important contributor to atmospheric lead concentrations,

In terms of concentrations, the Hayden site samples contain 88% and 86% of the As and Pb, respectively, in the fine size fraction (< 1 µm). Similarly, in Mount Isa, fine particulate accounts for 87% of As and 61% Pb. In Port Pirie, however, 72% of the As is in the fine size fraction while only 38% of the Pb is < 1 µm. Given that both Port Pirie and Mount Isa preform grinding of the ore that will later be refined for Pb, it is expected that coarse particle fractions will be enhanced in Pb concentration. Moreover, in Port Pirie the Pb concentrate feed stock has already been ground (~106 µm diameter) and concentrated by flotation, so it is reasonable to expect that mechanical action, including material handling and wind erosion gives rise to an enhanced concentration in the coarse mode (Jackson and Abbot, 2008), as observed here. Since Port Pirie is primarily a Pb Smelter, the fine fraction is also expected to contain relatively high Pb concentrations. While Mount Isa similarly refines Pb, the sampling site is 2.4 km further away from the activities when compared to Port Pirie. Therefore, the majority of the coarse particles have settled out of the atmosphere before reaching the receptor. For example, a 10 µm lead oxide particle has a terminal settling velocity of around 2.9 m s⁻¹, as calculated from Stokes law, assuming a density of 9,500 kg m⁻³ and spherical morphology. This particle would travel 0.4 km (the distance to the Port Pirie sampling location) with a sustained wind of 1.1 m s⁻¹ while the same particle would require a wind of 8 m s⁻¹ to travel 2.8 km (the distance to the Mount Isa sampling location). It is important to note that some studies show the MOUDI to be less efficient at collecting coarse particles than other samplers (Cabada et al. 2004), which would introduce a low bias in the coarse particles
Pb concentration. While PM$_{10}$ has been shown to provide good agreement with MOUDI measurements (Csavina et al. 2011), MOUDI samples may not provide total ambient contaminant concentrations as compared with those found in total suspended particulate collection.

We used the same procedures to perform a field site comparison for As and Pb concentrations. MOUDI observations are presented in Figure 7, including measurements from two urban locations. The concentrations of Pb and As were summed for particles with MOUDI cutpoint diameters $\leq 1$ and $\geq 1 \, \mu m$. All the smelting sites have higher Pb and As concentrations in the fine fraction except for Port Pirie, as discussed above. Figure 7 indicates that smelting heavily enriches concentrations of Pb and As in the atmosphere when compared to urban samples, with a particularly high impact on the fine size fraction.
Figure 7. Field site comparison of MOUDI observations of Pb and As concentrations summed according to two particle size fractions: < 1 µm and > 1 µm. Urban sites samples were collected for 96 hours on the following dates: Sydney – February 14, 2012; and Tucson – October 14, 2010. WHO guidelines: Pb – 500 ng/m³; As – 6.6 ng/m³ excess lifetime risk level 1:100,000.

Gravimetric analysis presented in Table 1 presents a field site comparison for the maximum mass concentration found for any individual MOUDI impactor stage. By weighing each filter (impaction stage) before and after exposures, it is possible to determine the total dust and aerosol mass collected on each stage, and thereby calculate the mass concentration (ppm) of Pb and As on each stage from the atmospheric concentration reported (Figures 2, 4 and 5). The Sydney and Tucson sites are included for comparison. The smelting sites are clearly enriched in Pb and As when compared to urban samples of Sydney and Tucson.
Table 1. Maximum mass concentration (ppm) found for any individual MOUDI impactor stage of As and Pb for field site comparison. Hayden, Port Pirie, and Mount Isa include smelting operations; Sydney, NSW AUS and Tucson, AZ USA represent an urban sample.

<table>
<thead>
<tr>
<th></th>
<th>Hayden</th>
<th>Port Pirie</th>
<th>Mount Isa</th>
<th>Sydney</th>
<th>Tucson</th>
</tr>
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<tbody>
<tr>
<td>As (ppm)</td>
<td>8,622</td>
<td>2,471</td>
<td>955</td>
<td>215</td>
<td>63</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>13,173</td>
<td>36,399</td>
<td>8,922</td>
<td>148</td>
<td>302</td>
</tr>
</tbody>
</table>

5.4 Conclusion

To our knowledge, this study is the first comparative analysis of the size-resolved concentrations of metal and metalloids around multiple smelting sites. Results in this study show the potential of smelting operations to affect nearby ecology and human health. Mine tailings alone can be a source of contaminants when present at high concentrations, but contaminants reside primarily in the coarse size fraction that will not travel as far in the environment. However, smelting emissions can have a much broader area of impact due to the fine size of the contaminated particles. In addition, when inhalation is a route of exposure for contaminated aerosols, fine particles are respired to the lungs which are thereby transferred to the blood stream via macrophages while coarse particles are removed by the upper respiratory tract and expelled through the digestive tract leading to lower associated dose when compared to lung deposition. The smaller size fraction also has a higher bioavailability due to higher surface to volume ratio.
Acknowledgements

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5.5 References


CHAPTER 6: Conclusions

Studies were performed at multiple sites having mining activities. Each of the sites had particular characteristics; however, all of them were sites with mining activities. Mining operations impact the environment in different ways. One of the environmental compartments more affected is the atmosphere. Aerosols are produced in a wide range of sizes depending on the type of processes. Some activities like crushing, grinding and mine tailings resuspension produce mainly coarse particles. On the other hand, smelting processes produce mainly fine particles. During this research a size resolved concentration of contaminants was determined at the different sites. For this purpose a Micro-Orifice Uniform Deposit Impactor (MOUDI) was utilized. Results obtained show a characteristic pattern in all the sites sampled. Fine particles have a higher concentration of contaminants than coarse particles. This represents a potential adverse health effect to the population exposed. Fine particles penetrate deeper in the respiratory system whereas coarse particles are generally filtered out by the upper respiratory tract. Another important aspect to consider is the fact that small particles can travel further in the environment. On the other hand coarse particles produced by mechanical action will not be able to travel as far as the fine particles.

Meteorological parameters play a key role in atmospheric dust transport, dry conditions and high wind speeds are ideal conditions for the transport of aerosols. A study that related the meteorological conditions with dust concentrations was performed at two different semi-arid sites. In this study we were able to show that both relative humidity and wind speed are determinants of dust generation.
One of the objectives of this research was to develop a technique that allows us to identify sources of lead in the environment. Lead isotopic analyses were done at multiple sites in order to identify possible sources of lead. These analyses were performed on MOUDI and soil samples. For the MOUDI samples the main objective was to investigate if the fine and coarse particles have the same origin or not. We found that fine particles have a different isotopic signature than coarse particles, by these differences it can be concluded that the lead contained in fine and coarse particles have different sources at Hayden. For the soil sample analysis, lead isotopic ratios were determined at different distances from the source of pollution, in this case mine tailings. A linear transect was studied, first the isotopic signature of the tailings was obtained. After this, the isotopic signature of a “background” site was determined. The “background” site was located 5 km away from the mine tailings. Multiple samples were taken in between these two points. Lead isotopic ratios similar to those of the mine tailings were observed in the samples closer to the tailings. As distance increased, the isotopic ratios were turning closer to those found at the “background” site. By knowing the difference in these ratios, a source apportionment calculation can be performed and the specific contribution of lead coming from the contaminated mine tailings can be determined. Overall, it was demonstrated that lead isotopes are a powerful tool to identify different sources of contaminants.

As it has been described before, this research is closely related to adverse effects on health. For this reason, we have had collaboration with researchers from toxicology and public health. Toxicological studies require a relatively large amount of sample to be performed. Unfortunately aerosols samplers usually are not capable of collecting the
large amount of dust required for these studies. For this reason a dust generator equipment was constructed. This equipment is able to aerosolize soil samples that are collected from the sites of concern, in this case, mine tailings. In addition to this, the equipment can be configured to produce large quantities of dust with a specific size distribution. During this research mine tailings were processed in the dust generator and a PM$_{10}$ cyclone was coupled to the equipment so PM$_{10}$ particles were generated. Besides the physical characterization of the particles (size distribution, morphology, etc.) the chemical composition was determined. From the analysis performed it can be concluded that PM$_{10}$ had much higher concentrations of contaminants like lead and arsenic than the actual soil samples. This is an interesting result due to the fact that fine particles can travel long distances and people nearby mine tailings might be exposed to high contaminant concentrations. With the equipment created for the production and selection of aerosols according to particle size, large quantities of dust have been generated and used for the development of toxicological studies.

With all the information generated during the development of this research as well as the treatment of meteorological information and the use of computational software, models have been created to predict concentrations of contaminants at different points from the source of contamination. The publications describing the models are presented in the appendix section. The author did not have a direct contribution in the development of the model; however, the data generated by the author was used for its creation.
Appendix A: Simulation of windblown dust transport from a mine tailings impoundment using a computational fluid dynamics model

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Abstract

Mining operations are potential sources of airborne particulate metal and metalloid contaminants through both direct smelter emissions and wind erosion of mine tailings. The warmer, drier conditions predicted for the Southwestern US by climate models may make contaminated atmospheric dust and aerosols increasingly important, due to potential deleterious effects on human health and ecology. Dust emissions and dispersion of dust and aerosol from the Iron King Mine tailings in Dewey-Humboldt, Arizona, a Superfund site, are currently being investigated through in situ field measurements and computational fluid dynamics modeling. These tailings are heavily contaminated with lead and arsenic. Using a computational fluid dynamics model, we model dust transport from the mine tailings to the surrounding region. The model includes gaseous plume dispersion to simulate the transport of the fine aerosols, while individual particle transport is used to track the trajectories of larger particles and to monitor their deposition locations. In order to improve the accuracy of the dust transport simulations, both regional topographical features and local weather patterns have been incorporated into the model simulations. Results show that local topography and wind velocity profiles are the major factors that control deposition.

Keywords: Aerosol transport, Dust, Deposition, CFD, Superfund
A.1 Introduction

The Iron King mine tailings site located in Dewey-Humboldt Arizona is a potentially hazardous source of contaminated aerosols. The Iron King Mine tailings and nearby inactive smelter site were officially added to the Environmental Protection Agency (EPA) national priorities list in 2008. The smelter was operational from 1904 till 1969. It was used to extract lead, gold, silver, zinc and copper at different times. The 220,000 m² tailings were impounded on property (EPA, 2010). Sediment from these mine tailings has significantly elevated concentrations of both lead (up to 0.20 wt%), and arsenic (up to 0.24 wt%), amongst other toxic species. Additional tests of top soil from nearby sampling sites have shown elevated contaminant concentrations outside the boundaries of the Iron King Mine property. The spread of the contaminants is in part caused by aeolian dust transport from the mine tailings.

Aerosol and dust transport is a potentially dangerous mechanism for spreading contamination because of the high mobility of the smaller suspended particulate, especially for accumulation mode aerosols (<1 µm diameter). This particle size range is potentially hazardous to human health since they have the potential to deeply penetrate in the respiratory system. The relatively large diffusivity of these aerosols causes them to have an increased likelihood to deposit in the smaller airways such as the alveolar regions of the lungs (Hinds, 1999). Long-term exposure to these aerosol and dust particles may cause adverse health effects. Lifetime excess cancer risks for a similar arsenic contaminated copper mine located in Hayden, Arizona, was estimated to be 1 in 5,000 by the Arizona Department of Health Services (Public Health Assessment, 2002), and up to 1 in 100, as estimated by EPA (Earth Justice, 2003).
In this work, we apply a Computational Fluids Dynamics (CFD) software tool, ANSYS FLUENT, to investigate aeolian transport and deposition rates of aerosols emitted from the Iron King Mine tailings to the surrounding region. The CFD is based on the turbulent Reynolds Averaged Navier-Stokes (RANS) equations. The complex topography of the terrain in the simulation area is included in the model. In addition, this CFD model can track both mixed gaseous species as well as predict the trajectories of individual particles (FLUENT Theory Guide). By utilizing these schemes within the CFD model, realistic simulations of aerosol and dust transport can be achieved.

A.2 Methodology

A.2.1 Site Description

The Iron King Mine Tailings are located in north central Arizona at 34.500 ° north latitude and 112.253 ° west longitude with an average altitude of 1436 m above sea level. The topography of the land directly adjacent to the mine tailing impoundment is characterized by rolling hills with the Chaparral gulch bordering the northern edge of the mine property and the Galena gulch bordering the southern edge. Larger mountains are located slightly further away in the surrounding Prescott and Tonto National Forests. It is a semiarid region that receives an annual average of 480 mm of precipitation (NCDC, 2004).

The tailings impoundment rises vertically from the hillside with a rectangular shape and flat top. The tailings material has regions of reddish brown color and consists of gravelly sands and silty sands (Remedial Investigation Report, 2010). The tailings have a loam texture that consists of 34.7 % sand, 44.8 % silt, and 20.4 % clay (Solis-Dominguez et al., 2012). The tailings are encrusted with white efflorescence deposits after rain storms.
A.2.2 Observations

Since December 2011, the Iron King Mine tailings have been equipped with two 10-m height towers fitted with meteorological instruments and dust monitors. Each tower has three anemometers located at 10 m, 3 m and 1 m heights. The north tower is equipped with all cup anemometers; while the south tower has a 3-D sonic anemometer located at 1 m above the ground. Additional meteorological instrumentation was used to measure wind direction, temperature, relative humidity, soil moisture and temperature. Three TSI DUSTTRAK II 8530 dust monitors were fitted to each tower at 10 m, 3 m, and 1 m heights. Each dust monitor utilizes an omnidirectional inlet that has a particle size cutoff of 27 μm aerodynamic diameter. Figure 1 shows four days of observations taken during 2012, including the 3-m height wind speed and direction, as well as the 1-m height DUSTTRAK data. As expected, there is a noticeable diurnal pattern in both in wind speed and direction with wind speed increasing during the morning hours and turning to calm conditions in the early evening. The dust monitor data show a similar diurnal pattern with higher dust concentrations as the wind speeds increase during the day. Occasional peaks in dust concentration during the day are due to brief wind gusts or top soil perturbations.
Figure 1: Time series of observations taken from the eddy flux tower located directly on the tailings from June 13\textsuperscript{th} to June 17\textsuperscript{th}, 2012. The top plot is the 1 m height dust concentrations with a 10 second sample frequency. The middle plot is a time series of the 3 m height wind speed with a 5 minute sample frequency. The bottom plot is the corresponding wind direction. The x axis represents time in days with integer values corresponding to midnight.

The region’s climate is characterized by two windy and dry seasons during spring and fall. This is ideal for producing aeolian dust. In this study, we focus on the 2012 spring windy season which we define as being from April 1\textsuperscript{st} to June 30\textsuperscript{th}. The end of the spring windy season coincides with the start of the North American Monsoon when convective outbreaks can cause localized heavy rains that increase soil moisture, which inhibits dust emission.

The average wind rose of the 2012 spring windy season can be seen in Figure 2. The wind rose was produced using the 10m anemometer daylight observations (8\textsuperscript{th} - 20\textsuperscript{th} hours local time). The dominant wind direction for all wind speed observations are
Southerly, Southwesterly, Southeasterly and Northerly. The northerly winds tend to be very low speed and occur during the overnight hours. When we take into consideration only wind speeds exceeding 4 m/s southerly wind direction dominates with 36% occurrence, while 85.2% of wind speeds that exceed 4 m/s come from one of the four wind directions: southeast, south, southwest or west. These observations were used in conjunction with the EPA AP 42 wind erosion model (EPA, 1988) to physically constrain the emission scheme that was used in the CFD species transport model.

**Figure 2:** Wind rose generated using daytime 10 m height anemometer observations taken on the mine tailings from April 1st to June 30th, 2012. Daytime observations are defined as 8:00 - 20:00 hours, local time. Wind speed in m/s.
A.2.3 Emission Scheme

The emission model used to estimate wind erosion of the mine tailings comes from the EPA AP 42 report (EPA, 1988). The friction velocity is estimated from the near-surface logarithmic wind profile (Eq. 1), where \( u(z) \) is the wind speed (m/s) at height \( z \), \( K \) is the von Karman constant, \( u^* \) is the friction velocity (m/s) and \( z_0 \) is the roughness height (m). The friction velocity is a measure of the shear stress exerted on the surface, and when this shear stress becomes sufficiently large and exceeds a critical threshold, \( u_T^* \), erosion of surface particles may occur. Portable wind tunnel experiments conducted on a similar copper mine tailing impoundment also located in Arizona found \( u_T^* = 0.172 \) m/s (Nickling and Gillies, 1986).

\[
    u(z) = \frac{u^*}{K} \ln \frac{z}{z_0}
\]  

The emission factor \( E \) (g/m\(^2\) per event) of a surface is defined in Eq. 2, where \( k \) is the particle size multiplier, \( N \) is the number of disturbances per event and \( P_i \) is the erosion potential for the \( i^{th} \) time period. The particle size multipliers for PM\(_{30}\), PM\(_{15}\), PM\(_{10}\) and PM\(_{2.5}\) are 1.0, 0.6, 0.5, and 0.075, respectively (Cowherd, 2006).

\[
    E = k \sum_{i=1}^{N} P_i
\]  

The erosion potential for each time interval is calculated using Eq. 3. In the case where \( u^* = u_T^* \), the erosion potential is zero. The friction velocity for each time interval is calculated from observed “fastest mile” within the time period. Fastest mile is defined as the shortest time required for a single mile’s worth of distance to be advected past the anemometer.
\[ p = \begin{cases} 
58(u^* - u^*_t)^2 + 25(u^* - u^*_t) & \text{for } u^* > u^*_t \\
0 & \text{for } u^* \leq u^*_t 
\end{cases} \] (3)

Frictional wind velocities were calculated using the fastest mile observations from the sonic anemometer located 1 m above the tailings because of its relatively high accuracy and since it requires less interpolation to the surface. An analysis of fastest mile friction velocities was conducted for one hour time intervals for the 2012 windy season. The resulting fastest mile friction velocities were used in the calculation of the erosion potential.

**A.2.4 Model Description**

FLUENT 12.0 (distributed by ANSYS Corporation) has been used in a variety of studies involving aerosol transport, including flow over stockpiles (Diego et al., 2009, Badr and Harion, 2005); quantification of the effect of industrial buildings on the wind erosion of stock piles (Turpin and Harion, 2010a 2010b); influence of the turbulent kinetic energy in the atmospheric boundary layer (Gorlé et al., 2009); and deposition and clearance of particles in human airways (Anthony and Flynn, 2006). Our simulations utilize a turbulent flow field, species transport and discrete phase modeling.

**A.2.4.1 Fluid Flow**

Fluid flow simulations used the k-ε turbulent kinetic model, a two equation method used to solve for the Reynolds stresses term of the Reynolds Average Navier-Stokes (RANS) equations of motion (Eq. 4). The Reynolds stresses (Eq. 5) are an apparent force that arises from the time averaging of the instantaneous Navier-Stokes equations and they are represented in terms of a turbulent viscosity (Eq. 6).
\[
\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j) = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j}\left[\mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \frac{\partial u_l}{\partial x_l}\right)\right] + \frac{\partial}{\partial x_j}(-\rho u_i' u_j') \tag{4}
\]

\[
-\rho u_i' u_j' = \mu_T \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \frac{2}{3} \left(\rho k + \mu_T \frac{\partial u_k}{\partial x_k}\right) \delta_{ij} \tag{5}
\]

\[
\mu_T = \rho C_u \frac{k^2}{\varepsilon} \tag{6}
\]

The k-ε turbulence model introduces two transport equations to solve for the Reynolds stresses, one describes the transport of turbulent kinetic energy (k), and the other the turbulent energy dissipation rate (ε). Using an iterative process, the turbulent kinetic energy and turbulent dissipation rate of the eddies is constrained.

The fluid flow boundary conditions used for the outer walls of the domain include velocity inlets, pressure outlets, zero-shear boundaries, and no-slip boundaries. The ground around the tailings was initialized as a no-slip boundary with a surface roughness of 0.1 m and roughness constant of 0.5 m. The tailing walls were also defined as no-slip boundaries; however, they were assigned a significantly small surface roughness of 0.0014 m because of the lack of vegetation. The top of the domain was chosen as the limit of the atmospheric boundary layer (ABL) and was set as a zero-shear boundary, and walls parallel to the mean flow were setup as zero-shear boundaries as well. The velocity inlet boundaries where initialized with a user defined logarithmic wind profile, with a 7 m/s wind speed at 10 m height, and surface roughness of 0.1 m was used in the logarithmic wind profile. The velocity inlet’s magnitude and direction can be controlled, allowing for non-orthogonal flows relative to the velocity inlet boundary. The lateral boundaries are modified from zero-shear boundary to periodic boundaries for these non-
orthogonal simulations. Pressure outlets oppose velocity inlets and are initialized with a constant static pressure of 0 Pa. The backflow direction is also appropriately specified for all pressure outlets. The inlet profile utilizes an isothermal temperature profile of 300 K. This will produce a stably stratified boundary layer and not include the effects of convective mixing.

For all the simulations, we specified uniform $k$ and $\varepsilon$ on inlet surfaces with values of 0.5 m$^2$/s$^2$ and 0.1 m$^2$/s$^3$, respectively. This was done following a recommendation by the FLUENT user guide, which states that for “flows where accurate profiles of turbulent quantities are unknown, uniform specification of turbulent quantities at a boundary are reasonable” (FLUENT User Guide). In addition, we also explicitly created a very large model domain with a significant run-up distance which allows the $k$ and $\varepsilon$ to fully develop from the specified inlet boundary values.

**A.2.4.2 Species Transport (Eulerian Approach)**

The species transport model within FLUENT uses the convective-dispersion mass transport equation (Eq. 7), where $Y_i$ is the local species mass fraction, $\nu$ is the velocity vector, $J_i$ is the dispersive flux, $R_i$ is the net rate of production via a chemical reaction ($R_i = 0$ in this case), and $S_i$ is the rate of creation from user defined sources (FLUENT Theory Guide). For the regional simulations, the mine tailings act as the source of the aerosols, $S_i$, utilizing a mass flow boundary condition. Considering that we are in a turbulent flow, the dispersive flux is obtained using Eq. 8, where $T$ is the temperature and $D_m$, $D_T$, $S_{ct}$ are the mass diffusivity, thermal diffusivity and turbulent Schmidt number, respectively. The default turbulent Schmidt number used is 0.7, and the thermal
diffusivity is calculated from the tracer species thermal conductivity (FLUENT User Guide).

\[ \frac{\partial}{\partial t} (\rho Y_i) + \nabla \cdot (\rho \nu Y_i) = - \nabla \cdot J_i + R_i + S_i \]  

(7)

\[ J_i = - \left( \rho D_{i,m} + \frac{\nu r}{Sc_i} \right) \nabla \cdot Y_i - D_{T,i} \frac{\nu T}{T} \]  

(8)

In this work, properties of the species were used to represent 1 µm diameter aerosol particles, so that particle advection and dispersion is representative of an accumulation mode dust plume. It is reasonable to assume that 1 µm aerosols are likely to remain airborne after suspension because of their high mobility and relatively long gravitational settling time (settling velocity = 7.5 × 10^{-5} m/s for particle density of 2.5 g/cm³) relative to the simulated time period of 900 s.

For the species transport simulations, a user defined inert species was created to act as a tracer for accumulation mode aerosols. The mass diffusivity of the tracer species was set equal to the diffusivity calculated for a 1 µm particle, 2.77 × 10^{-11} m²/s, its viscosity was set as 1.72 × 10^{-5} Pa s and its thermal conductivity at 0.0454 W/m K. The density is not defined for either the tracer species or the air because it is assumed they are homogenously mixed within each model element and that the fluid behaves as an incompressible ideal gas.

Species transport boundary conditions include inlet mass fraction, inlet mass flux, inlet direction specification and boundary species fraction specifications. A user defined function was used to define the inlet mass fraction and mass flux for the top of the tailings. Each simulation had an emission mass flux of 6.316 × 10^{-3} g/m² s and the
emission lasted for thirty seconds for total emission of 0.1895 g/m². The mass fraction boundary condition was set so 100% of the mass emitted was the tracer species and the emission occurred normal to the upper tailings boundary. A fixed zero mass fraction for the species tracer was used as the surrounding ground boundary condition, which implies complete capture of particles by the ground surface.

A.2.4.3 Discrete Phase Modeling (Lagrangian Approach)

FLUENT’s Discrete Phase Modeling (DPM) tracks the trajectory of individual particles as they are injected into the flow. This Lagrangian approach requires that the tracked particles have a very small volume number fraction relative to the fluid volume mesh cells. However, the volume mass fraction of the tracked particles relative to the fluid can be quite large without significant consequences (FLUENT Theory Guide). The DPM particles were released into the same steady flow field with the identical wind profile and turbulent parameter boundary conditions used in the species transport simulations.

The discrete phase modeling calculates the trajectory of a particle by using its equation of motion (Eq. 9), where \( u_p \) is the particle velocity, \( u \) is the fluid velocity, \( g \) is gravity, \( \rho_p \) is the particle density, \( \rho \) is the fluid density, \( F_D \) is the drag force and \( F_x \) represents additional forces. The drag force of the particles is calculated using the Stokes-Cunningham drag law, Eq. 10, where \( C_C \) is the slip correction factor, \( d_p \) is the diameter of the particle and \( \mu \) is the fluid’s dynamic viscosity

\[
\frac{du_p}{dt} = F_D (u - u_p) + \frac{g_x (\rho_p - \rho)}{\rho_p} + F_x \quad (9)
\]

\[
F_D = \frac{18 \mu}{\rho_p d_p^2 C_C} \quad (10)
\]
For particles of size less than 1 µm, the additional force, $F_x$, contains the Brownian force, Saffman’s lift force, and the thermophoretic force. The Brownian force is caused by random walk of highly mobile particles and the Saffman’s force represents a suspension (lift) force due to shear components of the flow. The thermophoretic force arises when sufficiently small particles are located within a thermal gradient and was, therefore, neglected in our simulations.

Particles were emitted from the upper surface of the tailings using a user defined file of injection points that were gridded with 5-m separation, covering the entire tailings. This resulted in 4080 particle injections per DPM simulation. Particles were released normal to the tailing surface with an initial velocity of 1 m/s. Multiple monodisperse DPM simulations were carried out for the four principal wind directions using 2.5 µm particles. Each boundary of the solution domain has a specific DPM condition in the case a particle comes into contact with the boundary. The ground surface, not including the tailings, used a deposition boundary condition; that is, particles that come into contact with the ground settle out. The tailings boundary condition was set to reflect all particles, which would represent bouncing. All the side boundaries of the domain were set to let particles escape.

**A.2.4.4 Mesh Generation**

Prior to running simulations with FLUENT, a model domain was created that was representative of the Dewey-Humboldt region, adjacent to the Iron King Mine tailings. To accurately represent the area of around the tailings, topographic data was gathered from the United States Geological Survey Seamless Data Server (USGS, 2012). Topographic data for a 25 km² area centered on the Iron King mine tailings that included
portions of the adjacent town of Dewey-Humboldt was downloaded with a horizontal resolution of 1/3 arc second or about 10.3 m. The topographic data underwent processing in Matlab to create a grey scale image representative of the regional elevation. The image had a buffer round the outer boundary that adds a 514.5 m run-up that slopes the edge of the topographic region down to a fixed elevation for the entire edge. The reason for adding this buffer region is to create a fixed flat edge that represented a base surface for mesh generation and processing. Following the Matlab processing, the regional grey scale image was converted to a Non-Uniform Rational B-Spline (NURBS) surface utilizing Rhinoceros, a 3-D NURBS based modeling software (Rhinoceros 4.0, 2008). The tailings were added by hand to the topographic surface using both satellite imagery and GPS coordinates that were collected on the tailings. Once the tailings were added, the ground surface was enclosed by a bounding box. The 5 km regional domain, with the buffer region included, had a total horizontal and vertical extent of 6750 m × 6300 m × 3780 m. The fully formed model domain was then imported into the ANSYS Design Modeler (2013) that was used to mesh the domain. Utilizing the ANSYS Mesher, the model domain was meshed using a tetrahedral meshing method. The most refined mesh used in the simulations had 450,899 nodes, and 2,463,913 tetrahedral finite elements. The meshes were then exported for use in the FLUENT CFD model.

A.2.4.5 Mesh Verification

Mesh verification is vitally important to maintain realism and repeatability of simulations. Two common techniques are used to verify the mesh accuracy, which include iterative convergence and mesh independence. In order to verify mesh independence three different meshes were created. The grid refinement ratio is defined
as the ratio of cell spacing for two separately sized meshes; for example, for meshes termed “fine” and “medium”, \( r_G = \Delta x_{\text{fine}}/\Delta x_{\text{med}} \). A grid refinement ratio of \((2)^{0.5}\) is recommended (Stern et al., 2001). However, due to computational limitations, a more reasonable refinement ratio of \((1.5)^{0.5}\) was used. The total number of nodes for the three meshes, coarse, medium and fine are 330,462, 390,778 and 450,899, respectively. The total number of tetrahedral finite elements for the three meshes are 1,796,275, 2,124,416 and 2,463,913.

The R\(_2\) value (Eq. 12) was used to determine if there is mesh independence. It was calculated by first estimating error quantities from three different sized mesh simulations for each degree of freedom. There are six degrees of freedom needed to fully describe the turbulent fluid motion, turbulent kinetic energy (k), turbulent dissipation rate (\(\varepsilon\)), static pressure, and the three components of the wind velocity vector. The error was calculated from Eq. 11, where \(e_{j,k}\) is the difference in value for a single degree of freedom simulated on two differently sized meshes, j and k (Roache, 1998). If the R\(_2\) values are less than one, the simulation is considered to be mesh-independent, indicating that an appropriate approximate solution has been found.

\[
||e|| = \sqrt{\sum e_{j,k}^2} \quad (11)
\]

\[
R_2 = \frac{||e_{\text{mid, fine}}||}{||e_{\text{course, mid}}||} \quad (12)
\]

Converge of the iterative procedure employed in the solution of the differential equations is calculated using the L\(_2\) error norm value, which is calculated by differencing a degree of freedom for two simulations using the same mesh but different global simulation error
(GSE) tolerances. Eq. 13 shows how the $L_2$ error norm is calculated, where $x_i$ and $x_{i-1}$ are degrees of freedom, $I$ represents the more strict GSE tolerance and $i-1$ represents the less strict GSE simulation tolerance. A strict limit of 5 percent or better was used to verify iterative convergence (Roache, 1998).

\[ L_2 = \frac{\left[ \sum (x_i - x_{i-1})^2 \right]^{0.5}}{\left[ \sum (x_i)^2 \right]^{0.5}} \]  

(13)

A.3 Results

A.3.1 Simulation Verification

Twenty locations within the model domain were randomly selected to verify mesh independence and iterative convergence. The locations were selected by dividing the model domain into 100 equal sized horizontal areas of which twenty were randomly selected for analysis. A vertical rake was used to sample the 6 degrees of freedom at 5 m intervals from the ground surface to a height of 3000 m. Figure 3 shows the locations of the 20 random rakes within the model domain.
Figure 3: Twenty randomly selected vertical rake sampling locations used for mesh verification. The vertical rakes are color mapped by elevation (in m). Image also includes the ground and tailing walls of the domain with each element face outlined. The finite elements corresponding to the mesh used in the simulation are outlined.

The finest mesh was used to determine iterative convergence. Three simulations were run using a GSE tolerance of $10^{-3}$, $10^{-4}$, and $10^{-5}$ for the six degrees of freedom. The $L_2$ iterative convergence parameter was then calculated for all six degrees of freedom using the three differently sized meshes (Table 1). Only the vertical component of the flow field did not meet the 5% criterion to show iterative convergence for the $(10^{-4}-10^{-5})$ $L_2$ error norm test. An additional simulation was conducted using a GSE of $10^{-6}$ which resulted in a $L_2$ value of less than 1%, which meets the 5% criteria to show iterative convergence. The $R_2$ values were calculated for the six degrees of freedom to show mesh
independence and can also be seen in Table 1. The $R^2$ values for all six degrees of freedom were less than 1, which confirms mesh independence. These verifications tests indicate that the finest mesh used represents accurately the solution of the problem within the tolerance limits selected.

Table 1. $L_2\%$ error norm and $R^2$ values for the six degrees of freedom and for three increasingly strict global simulation error residuals.

<table>
<thead>
<tr>
<th>$L_2%$ ($10^{-3}$-$10^{-4}$)</th>
<th>$k$</th>
<th>$\varepsilon$</th>
<th>$P$</th>
<th>$u_x$</th>
<th>$u_y$</th>
<th>$u_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12.022</td>
<td>8.455</td>
<td>13.155</td>
<td>1.875</td>
<td>2.230</td>
<td>60.290</td>
</tr>
<tr>
<td>$L_2%$ ($10^{-4}$-$10^{-5}$)</td>
<td>2.383</td>
<td>1.837</td>
<td>0.839</td>
<td>0.604</td>
<td>0.445</td>
<td>17.872</td>
</tr>
<tr>
<td>$L_2%$ ($10^{-5}$-$10^{-6}$)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.819</td>
</tr>
</tbody>
</table>

$R^2$

| $R^2$ | 0.819 | 0.813 | 0.842 | 0.918 | 0.819 | 0.610 |

A.3.2 Species Transport Simulations

Four simulations were conducted using the principal wind directions measured on the tailings during the 2012 spring windy season: northwestward, northward, northeastward and eastward wind directions. First, wind velocity profiles were generated using a logarithmic wind profile that was initialized with a 7 m/s wind speed at 10m height. This wind profile speed was selected from hourly fastest mile observations that had friction velocities large enough to produce wind erosion. The logarithmic profile was used as a boundary condition on the inlet surface, depending on wind direction. Figure 4a shows wind velocity vectors calculated from the CFD simulation at the centroid value of the elements directly adjacent to the tailings and ground boundaries for an eastward wind direction. The color mapping of the vectors represents the velocity magnitude (m/s). Eddies and sudden changes in the velocity vectors can be identified downwind of significant surface elevation variations, including an adjacent open pit mine, located
northwest of the tailings, and the tailing walls. Figure 4b shows wind speed contours along an eastward orientated vertical plane. The western edge of tailings creates oscillations in the vertical wind speed profile that propagate downwind. The tailings also generate a sheltered region of low wind velocities downwind of the eastern edge where elevation significantly drops compared to the top of the tailings. These results confirm the expected sensitivity of the CFD simulations to the local topography.

**Figure 4a:** Sample results from the FLUENT CFD computations: Wind velocity vectors at the centroid of the elements directly adjacent to the tailings and ground boundaries for an eastward (X direction) simulated wind direction. This wind simulation was initialized with a 7 m/s at 10 m height logarithmic wind profile along the eastern boundary. The color mapping of the vectors represents the wind magnitude (m/s). Eddies can be identified downwind of the tailings where changes in elevation occur, and near the open pit mine, located northwest of the tailings.
Figure 4b: Sample results from the FLUENT CFD computations: Wind speed contours along an eastward orientated vertical plane for an eastward (X direction) simulated wind direction. This wind simulation was initialized with a 7 m/s at 10 m height logarithmic wind profile along the eastern boundary. The color mapping represents the wind magnitude (m/s). The tailings effects on the wind field can be seen along western edge of tailings where the increase in elevation creates oscillations downwind. The tailings also generate a sheltered region of low wind velocities downwind of the eastern edge.

The species emission rate was calculated with the EPA AP42 wind erosion model using threshold friction velocities and sonic anemometer observations taken on the mine tailings from March 25, 2012 through June 26, 2012. The AP42 wind erosion model estimates that windy season average hourly emission for periods that generated soil erosion were 2.527, 1.516, 1.263, 0.190 g/m² for PM$_{30}$, PM$_{15}$, PM$_{10}$ and PM$_{2.5}$, respectively. PM$_{2.5}$ is the smallest particle size regime estimated by the AP 42 wind erosion model and has the largest mobility of all the classifications. PM$_{2.5}$ particles have long gravitational settling time and low rate of Brownian diffusion and can be transported long distances. For this reason the PM$_{2.5}$ erosion rate was used in the species transport
simulations. A 30 s emission event is used in the simulations. The transient species transport simulations were conducted for 900 s with 4 s time steps. The four second time step was selected to minimize the computational cost of the simulations while maintaining temporal resolution that allows us to observe the development of the species tracer plumes.

**Figure 5:** Contours of mass fraction of a northward species plume simulation, 90 seconds after emission from the tailings. Mass fractions are calculated for the centroid value of elements directly adjacent to the ground boundary. The contours of mass fraction are overlaid on a Google earth satellite image of the region. Concentration values are in kg_{species}/kg_{air}.
Figure 5 shows contours of the tracer species mass fractions calculated at the centroid of the elements directly adjacent to the ground boundary conditions, approximately 8 m elevation, 90 s after the beginning of the emission event. The mass fraction contours are shown on a logarithmic scale to accentuate the extent of the plume. To estimate deposition rates from these results, a series of vertical rakes with 5 m vertical resolution were sampled from the solution every 500 m downwind from the tailings, up to a distance of 2500 m. For each vertical rake the deposition rate was calculated using Fick’s law. Figure 6 shows the peak tracer species mass fraction profiles for the northward simulation at 500 m, 1000 m, 1500 m, 2000 m and 2500 m downstream from the center of the tailings. Peak mass fraction time step is defined as being the time step with the highest cumulative mass fractions within the profile for the respective location. Deposition rates were calculated at each rake location for each time step. Figure 7 shows the time series of capture rates for the five downwind rakes for the northward wind simulation. As expected, the deposition rates decrease with distance away from the tailings.
Figure 6: Vertical profiles of tracer species mass fraction for the northward transient species simulations. The vertical profiles coincide with the peak mass fractions measured during the simulation at each sample locations 500, 1000, 1500, 2000, 2500 m.
Figure 7: Time series of deposition rates calculated for the northward simulation at the 500, 1000, 1500, 2000, 2500 m sample locations. Deposition rates were calculated for each 4 s time step using Fick’s first law of diffusion.

Integration of the time series of deposition rates at each rake location gives the total deposition for each simulation. The cumulative deposition results for the four simulated wind directions are presented in Table 2. It is noticeable that the total deposition values for the rakes do not necessarily decrease with distance from the tailings. The northwestward wind simulation has the largest total deposition of the tracer species for all five of the downwind rake locations when compared to the other directional simulations. This is caused by the topography. In general, ground elevation increases with distance from the tailings in the northwestward direction, causing increased species concentrations near to the ground as the species is forced up the topographic slope. The elevation tends to decrease away from the tailings for the other three wind directions, which would
suggest the total deposition to be smaller than the northwestward wind direction. There are also seeming anomalies within each individual simulation; for example, the 1000 m rake for northward simulation, has a larger total deposition than the 500 m rake. This increased deposition at 1000 m is caused by the vertical rake being located on the upslope side of a hill, which serves as an enhanced interception surface, thus increasing deposition. The opposite argument can be made for the downslope side of the regional topography.

Table 2. Total downwind tracer species deposition values (pg/m²) for a single event as a function of distance from the tailings. Emission events were simulated for the four principal wind directions specified.

<table>
<thead>
<tr>
<th>Distance from tailings (m)</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northwestward Deposition</td>
<td>0.382</td>
<td>0.101</td>
<td>0.105</td>
<td>0.0979</td>
<td>0.0479</td>
</tr>
<tr>
<td>Northward Deposition</td>
<td>0.0534</td>
<td>0.0541</td>
<td>0.0255</td>
<td>0.0212</td>
<td>0.0196</td>
</tr>
<tr>
<td>Northeastward Deposition</td>
<td>0.0477</td>
<td>0.0315</td>
<td>0.0245</td>
<td>0.0269</td>
<td>0.0254</td>
</tr>
<tr>
<td>Eastward Deposition</td>
<td>0.143</td>
<td>0.0586</td>
<td>0.0795</td>
<td>0.0412</td>
<td>0.0321</td>
</tr>
</tbody>
</table>

Further investigation of the topographic effects on species tracer deposition was conducted by looking at the elevation and upslope information for the rake sample locations. Table 3 shows the elevation at the rake sample points and Table 4 presents the topographic upslope of the rake sample points. The topography of the terrain along the investigated directions is shown in Figure 8. The elevation information from Table 3 allows us to see if there is a correlation between the elevation and deposition totals from the simulations. The rake locations that observed increasing total depositions as the distance from the tailings increased included: the northwestward 1000 m and 1500 m
rakes, northward 500 m and 1000 m rakes, northeastward 1500 m and 2000 m rakes and eastward 1000 m and 1500 m rakes. There appears to be little correlation between the rakes elevation and total deposition because the northwestward 1000 m and 1500 m rakes have about a 29 m decrease in elevation between them and the northward 500 m and 1000 m rakes have an increase of about 26 m between the sample rakes locations. The last two seemingly anomalous rake pairs, northeastward 1500 m and 2000 m rakes and eastward 1000 m and 1500 m rakes, have small elevation differences between the rake locations on the order of 5.5 m to 7 m. For these simulations, there appears to be no correlation between higher deposition rates and elevation for the species transport method. Nevertheless, it topographic upslope of the landscape may shed light on the observed trends. The upslope of the ground at the rake sample locations is given in Table 4. The northwestward 1000-1500 m, northward 500-1000 m, and eastward 1000-1500 m seemingly anomalous sample locations have significant increases in upslope values, which are associated with the increase in total deposition. Topography, specifically the upslope degree of the ground surface, seems to play a major role in the spatial variability of species tracer deposition.

Table 3. Ground elevation of the 20 sample rake locations used in tracer species simulations.

<table>
<thead>
<tr>
<th>Distance from tailings (m)</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northwestward Elevation (m)</td>
<td>117.5</td>
<td>144.3</td>
<td>115.4</td>
<td>134.9</td>
<td>160.0</td>
</tr>
<tr>
<td>Northward Elevation (m)</td>
<td>96.7</td>
<td>122.6</td>
<td>140.6</td>
<td>111.7</td>
<td>142.2</td>
</tr>
<tr>
<td>Northeastward Elevation (m)</td>
<td>89.2</td>
<td>121.3</td>
<td>92.5</td>
<td>85.1</td>
<td>90.6</td>
</tr>
<tr>
<td>Eastward Elevation (m)</td>
<td>107.7</td>
<td>85.5</td>
<td>80.8</td>
<td>70.9</td>
<td>67.4</td>
</tr>
</tbody>
</table>
Table 4. Topographic upslope of the 20 sampling locations used in tracer species simulations. Positive values indicate increase in elevation along the specified direction.

<table>
<thead>
<tr>
<th>Distance from tailings (m)</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northwestward upslope (m/m)</td>
<td>-0.0246</td>
<td>-0.1472</td>
<td>-0.0141</td>
<td>0.0025</td>
<td>0.0345</td>
</tr>
<tr>
<td>Northward upslope (m/m)</td>
<td>-0.1553</td>
<td>0.2023</td>
<td>0.2707</td>
<td>0.0839</td>
<td>0.2131</td>
</tr>
<tr>
<td>Northeastward upslope (m/m)</td>
<td>-0.0445</td>
<td>0.1377</td>
<td>-0.1011</td>
<td>-0.1187</td>
<td>0.1694</td>
</tr>
<tr>
<td>Eastward upslope (m/m)</td>
<td>-0.1568</td>
<td>-0.0225</td>
<td>0.0199</td>
<td>-0.0381</td>
<td>-0.0485</td>
</tr>
</tbody>
</table>

Figure 8: Topographic elevation (in m) of the terrain following the indicated directions from the tailings. Specific values for the sampled locations (marked with asterisks) are shown in Table 3.

A.3.3 Seasonal Deposition Estimation

Seasonal deposition rates were estimated utilizing the species simulations and the observed seasonal wind data. The analysis of the windy season data found that 40.2\% of the hourly fastest mile friction velocities, from the spring windy season, were sufficient
to produce wind erosion according to the EPA AP42 wind erosion model. By scaling the single simulation results by the number of events predicted by the AP42 wind erosion model for that specific wind direction, we can estimate of the total seasonal PM$_{2.5}$ deposition for all the sample rake locations and for each wind direction simulation. Table 5 shows the 2012 windy season PM$_{2.5}$ deposition as estimated by using the AP42 wind erosion model and the FLUENT species transport model. Although these deposition values may seem quite small, they represent only the smallest size fraction aerosols, <2.5 µm diameter.

Table 5. Estimates of total PM$_{2.5}$ deposition for the 2012 spring windy season.

<table>
<thead>
<tr>
<th>Distance from tailings (m)</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northwestward Deposition (pg/m$^2$)</td>
<td>73.7</td>
<td>19.3</td>
<td>20.0</td>
<td>18.6</td>
<td>9.13</td>
</tr>
<tr>
<td>Northward Deposition (pg/m$^2$)</td>
<td>17.7</td>
<td>17.1</td>
<td>8.06</td>
<td>6.69</td>
<td>6.20</td>
</tr>
<tr>
<td>Northeastward Deposition (pg/m$^2$)</td>
<td>7.39</td>
<td>4.84</td>
<td>3.77</td>
<td>4.13</td>
<td>3.91</td>
</tr>
<tr>
<td>Eastward Deposition (pg/m$^2$)</td>
<td>12.6</td>
<td>5.15</td>
<td>6.98</td>
<td>3.61</td>
<td>2.82</td>
</tr>
</tbody>
</table>
A.3.4 DPM Simulations

To further investigate the spatial variations observed in the species transport simulations, we conducted a series of DPM simulations. Each DPM simulation emits 4080 particles (2.5 µm in diameter) from the tailings into the mean flow and one simulation is performed for each principal wind direction. Most of the injected particles tended to deposit very near to the tailings because of swirling winds that arise from the tailings having an elevated position relative to the surrounding ground. However, some particles managed to be transported further downwind and some, less than 5%, escaped the whole simulation domain; that is, were transported a distance of more than 3 km. The 5% escaped particle fraction is an underestimate because the thermodynamically stable boundary layer does not allow for vertical mixing that would be associated with a convective boundary layer typical of a clear day.

To study the effect of upslope on particle deposition, Figure 9 shows a distributed plot of the upslope value at the point where each particle deposits vs. the distance from the tailings where the particle deposited. From this plot it can be seen that once a particle gets far enough away from the tailings ( > 500 m), it tends to deposit on positive upslope regions. Even though the mean value of the upslope is positive for all particle deposition locations, which would be consistent with an upslope bias for deposition, the standard deviation is so large that a general quantitative conclusion is not possible. However, the average and standard deviations of the upslope value for particles that settled more than 500 m away from the tailings show that particles that escape the swirling eddies created by the tailings topography preferentially deposit in areas of topographic upslope. Additional sensitivity tests occurred that looked at the effect that injection location and
injection velocities have on deposition location. Results showed that variations of injection locations and injection velocity produced minimal effects on the deposition location. These DPM results reinforce the results gathered from the species transport simulations, which showed that topography plays a major role in the deposition of fugitive aerosols from the Iron King Mine tailings.

![Figure 9: DPM particle deposition location ground upslope versus distance from deposition to the tailings. This plot includes the particles released from the tailings for the northwestward, northward, northeastward and eastward wind directions.](image)

A.4 Concluding Remarks

Utilizing in situ observations and the EPA AP 42 wind erosion model, we were able to estimate wind erosion and local deposition of dust and aerosol from a chemically contaminated mine tailings site. The model coupled three-dimensional velocity fields obtaining from CFD calculations employing the k-ε turbulence model with either the
species transport equation (for particles of size less than 1 \(\mu\)m diameter) or the equations of motion for individual particles (for 2.5 \(\mu\)m diameter particles). The simulations showed significant heterogeneity in deposition patterns in the regions surrounding the tailings, with topographic upslope and wind velocity fields playing a major role in the deposition variability. These results show that future predictions of deposition from this and similar sites must rely on accurate descriptions of wind velocity and surrounding terrain.

The calculations presented in this work are preliminary in nature. Further work will be done towards validating the accuracy of the emissions model, which relies on empiricisms that may not be applicable to a specific location. In addition, processes such as saltation and particle creep have not been considered in detail, and they may play an important role in total emissions. Despite the limitations, the results give an estimate of the relative strength of deposition patterns in the region surrounding the tailings which, in turn, can be translated into deposition patterns of contaminants such as lead and arsenic, present at relatively high concentrations in the top soil of the tailings.

**Acknowledgements**

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Rhinocerous Release 4.0, Robert McNeel & Associates.


Appendix B: Development of a dust deposition forecasting model for a mine tailing impoundment using in situ observations and particle transport simulation

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Abstract

Mine tailings impoundments in arid and semiarid environments are susceptible to wind erosion due to their fine grain silt and sandy composition and lack of vegetative coverage. Aeolian transport of particulate matter from these mine tailings impoundments are potential hazards to human health due to the presence of metal and metalloid contaminants. Predicting windblown transport of mine tailings material can be a useful tool in characterizing the risk and environmental impact on neighboring communities. This work presents a model that can be used to forecast the transport and deposition of windblown dust from mine tailings impoundments. The deposition forecast model uses in situ observations from a tailings field site and theoretical simulations of aerosol transport to parameterize the model. The model was developed using data from the Iron King Mine tailings in Dewey-Humboldt, Arizona, a Superfund site that is heavily contaminated with lead and arsenic. The model methodology, development and preliminary verification are presented.

Keywords: Deposition, Dust, Wind erosion, Aerosol transport, Superfund
B.1 Introduction

Aeolian transport of dust from mine tailings can be a significant problem in arid and semiarid regions, where the naturally dry and windy environment makes the tailings increasingly susceptible to wind erosion. Dust particles can have deleterious health effects and, as a result, particulate matter, specifically PM$_{2.5}$ and PM$_{10}$, are one of six air pollutants regulated under the National Ambient Air Quality Standards NAAQS (USEPA, 2011).

The US Environmental Protection Agency recommends two models for predicting the dispersion of pollutants, including particulate matter: AERMOD and CALPUFF. AERMOD is a steady state Gaussian plume model designed for industrial sources (Cimorelli, 1998). CALPUFF is a non-steady state plume dispersion and transport model that works best on long range transport simulations over scales of 50 km or more (Scire et al., 2000). Although both of these models have their strengths, they were designed to maximize their accuracy for general use in a variety of environments and conditions, which do not include site specific factors that affect windblown deposition patterns.

In this work, we developed a site-specific dust transport and deposition forecast model (DFM) for a mine tailings impoundments. The model simulates multiple emission events and is parameterized using empirical relations derived from field observations. The tailings are a part of the Iron King Mine and Smelter area, an EPA Superfund site since 2008 (EA Engineering, 2010). The Iron king mine tailings impoundment is contaminated with arsenic and lead and located near the town Dewey-Humboldt with a population of 3,951 (US Census, 2005).
B.2 Methodology

B.2.1 Site Description

The Iron King Mine site is adjacent to Dewey-Humboldt, located about 90 miles north-northwest of Phoenix, Arizona. The region is semiarid with an average annual rainfall of 47.7 cm (NCDC, 2004). The vegetation is largely composed of grasslands, chaparral, and pinyon/juniper woodlands, but the mine tailings impoundment is devoid of vegetation. The topography generally ranges from rolling hills to rugged mountainous terrain with an average elevation of 1436 m above mean sea level (EA. Engineering, 2010).

The Iron King tailings impoundment is located 1.5 km west-southwest of Dewey-Humboldt and has two adjacent waterways that are dry except during precipitation events, the Galena Gulch south of the property and the Chaparral Gulch along the northern boundary. The tailings impoundment has a reddish brown color and rises vertically from the hillside with sloped sides and flat top. Figure 1 is a visual satellite image of the Iron King tailings and surrounding area. The tailings material consists of gravelly and silty sands with a loam texture that consists of 34.7 % sand, 44.8 % silt, and 20.4 % clay (Solis-Dominguez et al., 2012). The tailings material is acidic with a pH of 2.5 and is contaminated with lead and arsenic (Ramirez-Andreotta et al., 2013). Surface soil measurements of lead and arsenic in the tailings pile were observed to be as high as 9830 mg/kg and 6300 mg/kg, respectively (EA Engineering, 2010). Elevated concentrations of arsenic and lead in adjacent offsite soils are indicative of aeolian and ground water transport (Ramirez-Andreotta et al., 2013).
B.2.2 Instrumentation

Two eddy flux towers were installed on the Iron King tailings in 2012 (Figure 1). Instrumentation on the towers includes: three TSI DUSTTRAK II 8530 with omnidirectional inlets located at 1-m, 3-m and 10-m heights, cup anemometers at 3 and 10-m, a sonic anemometer at 1-m height on the south tower only, thermometers and hygrometers at 3 and 10-m height. The DUSTTRAKs are designed to sample PM$_{27}$ (particulate matter with an aerodynamic diameter of 27 µm or less). The DUSTTRAK and sonic anemometer observations are recorded with 10 s resolution. In order to extend the battery life of the DUSTTRAKs they are down for 8 h a day, 9:00 pm to 5:00 am, when winds are typically stagnant. Temperature and relative humidity meters as well as the cup anemometers operate 24 h a day at 5 min resolution. The instruments are solar powered with a 48 h reserve for cloudy days. A cell phone modem was used to remotely download the data.
A Multiple Orifice Uniform Depositing Impactor (MOUDI) was used to determine aerosol size distributions. The MOUDI has been shown in several studies to be useful in determining contaminant distribution in dust and aerosol by particle size (Querol et al., 2000; Allen et al., 2001; Tursic et al., 2008; Csavina et al., 2011). The MOUDI model used is the MOUDI-II and is distributed by MSP corp. It has eleven stages that collect particles with an aerodynamic cut point diameter: 18, 9.9, 6.2, 3.1, 1.8, 1, 0.55, 0.32, 0.18, 0.1, 0.054-μm and ultrafine particles collected on an “after filter”. The MOUDI was located along the northern edge of the tailings impoundment (Figure 1).
B.2.3 Idealized particle trajectory

Idealized particle trajectory simulations were conducted in order to create a model that predicts the deposition locations of aerosol released from the tailings. These simulations predict the trajectories and deposition patterns for spherical particles of varying aerodynamic diameters in a convectively turbulent logarithmic wind profile. These simulations are conducted in a 2-dimensional framework where particles trajectories are determined in terms of downwind and vertical directions.

The trajectory simulations include the following forces: gravity, Stokes air resistance and Brownian and eddy diffusion. Eddy diffusion has a significantly larger impact on aerosol trajectories than Brownian diffusion, especially in a convectively turbulent environment. The trajectory of a particle under the influence of gravity and Stokes air resistance can be determined by integrating the force balance on the particle,

\[
m \frac{dv}{dt} = gm + 3\pi \mu D_p (v_a - v)
\]

where \(m\) is the mass of the particle, \(v\) is the particle velocity vector, \(g\) is gravity acceleration, \(\mu\) is the air viscosity, \(D_p\) is the particle diameter and \(v_a\) is the air velocity vector.

For very small (sub-micron) particles the Brownian force may cause variations in the trajectory of the particles. The effect of Brownian motion on a particle is included by calculating its mean displacement, \(X\),

\[
X = (2D_b \Delta t)^{1/2}
\]
where $D_b$ is the molecular diffusivity and $\Delta t$ is the time scale. Over a time scale of 1 s, a 2-μm diameter spherical particle ($\rho_p = 2500 \text{ kg/m}^3$) diffuses 5 μm while falling 300 μm due to gravity. This shows that Brownian diffusion is insignificant under the conditions explored in this work.

Eddy diffusion is added to the particle trajectory model as a way of including the effects of convective turbulent eddies in the wind field. The eddy diffusivity is modeled by

$$D_{eddy} = \frac{K u^* Z}{\phi_m}$$  \hspace{1cm} (3)

where $K$ is the von Karman’s constant, $u^*$ is the friction velocity, $Z$ is the height above the ground and $\phi_m$ is the momentum similarity function determined by Monin-Obukhov similarity theory (Shao, 2000). The Monin-Obukhov length, $L$, is given by

$$L = \frac{u^3}{\kappa g \overline{w' \theta'}}$$  \hspace{1cm} (4)

where $\overline{w' \theta'}$ is the surface buoyancy flux based on temporal deviatory variables, $\theta$ is potential temperature and $w$ is vertical component of the wind velocity (Shao, 2000). The similarity function in equation (3) is given by

$$\phi_m = \begin{cases} 1 + \beta_m \zeta & \zeta > 0 \\ (1 - \gamma_m \zeta)^{-1/4} & \zeta < 0 \end{cases}$$  \hspace{1cm} (5)

where

$$\zeta = \frac{Z}{L}$$  \hspace{1cm} (6)
The cyclical dependence of $L$, $\zeta$ and $u^*$ requires using an iterative process to solving for the Monin-Obukhov Length. We used Zeng et al.’s (1998) method to iteratively solve for the nondimensional term $\zeta$. The momentum similarity function $\phi_m$ is determined using equation 5 with $\beta_m$ and $\gamma_m$ are 5 and 16 respectively (Shao, 2000). For typical daytime conditions measured using the eddy flux towers, we have found that the momentum similarity function typically has values in the range of 0.6 to 0.8. For the idealized simulations we use a fixed value of 0.7 for the momentum similarity function.

The eddy diffusivity calculated by equation 3 is valid for the fluid itself. However, particles do not instantaneously relax to changes in the fluid flow, so an adjustment must be made to the eddy diffusivity to make it applicable to aerosol particles. Particle eddy diffusivities are calculated from

$$K_{pz} = D_{eddy} (1 + \frac{\beta^2 \omega_t^2}{\sigma^2})^{-0.5} \quad (7)$$

$$K_{px} = D_{eddy} (1 + 4 \frac{\beta^2 \omega_t^2}{\sigma^2})^{-0.5} \quad (8)$$

where $\omega_t$ is the terminal velocity of the particle, $\sigma$ is the standard deviation of turbulent wind velocity and $\beta$ is a dimensionless coefficient. The standard deviation of daytime turbulent wind velocities, measured at 10-m height over an hour, is on the order of 0.8 m/s and $\beta$ is of the order 1 (Shao, 2000). The particle eddy diffusivities can be used in equation 2 to determine the mean displacement of a particle caused by turbulent eddies in the boundary layer.

We included the effects of eddy diffusion to the 2-D particle trajectory model by adding a displacement to the particle’s location after each time step. The displacement of the
particle is calculated by generating two random numbers. The first is from a normal distribution with a mean displacement calculated using equation 2 and the particle eddy diffusivity with a standard deviation that is half of the mean. The second random number is uniformly generated on the range $-\pi$ to $\pi$ and this is used to determine the direction of the random motion.

**B.2.4 Assimilation of topography into deposition model**

The topography of the study area is complex. Stovern et al. (2014) employed a CFD model to simulate the transport of windblown particles from the Iron King Mine tailings impoundment using both individual particles (Lagrangian approach) and species plumes (Eulerian approach). Their results showed that particles preferentially deposit on areas of up-sloping terrain. To include these effects on the deposition model we use a weighted interpolation technique to assimilate topographic upslope data. To calculate the regional topographic upslope we first collected 1/3 arc s (10.3-m) horizontal resolution topographic elevation data (USGS, 2013) for the Iron King Mine and the adjacent town of Dewey-Humboldt area (5250-m x 5700-m). The upslope of each pixel is generated using a 5 pixel (51 m) radial cross section to estimate the slope. Radial position is defined from the central location of the tailings pile. The upslope values were assimilated into a map of background isotropic deposition estimates that is generated using the idealized particle trajectory results over a flat surface.

The deposition forecasting model’s spatial resolution is limited by the topographic data’s 10.3-m resolution. Hence, each pixel of the upslope and DFM matrix represents a 10.3-m $\times$ 10.3-m area. The upslope map was linearly weighted prior to being assimilated to the
background deposition map, so that positive upslope values increase the deposition linearly with upslope value through the relation

\[ U_{w(i,j)} = (U_{i,j} * W) + 1 \]  \hspace{1cm} (9)

where \( U_{ij} \) is the upslope value of the \( i \)-th row and \( j \)-th column, \( W \) is a weighting constant with a value of 0.5 and \( U_{w(i,j)} \) is the new weighted upslope matrix value of the \( i \)-th row and \( j \)-th column. Slope values in the 25-km\(^2\) area centered on the tailings ranges from -0.6 to +0.6. By applying a 0.5 weighting constant and adding 1 we shift the distribution of slope values to range between 0.7 and 1.3 with flat ground having a value of one. The value of the weighting constant (\( W \)) controls the influence of topography on deposition of aerosols. The larger weighting constant means topographic slope has a greater impact on the deposition rate. A weighting constant of zero would mean there is no influence of topographic slope on aerosol deposition. Assimilating topography into the model is a vital step to accurately representing the deposition pattern of aerosols in a topographically complex environment.

**B.3 Results and Discussion**

**B.3.1 Analysis of observations**

We analyzed field observations collected from April 2012 to August 2013. Periods of observational down time, days when the tailings were disturbed by human activity, such as during sampling, rainy days and subfreezing temperature periods were ignored. The remaining data, amounting to 46.7% of the total, were analyzed in hourly intervals from 9:00 AM to 9:00 PM. Analysis of data in hourly intervals allows us to develop empirical
relations for dust emission fluxes in conjunction with hourly-based weather forecasting, which will be used to predict deposition patterns.

Typically, DUSTTRAK data show sporadic dust spikes separated by long periods of little or no dust, as illustrated in Figure 2. After deployment in the field for several weeks, baseline drift in dust concentration is especially noticeable (note that dust concentration does not reach zero during operation) but can be accounted for by subtracting the baseline observed immediately prior to and after every dust spike.

![Figure 2](image_url)  
**Figure 2.** Three days of DUSTTRAK data measured on the tailings, which shows sporadic dust spikes separated by long periods of little to no elevated dust concentrations.

We integrated the measured dust concentrations of the dust spikes over one-hour periods to find hourly cumulative dust concentrations. An observation was considered a dust spike if either a 50-s average of dust concentration or a 50-s standard deviation exceeded
the critical values of 0.015 mg/m$^3$ and 0.005 mg/m$^3$, respectively (the standard deviation criterion was used to identify the onset of the dust spike). These values were determined by analyzing the variability of baseline DUSTTRAK data. Analysis of hourly meteorological observations was also conducted to determine mean wind speed and relative humidity. For wind direction, both hourly averages and standard deviations were calculated. Using these hourly meteorological observations in combination with the hourly cumulative dust concentrations, we derived empirical relationships to describe how dust concentrations relate to meteorological conditions (see next section).

Four sets of MOUDI samples were taken on the tailings to help determine dust particle size distributions. The MOUDI samples were taken between April 2013 and January 2014 and were analyzed to determine the dust mass and contaminant (lead and arsenic) concentrations as a function of aerodynamic diameter. The MOUDI was programmed to turn on from 11:00 AM to 3:00 PM for each set of observations. For each sample, the MOUDI operated continuously for approximately 30 days to gather enough sample material for analysis in all stages.

In the following sub-sections we develop several empirical relationships derived from direct observations. First we look at the relationship between observed dust concentrations, wind speed and relative humidity. Secondly, we determine the average vertical profile of dust by comparing 1-m, 3-m and 10-m dust observations. Thirdly, we determine the average aerodynamic size distribution of dust collected on the tailings via a MOUDI. Finally, we look at the correlation between the average wind speed and the variance in observed wind direction. These empirical relations will be used to construct the deposition forecasting model.
**B.3.1.1 Correlation of dust concentration with wind speed and relative humidity**

To investigate the relationship between observed wind speed and dust concentration, we first compared the hourly accumulated dust concentrations with the associated hourly averaged wind speed over the daytime period 9:00 AM to 5:00 PM. A scatter plot of 10-m wind speed versus the 3-m height hourly accumulated dust concentrations for all the hourly observations is shown in Figure 3a. Figure 3b shows the average 3-m hourly accumulated dust concentrations when the observations are binned by 1 m/s wind speed intervals. As expected, dust concentrations increase monotonically with winds speed.
Figures 3a and 3b. 3a is a scatter plot of hourly averaged 10-m wind speed versus the 3-m hourly accumulated dust concentrations for all the hourly observations between 9 AM-5 PM local time. 3b is the average hourly cumulative dust concentrations when portioned into 1 m/s wind speed bins.
Csavina et al. (2014) showed the important role that relative humidity can play on wind erosion in semi-arid environments. Since the Iron King mine tailings site is located in a semi-arid environment, the effect of relative humidity should also be considered. Dust concentrations and relative humidity were inversely correlated, as shown in Figure 4a. Partitioning the cumulative dust concentrations into 5% relative humidity bins gives a better representation of the observed trend (Figure 4b). The highest average cumulative concentrations occur at low relative humidity (5-25%) and there is a decline until 75% where the average dust concentrations go to zero. The low value in Figure 4b at relative humidity < 5% reflects an average over relatively few data and was discarded due to the low occurrence of that specific condition. The effects of wind speed and relative humidity on dust concentration were correlated as follows,

$$C_{dust} = A_2 A_1 U^B$$

(10)

where $C_{dust}$ is the cumulative hourly dust concentration, $U$ is the average hourly wind speed, fitted power law constants were obtained by considering data at relative humidity $< 25\%$ yielding values $A_1 = 0.05677$ and $B = 1.246$, and $A_2$ is a function of relative humidity given by

$$A_2 = \begin{cases}
1 & \text{for } RH \leq 25\% \\
(50 - (RH - 25))/50 & \text{for } 25\% < RH \leq 75\% \\
0 & \text{for } RH > 75\%
\end{cases}$$

(11)

This conditional weighting function provides a method to include relative humidity’s effect on cumulative dust concentrations and matches the observational patterns of wind speed and relative humidity’s effect on aeolian dust concentrations.
Figure 4a and 4b. 4a is the hourly cumulative dust concentrations versus hourly average relative humidity. 4b is the average hourly cumulative dust concentrations when portioned into 5% relative humidity bins.
B.3.1.2 Vertical profile of dust concentrations

Comparisons of dust concentrations recorded by the DUSTTRAKs located at different heights (1, 3 and 10 m) in the eddy towers can be used to assess vertical variations of dust concentration. Figure 5 shows that dust concentrations measured at 1-m and 3-m above ground are correlated linearly with a slope close to one, which indicates that they are approximately the same. However, at 10-m above ground, the cumulative dust concentration is approximately 50% of that measured at 3-m above ground (Figure 6).

Equation 12 shows that cumulative column abundance of airborne dust \( D_{\text{column}} \) (mg/m\(^2\)) is solved by integrating the cumulative dust concentration, \( C \) (mg/m\(^3\)), from the surface \((z=0)\) to the altitude where concentration of aerosols goes to zero \((z_c=0)\). Using the average vertical profile of cumulative dust concentrations and linearly extrapolating we solved for the cumulative column abundance. Cumulative column abundance is used to determine the total mass of dust emitted by the tailings impoundment in the deposition forecast model.

\[
D_{\text{column}} = \int_{z=0}^{z_c=0} C \times dz
\]  
(12)
Figure 5. Correlation of cumulative dust concentrations measured at 1-m and 3-m above ground. The red line indicates the linear fit of the data forced through the origin ($R^2 = 0.7739$; slope = 0.9664).

Figure 6. Correlation between the cumulative dust concentrations measured at 3-m and 10-m above the ground. The red line indicates the linear fit of the data forced through the origin ($R^2 = 0.61$; slope = 0.4434).
**B.3.1.3 Particle size distribution of dust**

We utilized a MOUDI to determine the fractionated size distribution of the Iron King mine tailings dust. The observed size distribution is presented in Table 1. For our use, the stages were grouped into three categories where, coarse = TSP-PM$_{18}$ (first stage), medium = PM$_{18}$-PM$_{3.1}$ (second to fourth stages), and fine = PM$_{3.1}$ (all stages below 3.1-$\mu$m). The average mass fractions for the three categories, coarse, medium, fine, are 30.1%, 30.0%, and 39.9% respectively. For simplicity, we will refer to these three size fractions as coarse, medium and fine.

<table>
<thead>
<tr>
<th>Aerodynamic cut point diameter (µm)</th>
<th>Sample 1 (µg)</th>
<th>Sample 2 (µg)</th>
<th>Sample 3 (µg)</th>
<th>Sample 4 (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>741</td>
<td>690.5</td>
<td>557.45</td>
<td>609.3</td>
</tr>
<tr>
<td>9.9</td>
<td>367</td>
<td>154</td>
<td>99.6</td>
<td>339.5</td>
</tr>
<tr>
<td>6.2</td>
<td>232.5</td>
<td>284.5</td>
<td>117.4</td>
<td>325.25</td>
</tr>
<tr>
<td>3.1</td>
<td>176</td>
<td>251</td>
<td>137.4</td>
<td>230.8</td>
</tr>
<tr>
<td>1.8</td>
<td>174</td>
<td>147.5</td>
<td>107.25</td>
<td>2.8</td>
</tr>
<tr>
<td>1</td>
<td>112.5</td>
<td>127.5</td>
<td>70.45</td>
<td>122.4</td>
</tr>
<tr>
<td>0.55</td>
<td>145</td>
<td>121</td>
<td>91.6</td>
<td>103.25</td>
</tr>
<tr>
<td>0.32</td>
<td>199</td>
<td>179</td>
<td>86.9</td>
<td>147.1</td>
</tr>
<tr>
<td>0.18</td>
<td>118</td>
<td>117.5</td>
<td>54.5</td>
<td>69.9</td>
</tr>
<tr>
<td>0.1</td>
<td>147</td>
<td>91</td>
<td>46</td>
<td>68.25</td>
</tr>
<tr>
<td>0.054</td>
<td>228</td>
<td>91.5</td>
<td>50.9</td>
<td>72.6</td>
</tr>
<tr>
<td>AF</td>
<td>48</td>
<td>79.5</td>
<td>50.6</td>
<td>302.95</td>
</tr>
</tbody>
</table>

The deposition rates of each size fraction are simulated within deposition forecasting model individually. By separating the dust into three different size fractions we are able to simulate the deposition of aerosols with similar aerodynamic diameters. This avoids
the problem of determining the deposition of windblown dust that has a large size range (sub-micrometer to 10’s of micrometers in diameter) in a single simulation.

**B.3.1.4 Standard deviation of horizontal wind direction**

It is widely observed that the variability in wind direction is dependent on the wind speed. In order to quantify this relationship we directly compared the standard deviation of horizontal wind direction to the average wind speed. To calculate the standard deviation of horizontal wind direction, we first determine the mean wind direction, $\theta_C$ by

$$
\theta_C = \arctan\left(\frac{\sin(\theta)}{\cos(\theta)}\right)
$$

where $\theta$ is a time series of observed wind directions (Weber, 1997). Once the average wind direction has been determined, one can perform a typical standard deviation calculation. For example, we analyzed the meteorological observations to calculate both mean wind direction and standard deviation of wind direction for the period, April 2012 to August 2013. Figure 7 shows the average standard deviation of wind direction when all samples are binned using 1 m/s wind speed intervals. There is a noticeable decrease in the average standard deviations relative to increasing wind speed. These data support the common observation that high wind speeds have less variability in direction than winds with a lower speed. The data were fitted to an exponential function,

$$
\sigma_\theta = Ae^{BU}
$$
where $U$ is wind speed in m/s, $\sigma_0$ is the standard deviation of wind direction, and $A = 66.28$ and $B = -0.2137$. This empirically fitted exponential function will be used to control the angular distribution of the deposition pattern within the dust deposition forecast model.

The standard deviation of the wind direction is assimilated into the forecast deposition model by assuming that the angular deposition pattern has a Gaussian shape with standard deviation given by equation 14. This trend is incorporated through the following weighting function:

$$ W_{\theta_i} = 1 \ast e^{(\theta_e - \theta_i)^2 / 2\sigma_\theta} $$

(15)
where \( i \) is the pixel index, \( \theta_i \) is the angle between the \( i^{th} \) pixel and the center of the tailings, \( \theta_c \) is the mean wind direction determined by the forecast wind direction and \( \sigma_0 \) is calculated using equation 14. This weighting method gives 100% weight to all the pixels directly downwind and creates a bell curve that reduces the weighting of the background isotropic deposition pattern as one moves angularly away from the mean wind direction.

**B.3.2 Idealized particle trajectory results**

Since we are simulating the deposition patterns of dust particles using 3-m observations, we initialized the particle transport by freely releasing the particles at 3-m height. Figure 8 shows the trajectory of a 10 \( \mu m \) diameter particle released in an atmosphere with a logarithmic wind profile. Stokes air resistance, turbulent eddy diffusion and gravitational settling are acting on the particle. The logarithmic wind profile was initialized with a 5 m/s at 10-m height wind speed and a surface roughness of 0.141 mm. The particles in the simulations traveled significantly further than they would have if they freely released and gravitational settling occurred without eddy diffusion. It is interesting to note that, since random motions generated by eddies affect the trajectory, no two particle trajectories are the same and the result in Figure 8 is a single sample of the results.
Figure 8. Trajectory of a 10 µm diameter particle released in a logarithmically profiled wind field with gravitational settling, Stokes air resistance and eddy diffusion acting on the particle. The logarithmic wind profile was initialized with a 5 m/s at 10-m wind speed and a surface roughness of 0.141 mm.

A simulation of 5000 individual particles was conducted to determine the deposition patterns for spherical particles of fixed diameter. The simulations were conducted for three different particle diameters of 2.5-µm, 10-µm, and 25-µm. Figure 9 shows two histograms of the deposition locations for 5000 simulated 2.5-µm and 25-µm particles released in a convective wind field with a 5 m/s at 10-m height wind speed. As expected, there were significantly more 2.5 µm particles that reached the 2000 m limit than for the 25-µm particles. The histogram data were fitted to an exponential curve relating particle deposition distance \( Y \), in m and distance from source \( X \), in m,

\[
Y = Ae^{BX}
\]  

(16)
Figure 9. The top two histograms are of the deposition locations for 5000 simulated 2.5-μm and 25-μm particles released in a convective wind field with a 5 m/s at 10 m height wind speed. The bottom two plots (Figure 9) show the 2.5-μm and 25-μm diameter particle’s histogram data fitted with an exponential curve (black line).

Table 2 shows the fitted coefficients, A and B, for the three particle fractions. We can use these empirically derived functions as a first guess for the radial deposition pattern for the three particle sizes. By applying the MOUDI mass distribution of particle size fractions to the predicted airborne dust concentrations, we generate an isotropic background best estimate of the radial deposition pattern for each size fraction; coarse, medium and fine.
Table 2: Fitted exponential coefficients, A and B, and the number of particles that did not deposit, determined by 5000 individual particle trajectories for spherical particles with diameters 2.5-μm, 10-μm and 25-μm

<table>
<thead>
<tr>
<th>Dp</th>
<th>A</th>
<th>B</th>
<th># in last bin</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>92</td>
<td>-0.001977</td>
<td>695</td>
</tr>
<tr>
<td>10</td>
<td>111.4</td>
<td>-0.00229</td>
<td>459</td>
</tr>
<tr>
<td>25</td>
<td>241.4</td>
<td>-0.004277</td>
<td>58</td>
</tr>
</tbody>
</table>

B.3.3 Dust forecast model

Integrating the empirically derived meteorological functions for wind speed, wind direction and relative humidity with the idealized particle simulations, we can forecast regional dust deposition caused by wind erosion of the tailings. The deposition model is initialized by the generation of 105 individual emission events that are evenly spaced 31 m apart covering the entire tailings pile. For each emission event the total deposition map is comprised of three components, the deposition maps for the coarse, medium and fine airborne particulates.

The first step is generating the deposition map is to estimate the total hourly dust concentration (μg/m³) by using equation 10. The calculated hourly mass concentration is converted to column abundance, defined as the total dust mass of a column of air found by integrating the vertical dust profiles divided by the projected surface area of ground,
and then multiplied by the area of the tailings pile, ~95,000 m$^2$, to get the total mass of dust that is transported from the mine tailings pile. This assumes that the wind erosion and transport is uniform over the entire tailings impoundment. Using the fractional distribution determined by MOUDI observations, the total mass of windblown particulate matter for the three size fractions is then calculated.

Having estimated the total mass of the windblown particulate matter for the three size fractions, we generate a deposition map. ‘First guess’ dust deposition patterns are generated for each of the 105 individual emission events for three size fractions. We assume an isotropic dust pattern from the point source using the exponential functions derived from the individual particle simulations (Table 2). The ‘first guess’ deposition maps have the same horizontal resolution as topographic data (10.3 m). The model’s calculation procedure is illustrated by the results in Figure 10. Figure 10a shows an example of a ‘first guess’ dust deposition map for medium size particles. Figure 10b shows the map of weighted upslope values that are assimilated into the ‘first guess’ deposition map to modify the deposition estimates to include the effects of topography. Figure 10c shows a representation of the angular weighting matrix that is created using wind direction and the empirical relation relating standard deviation of wind direction to wind speed. When the angular weighting matrix and weighted upslope matrix are assimilated into the ‘first guess’ deposition map, we get the calculated deposition pattern for the specific size fraction and for the point source (Figure 10d). These results were generated by using an average hourly wind speed of 5 m/s towards 324° (west of north) and a relative humidity of 20%, corresponding to prevailing observations. The three size fractions were summed to create hourly deposition (μg/m$^2$) estimates of PM$_{2.7}$ transported
from the mine tailings. Figure 11 shows the resulting calculated dust deposition maps for the three size fractions and the cumulative PM$_{27}$ deposition. It is easily noticeable that the spatial distributions of the fine and medium particle size fractions are much larger than the coarse size fraction. However, because of the larger spatial distributions of the fine and medium size fractions the maximum deposition amounts attributed to the fine and medium particles are about 70% less than the coarse size fraction. This is expected because the coarse size fraction particles cannot travel very far because of their fast gravitational settling velocity and, as a result, most will deposit very close to the source.
Figure 10. 10A shows an example of a ‘isotropic background dust deposition map for medium size particles. 10B shows the map of weighted upslope values. 10C is the angular weighting matrix that is created using wind direction and standard deviation of wind direction. 10D the expected deposition pattern for a point source and the fine size fraction. These images were generated by initializing the model with an average hourly wind speed of 5 m/s towards 324° (west of north) and a relative humidity of 25% corresponding to prevailing observations. The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.47639° to 34.52380° latitude and -112.27639° to -112.22491° longitude.
Figure 11. The resulting dust deposition maps for the three size fractions coarse (upper left), medium (upper right), fine (lower left) and the total dust deposition (lower right). The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.49610° to 34.52380° latitude and -112.27639° to -112.24869° longitude.

B.3.4 Model Verification

In order to determine how well the simulations capture the true deposition patterns of windblown dust we compared our predicted deposition maps to observed topsoil samples of tracer species that originated from the tailings. The mine tailings contain both arsenic and lead at concentrations that are three orders of magnitude greater than the background levels in the region. By taking the surface soil (topsoil) measurements of arsenic and lead we created ‘smoothed’ arsenic and lead concentration maps in the region around the tailings. Most of the topsoil sample data were obtained from the EPA IK remediation report (EA. Engineering, 2010), where 374 soil samples were collected at distances up to
2.5 km from the tailings pile. Our deposition model, combined with the use of an average concentration of lead and arsenic of the topsoil of the mine tailings, can be used to predict the deposition pattern of the two contaminants. It is important to point out that this model verification will be based on comparison of observed spatial trends to model calculations, since topsoil is subject to other potential contaminant transport mechanisms like liquid runoff during rainy periods.

An optimal interpolation scheme was used to assimilate the heterogeneous data to produce a contour map of arsenic and lead concentrations as measured in the topsoil samples. The soil samples were assimilated into a map of the region with 10.3-m horizontal spatial resolution. The optimal interpolation scheme was based in the following equations

\[
X_{post} = X_{prior} + W[Y - (HX_{prior})]
\]  

(17)

\[
W_{i,j} = e^{dx/L}
\]  

(18)

where \(X_{post}\) is the interpreted soil sample matrix, \(X_{prior}\) is the background matrix, \(W\) is the weighting matrix, \(Y\) is the observation vector and \(H\) is the matrix that identifies the nearest neighbor for the soil sample locations. We assumed a flat background matrix with zero concentrations for both lead and arsenic (even though background concentrations are not zero, they are less than 0.1% of the tailings averages). The weighting matrix is determined by the distance between the sample locations and the map pixels. An exponential function was used to determine the weights within the weighting matrix (equation 18) where \(W_{i,j}\) is the weight given to the \(i^{th}\) pixel influenced by the \(j^{th}\) soil sample, \(dx\) is the distance between the \(i^{th}\) pixel and the \(j^{th}\) soil sample and \(L\) is the
correlation length. The correlation length was set to 100 m for both the arsenic and lead soil sample interpolation maps.

Figures 12 and 13 are maps of the natural log of the interpolated arsenic and lead concentrations in topsoil, respectively. There are several areas that are high in both arsenic and lead concentrations, including the main mine tailings pile, the operations area just west of the main tailing pile and the smelter area, located about 2 km east of the main tailings pile. Note that, despite the smoothing, there are certain areas that are biased towards higher concentrations than their surroundings by specific measurements (notably two areas NE and SE of the tailings).

Figure 12. Map of the natural logarithm of arsenic concentrations (ppm) measured in top soil samples and interpolated using optimal interpolation method. The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.47639° to 34.52380° latitude and -112.27639° to -112.22491° longitude.
Figure 13. Map of the natural logarithm of lead concentrations (ppm) measured in top soil samples and interpolated using optimal interpolation method. The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.47639° to 34.52380° latitude and -112.27639° to -112.22491° longitude.

To verify the deposition model, we looked at arsenic and lead concentrations in transects originating at the tailings and following a specific direction. By looking at transects generated by the surface soil concentrations, our expectation is that they should match the pattern determined by the particle transport simulations. Eight transects were plotted for arsenic and lead surface soil concentrations in the north, northeast, east, southeast, south, south west, west and northwest directions. The radial transects were collected from the center of the tailings pile and extended out to 1 km. Figures 14 and 15 show the average of all eight transects of natural log concentration for arsenic and lead versus distance from the tailings. Also plotted on the graph are two straight lines that have the same slope as the exponential coefficients B from Table 2 for particles with diameters 2.5-μm and 25-μm. For arsenic (Figure 14), the average transect fall between the deposition patterns
predicted by a 25-μm diameter particles and a 2.5-μm diameter particles. For lead (Figure 15), the average of the log concentration transects is slightly higher and follows the deposition pattern of particles with a diameters 2.5-μm up to 300-m from the tailings. The elevated lead concentrations near the tailings are caused by the westward and southwestward transects that cut through the operations area of the property. The operations area has anomalously high values of lead that were not caused by windblown transport and instead by anthropogenic mining activity. For distances greater than 300-m, the average lead transect falls between the predicted deposition patterns by the 25-μm diameter particle and a 2.5-μm diameter particle deposition decay rate. The comparison of surface soil concentrations of arsenic and lead seem to reinforce the predicted radial deposition patterns from the idealized simulations. This gives us confidence in our deposition model and allows us to suggest that the elevated arsenic and lead concentrations in the surface soils surrounding the tailings are most likely caused by aeolian transport.
Figure 14. Average radial transects of arsenic natural log concentrations (ppm by mass) versus distance from the mine tailings. Data points represent topsoil concentrations interpolated from the topsoil data. Solid lines represent deposition model predictions for 2.5-μm (red) and 25-μm (black) particles.

Figure 15. Average radial transects of lead natural log concentrations (ppm by mass) versus distance from the mine tailings. Data points represent topsoil concentrations interpolated from the topsoil data. Solid lines represent deposition model predictions for 2.5-μm (red) and 25-μm (black) particles.
B.4 Conclusions

This work presents a mathematical model that relies on in-situ measurements to develop a predictive tool to quantify transport and deposition of PM$_{2.5}$ dust from a contaminated source. The model includes the effects of wind speed and relative humidity, which improves on previous efforts that use a single threshold friction velocity, such as the EPA AP42 wind erosion model. This model also incorporates regional topographic information and its impact on dust deposition, which has proven to yield significant effects. The method used to generate the model can be translated to other regions and applied to different windblown dust sources. Source apportionment techniques (such as lead isotope analysis) could potentially be used in future model validations. Overall the deposition model is a practical method to predict deposition of several aerosol size fractions by incorporating empirically derived relations and site specific topographic effects.

Acknowledgements

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Appendix C: Verification of windblown dust deposition forecasting model using inverted-disc samplers

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Abstract

Wind erosion, transport and deposition of particulate matter from windblown dust sources such as mine tailing impoundments can have significant effects on the surrounding environment. Mine tailings are fine grain silty material that is a waste product from the mineral ore refinement process. The tailings are usually stored in very large piles with sloped sides and flat tops. This material usually lacks the nutrients and microbial activity required to sustain vegetation so most tailing piles lay barren. The lack of vegetation and the way they protrude vertically above the neighboring terrain makes them extremely susceptible to wind erosion. Modeling the erosion, transport and deposition of particulate matter from mine tailing piles is very difficult for many reasons including heterogeneity of the soil surface, vegetative canopy coverage, dynamic meteorological conditions and topographic influences. Stovern et al. (2014) created a deposition forecasting model that is specifically designed to model the transport of arsenic and lead contaminated particulate matter from the Iron King Mine tailing impoundment, an EPA Superfund site. Using inverted-disc deposition samplers it is our goal to verify the accuracy of the deposition model. The deposition forecasting model will be initialized using data from an operational Weather Research and Forecasting (WRF) model. The forecast deposition patterns are compared to the inverted-disc samples through gravimetric, chemical composition and lead isotopic analysis.

Keywords: Dust transport, Deposition, Forecasting, Inverted Frisbee
C.1 Introduction

Wind erosion, transport and deposition of particulate matter can have significant effects on the surrounding environment especially in the semi-arid regions located in the southwestern US. The semi-arid regions are especially susceptible to wind erosion because of the dry climate and lack of vegetation with increased likelihood of wind erosion. Wind erosion occurs on a variety of spatial scales from the very large dust storms that can travel thousands of kilometers (Wilkening et al., 2000) to the small local sources whose impact is much more regionally confined. Some of the human health concerns associated with elevated concentrations of particulate matter include fungi and bacteria transport (Sprigg et al., 2014), respiratory stress and cardiovascular disease (Brook et al., 2010). Local sources of windblown dust such as dry lake beds, plowed fields and stock piles can regularly produce windblown particulate matter and have significant effects on their local surroundings. In Arizona, where mining plays a significant role in the economy, mine tailing impoundments can be a significant anthropogenic source of windblown particulate matter. There have been several studies that investigate wind erosion of stoke piles and tailings impoundments through the use of computational modeling (Badr and Harion 2005, Turpin C. and J. L. Harion 2010, Diego et al. 2009, Stovern et al. 2014).

Being able to predict the transport and deposition of windblown dust from mine tailing impoundments is vital in determining the exposure risks on neighboring communities. Forecasting windblown dust transport and deposition can be difficult for many reasons including the heterogeneity of the soil surface, vegetative canopy coverage, dynamic meteorological conditions and topographic influences. Stovern et al. 2014 created a
windblown deposition forecasting model (DFM) for a specific tailings impoundment. The model is based on empirical relations derived from eddy flux tower observations and physical models. The DFM was developed for the Iron King Mine and Humboldt smelter tailings impoundment, an US Environmental Protection Agency (EPA) Superfund site that has elevated concentrations of toxic species such as lead and arsenic on the property and surrounding areas.

We will assess the accuracy of the DFM through the use of in situ deposition samplers. Two, month long field sampling campaigns were conducted, from April 21st till May 22nd and June 11th till July 9th 2014, during which aerosols were collected by inverted-disc samplers and analyzed for weight, chemical composition and lead isotopes. The inverted-disc samples are compared to the deposition amounts predicted from DFM. The deposition forecasting model is initialized using an operational Weather Research and Forecasting (WRF) model. We hypothesize that forecast spatial deposition patterns generated by the DFM will agree with arsenic and lead tracers captured by the inverted-disc samplers.

C.2. Methodology

C.2.1 Site description

The Iron King Mine tailings and Humboldt smelter located in central Arizona are a legacy of lead, gold, silver, zinc and copper production from 1906-1969. The area was classified as a Superfund site by the US EPA in 2008 (EPA, 2010) after it was discovered that both areas are heavily contaminated with both lead and arsenic.

The area is classified as semiarid with an annual rainfall of about 0.48 meters a year (NCDC, 2004). The vegetation is classified as Pinyon Juniper woodlands with limited
desert grasses and other bushes (EA Engineering Science and Technology, 2010). Most
of the land adjacent to the northern, western and southern edges of the tailings and mine
operations property is publicly owned state trust and grazing land. There is residential
property located east of the mine property where Arizona state highway 69 separates the
mine property from the town of Dewey-Humboldt. The close proximity of residential
structures to the Iron King Mine and Humboldt smelter may put them at risk of heavy
metals exposure.

The main tailings impoundment has a total aerial extent of 96,000 square meters and is
devoid of vegetation except where a phytoremediation project is attempting to reestablish
native vegetation. The revegetation project has been in progress since May 2010 and is
confined to an area of 7,200 square meters on top of the tailings (Maier and Chorover,
2011). The surface of the impoundment is made up of silty, clay and sandy soils and has
a reddish discoloration (Solis et al, 2012). The tailings are typically covered in a crust
with salty efflorescence that usually forms following rain events. This crust can be easily
broken up and results in very fine powdery material that is easily eroded by the wind.

The average arsenic and lead concentrations measured in several bulk samples of the
mine tailing material is about 0.12% and 0.10% by mass and the efflorescence salts have
average arsenic and lead concentrations of 0.22% and 0.24%.

A suite of meteorological and aeolian dust monitoring instruments was installed on the
tailing impoundment in 2009. The setup consists of two eddy flux towers, equipped with
a variety of meteorological and six DUSTTRAK dust monitors for PM$_{2.5}$, anemometers,
wind vanes, thermometers, hygrometers, soil moisture probe and soil radiometer
(Stovern, 2015). In addition, a Micro-Orifice Uniform-Deposit Impactor (MOUDI) was
deployed to measure size fractionated distribution of aeolian dust from January 24 to July 9, 2014.

**C.2.2 Deposition forecasting model description**

The DFM predicts the deposition of PM$_{2.7}$ windblown dust from the Iron King tailings impoundment. The DFM is a hybrid model that utilizes both empirically derived relations and physics based particle simulations.

The nearly two years of meteorological and dust monitoring data collected from the eddy flux towers was used to derive empirical relationships between meteorological conditions and windblown dust generation. These empirical relations include the effects of wind speed and relative humidity on airborne dust, particle size fractionation and the vertical profile of dust measured on the tailings and wind speed effects on wind direction variability (Stovern, 2014). The empirical relations are used in conjunction with high resolution WRF operational weather forecasts to predict PM$_{2.7}$ generated by the tailings.

The DFM also includes the effect topography has on aerosol deposition. Stovern et al. (2014) simulated windblown transport of fugitive aerosols from the Iron King Mine tailings. They found that windblown dust preferentially deposits in regions of topographic upslope relative to the mean flow. Due to the complex topography of the site these effects are included in the model.

The DFM results for each forecast period are produced for three particle size ranges and are generated on a spatial grid that is approximately $\sim 25$ km$^2$ with 10.3 meter spatial resolution. These simulations include the effects that a convectively turbulent boundary layer has on particle trajectories. This includes all of the Iron King tailings and most of the adjacent town of Dewey-Humboldt. The model is initialized using the 48-hour
forecasts from an operational version of the WRF model produced by the department of Atmospheric Sciences at the University of Arizona.

**C.2.3 WRF model forecasts**

The WRF model is used to initialize the DFM. It is configured with two nested grids that cover the entire state of Arizona, and portions of California, Colorado, Nevada, New Mexico, Utah and Mexico. The inner and outer domains have horizontal resolutions of 1.8-km and 5.4-km respectively. Model forecasts are produced daily at 12Z and 6Z, using both GFS and NAM initializations. Each forecast run is 48 hours long at one hour intervals. The DFM was initialized using the WRF forecast conditions predicted 28-39 hours in advance.

We used the daily 12Z GFS WRF runs during the periods April 21st till May 22nd and June 11th till July 9th 2014 to tabulate the U- and V- components of the 10-m winds, 2-m specific humidity, the 2-m temperature and the surface pressure for each hour between 9 AM and 9 PM. We then calculated the wind speed and wind direction and relative humidity for each hourly interval by averaging the five nearest-neighbor WRF grid points at the tailings location which was used to initialize the deposition forecasting model.

**C.2.4 Comparison of direct observations and WRF model forecasts**

WRF model forecasts and observed meteorological conditions on the tailings were compared to test for systematic biases over a period of 163 days (June 2012 to August 2013). This period coincides with the same observing period used to determine the empirical relations used in the creation of the deposition forecasting model (Stovern et al., 2014).
As described later, determining the slope of the trend line for the forecast and observed wind speed and relative humidity we corrected for systematic bias. Wind direction is a circular variable so in order to calculate bias we first calculated the residual for each model and observation pair which fall within the range of -180 to +180 degrees. A positive residual indicates counter-clockwise rotation between the WRF model and observed wind direction and vice versa. A perfectly nonbiased data set would produce an average residual of zero.

Inverted-disc samplers have been used in several deposition experiments including, aeolian deposition near an eroding source field (Hagen et al., 2007) and dry deposition of polychlorinated organics (Koester, 1992). The collection efficiencies of inverted-disc samplers have been studied extensively (Hall, 1986; Hall, 1988; Vallack, 1995; Sow et al., 2006 and Goossens and Rajot, 2008) and are dependent on wind speed and particle diameter. However there appears to be general consensus that the collection efficiency falls within the range of 5-40% (Sow et al., 2006). For this study collection efficiency is unimportant because we compare relative deposition amounts. Hall (1986) showed that an inverted-disc sampler has a significantly higher blowout wind speed than both the flat disc and the British Standard deposit gauge. This reduces re-suspension and loss of particulate matter.

The plastic discs (Frisbees) were purchased from discountmugs.com. They have a diameter of 233 mm and a depth of 25 mm. The discs were glued to the lids of high density polyethylene 500 ml sample bottles (Thermo Scientific) using Loctite plastic bonder. A 8.47 mm hole was drilled through the disc into the bottle. The samplers were mounted to iron stakes and placed at 1 meter height above the ground.
A set of 20 inverted-disc samplers were placed around the Iron King property and surrounding area. The disc samplers were placed along three transects to measure deposition in the northward, eastward and southward directions starting from the main tailings and extending up to 1 km away. A majority of our samplers were located north of the main tailing pile, along the dominant wind direction. There is also significant topographic variation north of the tailings which is used for testing the effect topographic upslope has on dust deposition. The pins on the visible satellite image denote the locations of the inverted-disc samplers and the tailings pile is identified by the discoloration (Figure 1). Arizona highway 69 and the town of Dewey-Humboldt can be seen along the eastern edge of the mine property.

Figure 1. Google Earth visible satellite image of the Iron King Mine tailing impoundment and the town of Dewey-Humboldt. The location of the inverted-disc samplers are denoted by yellow pins.
C.2.5 Sample analysis

In the field, deionized water was used to flush all the dust captured on the inverted-disc into the attached 500-mL bottle. The bottles were unscrewed from the attached inverted-discs and capped for transportation to the laboratory where each sample was partially dried in the 500-ml bottle in an oven (60 °C) and then transferred quantitatively into a pre-weighed 50-mL glass vial.

The dried samples were weighed using a Mettler AE100 balance (±0.1 mg). The sample masses were normalized to the area of the disc giving the mass deposition per unit area for each sample location.

The samples were then prepared for metal and lead isotopes analysis by extraction with 15 mL of \textit{aqua regia} (1.03 M HNO$_3$/2.23 M HCl, trace-metal grade) with sonication at 80 °C for 60 minutes. 1.2 mL of solution were extracted and diluted to 4 mL with deionized water before the analysis. Due to the relatively low concentrations of lead in some of the samples the lead isotope analysis samples were concentrated on a hot plate (Felix et. al, 2014). An ICP-MS (Agilent 7700X with an Octopole Reaction System) was used to analyze for metal concentrations and lead isotopic composition. MiliQ water, 0.669 HCl (Fisher, trace-metal grade) and 0.309 M HNO$_3$ (EMD, Omnitrace) were used to create the certified calibration standards from Accustandard. In addition to each sample, the National Institute of Standards and Technology (NIST) standard reference material (SRM 1643e trace elements in water) was also analyzed. We used the same operating condition for the analysis of both elemental concentrations and the lead isotopic ratios. NIST SRM 981 (Lead isotopic standard) was used for validation and calibration and the analytical precision of lead isotopic ratios was under 0.5 %. (Felix et al., 2014).
C.3 Results

C.3.1 WRF model verification

Biases in the WRF forecast wind speed, wind direction and relative humidity are determined by direct comparison to in situ observations. All three parameters showed strong positive correlations, which is notable considering we are comparing point observations to weather forecasts generated at least 24 hours in advance. The forecast of relative humidity showed good agreement with the observations (Figure 2) with a slope of 0.9736 and a $R^2$ value of 0.59. This shows that the WRF model slightly under predicts the observed relative humidity. This small bias is influenced by just a few forecasts with significantly lower relative humidities than those observed. This was caused by precipitation events that the WRF model failed to forecast. To adjust for this slight bias, the model-predicted relative humidity is multiplied by a correction factor of $1/0.9736$. 
Figure 2. Comparison of hourly averaged observed relative humidity and WRF model forecast relative humidity for the period of May 29, 2012 to August 4, 2013.

The forecast and observed hourly averaged wind speeds are also positively correlated but with much more scatter (Figure 3). The slope of a linear fit to the data forced through the origin is 0.838 with a $R^2$ value of 0.230, which means the WRF forecast winds are systematically lower than those observed. The low $R^2$ value is indicative of the difficulties when comparing model forecasts using 1.8-km grid spacing to point observations where boundary layer mechanics and surface roughness play an important role. The model-predicted wind speed is corrected by multiplying by $1/0.838$. 
Figure 3. Comparison of hourly averaged 10-m observed wind speed versus WRF model forecast wind speed for the period of May 29, 2012 to August 4, 2013.

The histogram of the hourly wind direction residuals, is shown in Figure 4. The histogram was generated using 10 degree bins from -180 degrees to 180 degrees. The histogram is shifted to the right of zero which means the model-predicted wind direction is systematically biased counter clockwise from the observed. The median of the residuals is +14.71°. So by adding 14.7 degrees of clockwise rotation to the forecast wind direction we account for the apparent bias between model forecast and observed conditions.
Figure 4. Histogram of residuals generated using the observed wind direction and WRF modeled wind direction for the period of May 29, 2012 to August 4, 2013.

C.3.2 Deposition model prediction

The DFM simulations were initialized using the corrected WRF model forecasts. Figure 5 is a box plot of the deposition predicted by the DFM for the fine (PM$_{3.1}$), medium (PM$_{18}$-PM$_{3.1}$), coarse (PM$_{27}$-PM$_{18}$) and total suspended fine particulate (PM$_{27}$) for the period April 21$^{st}$ till May 22$^{nd}$ 2014. A majority of the deposition occurs in the northward direction forced by the dominant wind direction. However, there is significant forecast deposition in the southeastward and southwestward directions. This was the result of several synoptic scale troughs that shifted the daytime wind direction to a more southwesterly and southeasterly flow for several days during the month. One of these troughs was accompanied by precipitation on April 27, 2014. The WRF model predicted the strong wind speeds associated with the trough but failed to accurately forecast the
precipitation that was observed at the site. The increased soil moisture caused by the precipitation greatly reduces windblown erodibility. Hence the deposition in the southwesterly direction was significantly over estimated.

![Image of deposition maps](image)

**Figure 5.** Maps of deposition for three size fractions and PM$_{27}$ predicted by the DFM for the forecast period April 21 to May 22, 2014. The fine size fraction is located in the upper left, medium size fraction in upper right, coarse size fraction in lower left and total in lower right. The tailings impoundment is outline in black and the color scale is in mg/m$^2$. The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.47639° to 34.52380° latitude and -112.27639° to -112.22491° longitude.

The maximum forecast deposition of fine, medium, coarse and PM$_{27}$ for the May sampling period are 36, 34, 104 and 185 mg/m$^2$ respectively. The maximum coarse particle deposition was mainly constrained to the immediate tailing region due to their large size and fast settling times which do not allow them to be transported long distances. However, the fine particles have a much smaller terminal velocity which
scales with $Dp^3$, and are transported much further down wind. The fine particles have a max deposition location that is located about three hundred meters from the tailings in the northward direction. There are slight variations in the deposition patterns caused by the impact of topographic slope of the surrounding region.

The resulting DFM simulations for the sample period June 11th till July 9th 2014 can be seen in Figure 6. Figure 6 is a box plot of the deposition predicted by the DFM for the fine, medium, coarse and $PM_{27}$ suspended particulate. Compared to the May sampling period the forecast weather conditions at the site were consistent with predominantly southerly winds that caused almost all the deposition to be in the northward direction. The maximum forecast deposition of fine, medium, coarse and $PM_{27}$ particles for the June sampling period are 38, 37, 89 and 157 mg/m$^2$ respectively and located directly north of the tailing impoundment.
Figure 6. Maps of deposition for three size fractions and PM$_{27}$ predicted by the DFM for the forecast period June 11 to July 9, 2014. The fine size fraction is located in the upper left, medium size fraction in upper right, coarse size fraction in lower left and total in lower right. The tailings impoundment is outline in black and the color scale is in mg/m$^2$. The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.47639° to 34.52380° latitude and -112.27639° to -112.22491° longitude.

C.3.3 Inverted-disc analysis

C.3.3.1 Mass analysis

The mass deposited on the inverted-disc samplers were measured for the sampling periods, April 21$^{st}$ till May 22$^{nd}$, 2014; and June 11$^{th}$ till July 9$^{th}$, 2014. Table 1 shows the total mass collected by each disc sampler for both periods. Mass deposition for the sampling periods ranged from 178-1039 mg/m$^2$ and averaged 482 mg/m$^2$. The highest mass deposited was measured at location N for the May sampling period and location B for the June sampling period. Sample N is located adjacent to the highway while sample
B is located on the tailings impoundment. Because roadways are well documented as production source of atmospheric aerosols it follows that we would expect larger amounts of deposition to be captured with the N sampler. There is a large amount of heterogeneity in the absolute deposition amounts and there is no distinguishable spatial pattern in absolute deposition mass captured by the samplers.

Table 1. Total mass of deposition captured using inverted-disc samplers

<table>
<thead>
<tr>
<th>Location</th>
<th>4/21 till 5/22 Deposition (mg/m²)</th>
<th>6/11 till 7/09 Deposition (mg/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>483.1</td>
<td>476.1</td>
</tr>
<tr>
<td>B</td>
<td>750.5</td>
<td>1039.0</td>
</tr>
<tr>
<td>C</td>
<td>213.4</td>
<td>731.7</td>
</tr>
<tr>
<td>D</td>
<td>806.8</td>
<td>832.6</td>
</tr>
<tr>
<td>E</td>
<td>290.8</td>
<td>337.7</td>
</tr>
<tr>
<td>F</td>
<td>440.9</td>
<td>295.5</td>
</tr>
<tr>
<td>G</td>
<td>382.3</td>
<td>239.2</td>
</tr>
<tr>
<td>H</td>
<td>562.9</td>
<td>227.5</td>
</tr>
<tr>
<td>I</td>
<td>311.9</td>
<td>354.1</td>
</tr>
<tr>
<td>J</td>
<td>501.9</td>
<td>253.3</td>
</tr>
<tr>
<td>K</td>
<td>931.1</td>
<td>485.5</td>
</tr>
<tr>
<td>L</td>
<td>506.6</td>
<td>433.9</td>
</tr>
<tr>
<td>M</td>
<td>497.2</td>
<td>N/A</td>
</tr>
<tr>
<td>N</td>
<td>1006.1</td>
<td>178.2</td>
</tr>
<tr>
<td>AA</td>
<td>N/A</td>
<td>335.4</td>
</tr>
<tr>
<td>BB</td>
<td>N/A</td>
<td>243.9</td>
</tr>
<tr>
<td>CC</td>
<td>N/A</td>
<td>307.2</td>
</tr>
</tbody>
</table>

Assuming a 20% collection efficiency of the inverted-disc samplers, the directly observed deposition for the two sampling periods is within an order of magnitude of the peak forecast deposition flux. The peak forecast deposition is approximately one quarter of the mass directly measured using the samplers, which is actually quite close agreement. When comparing the peak DFM deposition amount to the observed deposition in the
inverted-disc samplers is important to consider the fact that wind erosion occurs from a variety of sources within the region and each deposition sampler is collecting aerosols from all of them not just aerosols resulting from the tailings. The deposition forecasting model only simulates the transport of windblown particulate matter from the tailing impoundment and for particles with an aerodynamic diameter \( \leq 37\text{-μm} \). A few larger particles generated at the sampler site could highly skew the mass collected. For example, a single spherical particle with 500-μm diameter and a density of 2500 kg/m\(^3\) has a mass of 0.16-mg which could add 1.7% to the lowest observed mass collected. The compounding factors of possible multiple aerosol sources and the modeling of PM\(_{27}\), not TSP, makes our DFM estimate of deposition very reasonable when compared to the total deposition amounts measured by the inverted-disc samplers. Through the use of elemental analysis we can partition the captured dust and determine what influence the tailings have on each sampler.

### C.3.3.2 Lead and arsenic analysis

In this part of the study we examine arsenic and lead collected by the inverted-disc samplers. The tailings have significantly elevated arsenic and lead when compared to the natural surroundings (EA Engineering Science and Technology, 2010). By analyzing the dust collected by the inverted-discs we can determine the fractional contribution of dust originating from the tailings using these “tracers”. The arsenic and lead concentrations (ppm) measured by the inverted-disc samplers for both sampling periods can be seen in Table 2. The May arsenic data is absent due to erroneous ICP-MS results.
Table 2: Total As and Pb (ppm) measured in the dust collected by the inverted-disc samplers

<table>
<thead>
<tr>
<th>Location</th>
<th>May (4/21 to 5/22) Pb (ppm)</th>
<th>June (6/11 to 7/09) Pb (ppm)</th>
<th>June (6/11 to 7/09) As (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>332.00</td>
<td>902.56</td>
<td>1826.01</td>
</tr>
<tr>
<td>B</td>
<td>980.54</td>
<td>1743.46</td>
<td>3856.23</td>
</tr>
<tr>
<td>C</td>
<td>317.47</td>
<td>1036.88</td>
<td>1406.30</td>
</tr>
<tr>
<td>D</td>
<td>454.13</td>
<td>774.63</td>
<td>1388.58</td>
</tr>
<tr>
<td>E</td>
<td>130.34</td>
<td>317.04</td>
<td>132.15</td>
</tr>
<tr>
<td>F</td>
<td>39.34</td>
<td>71.24</td>
<td>46.37</td>
</tr>
<tr>
<td>G</td>
<td>505.51</td>
<td>1613.84</td>
<td>1311.74</td>
</tr>
<tr>
<td>H</td>
<td>481.83</td>
<td>837.61</td>
<td>587.53</td>
</tr>
<tr>
<td>I</td>
<td>216.56</td>
<td>434.59</td>
<td>586.08</td>
</tr>
<tr>
<td>J</td>
<td>217.93</td>
<td>383.27</td>
<td>504.37</td>
</tr>
<tr>
<td>K</td>
<td>234.20</td>
<td>341.99</td>
<td>464.51</td>
</tr>
<tr>
<td>L</td>
<td>291.82</td>
<td>438.81</td>
<td>648.94</td>
</tr>
<tr>
<td>M</td>
<td>41.89</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>N</td>
<td>41.18</td>
<td>137.72</td>
<td>155.95</td>
</tr>
<tr>
<td>AA</td>
<td>N/A</td>
<td>383.53</td>
<td>449.05</td>
</tr>
<tr>
<td>BB</td>
<td>N/A</td>
<td>453.17</td>
<td>594.62</td>
</tr>
<tr>
<td>CC</td>
<td>N/A</td>
<td>301.92</td>
<td>435.08</td>
</tr>
</tbody>
</table>

The best way to assess the heterogeneous results is to compare transects of relative concentrations of observed As and Pb (ppm) with forecast PM$_{2.7}$. The relative Pb and As concentration transects are calculated by normalizing each sampler to the average concentrations measured by inverted-disc samplers A and B located on the tailings pile. Transects of the DFM PM$_{2.7}$ are normalized by the forecast deposition at the location of sampler B (34.50087° latitude and -112.25305° longitude). All radial distances of the sample locations are calculated from sample point B. Figure 7 and 8 shows the DFM results of total deposition for the May and June sample periods. The black stars represent the locations of inverted-disc samplers. Three transects are evaluated in the southwestward, eastward and northward directions.
Figure 7. Map of PM$_{2.7}$ deposition predicted by the DFM for the forecast period April 21 to May 22, 2014. The color scale represents the natural log of deposition. The tailings impoundment is outlined in black and the locations of the inverted-disc samplers are marked by white stars. The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.49142° to 34.51452° latitude and -112.26247° to -112.23939° longitude.
Figure 8. Map of cumulative deposition generated by the DFM for the forecast period June 11 to July 9, 2014. The color scale represents the natural log of deposition. The tailings impoundment is outlined in black and the location and sample label of the inverted-disc samplers are marked by white stars. The grid points are spaced by 10.3-m and the domain has a total horizontal extent of 34.49142° to 34.51452° latitude and -112.26247° to -112.23939° longitude.

For the June sampling period the southward transect is calculated using the tailings average samples A and B, sample E (366-m downwind) and F (538-m downwind). For the eastward transect we use the tailing average, sample C (377-m downwind), sample D (657-m downwind) and sample N (786-m downwind). For the northward transect was generated using the tailing average samples, the average of samples H and AA (205-m downwind), the average of samples I, J and BB (300-m downwind) and the average of sample points K, L and CC (379-m downwind). For the May sampling period the northward transect was generated using the tailing average samples, sample H (205-m
downwind), the average of samples I and J (300-m downwind), the average of samples K and L (379-m downwind), and the sample point M (1027-m downwind).

The southward eastward and northward cross sections for the May and June sample periods can be seen in Figure 9. The southward cross sections of the model-predicted fractional reduction in deposition match very closely with the observed fractional reduction of ppm of As and Pb measured in the inverted-disc samplers. For the May sampling period, the forecast overestimated the relative amount of deposition located at the sample locations E and F. This was caused by strong northeasterly winds associated with a synoptic scale weather system. This weather system produced precipitation in the region which the WRF model failed to predict. The erroneous WRF weather forecast yielded an overestimation of windblown dust transport in the southwestward direction. For June the DFM model accurately forecasts the relative reduction in As and Pb at the E and F sample locations.
Figure 9. Comparison of relative decreases in arsenic (blue dashed lines) and lead (blue solid lines) concentrations measured by the samplers versus the relative decreases of deposition forecast by the DFM (red dashed lines) for the southward (Top) eastward (middle) and northward (bottom) cross sections and the April 21 to May 22, 2014 (left) and June 11 to July 9, 2014 (right) sample periods.

The eastward transect shows that the model grossly underestimated the amount of deposition for the C and D locations for both the May and June sampling period. However, it was quite accurate with the prediction at location N located approximately 786 meters away from the tailings. The reason for the underestimate of the relative As and Pb concentrations at locations C and D is because the area located directly east of the
tailing impoundment is also heavily contaminated with As and Pb. The deposition forecasting model only predicts the transport of fugitive dust from the main mine tailing pile and does not take into consideration other sources of As and Pb, such as the operations and lower tailing area. Figure 10 shows DFM results for the May and June sample periods when the source area is extended to contain the lower eastern operations area as well as the new eastern transect for the extended area simulations. With the addition of the lower tailing/operations area there is significantly better agreement between the DFM model and the inverted-disc samplers. In addition the sample location N had a fractional As and Pb concentrations that matched very well with the predictions made by the DFM for both sampling periods.
Figure 10. The top two figures are the DFM results for the April 21 to May 22, 2014 (left) and June 11 to July 9, 2014 (right) sample periods when the source area is extended to contain the lower eastern operations area. Black stars represent the locations of the inverted-disc samplers. The bottom two figures are the new eastern cross section of relative decreases in arsenic (blue dashed lines) and lead (blue solid lines) concentrations measured by the samplers versus the relative decreases of deposition forecast by the DFM (red dashed lines).

The northward transect shows a similar downwind pattern of reduction in the fractional As and Pb concentration. The DFM overestimates the fractional reductions of Pb for the May sampling period and both As and Pb for the June sampling period. However, the DFM was significantly better estimating the relative reduction of As and Pb for the May sampling period when compared to June. For the May sampling period the DFM accurately predicted the fractional reduction in Pb concentrations for sampler M located approximately 1-km north of the tailings.
The highest concentrations of both As and Pb were measured by the inverted-disc samplers located on the tailings (A and B). In comparison, the DFM model predicts that the highest amount of tailing dust deposition should occur approximately 150 meters north of sample point B. However the inverted-disc samplers show significant reduction in relative As and Pb between the tailings (A and B) and the points located about 205-m north (H and AA). This mismatch may be influenced by the capture of large particles by the inverted-discs. Dilution of disc samples by few large local clean particles can explain the large relative decrease between the tailing located samples and the samples located 205-m north.

The DFM includes topographic slopes when calculating deposition rates to the surface. Through computational fluid dynamics modeling Stovern et al. (2014) showed that the slope of the ground significantly impacts deposition in this topographically complex region. The inverted-disc samplers were strategically placed in locations that were sloped for the northward transect. The samples located at 205-m, 300-m and 379-m were in a down-sloping, up-sloping and down-sloping regions, respectively. Thus we would expect that the samples collected at 300-m should have systematically more deposition than the samplers at 379-m. However we appear to see the opposite occurring in the May sampling period and relatively equal amounts of deposition in the June sampling period. One reason why we are not seeing the effects of topographic slope on deposition patterns may be due to changes in surface roughness between the sampler locations at 300-m and 379-m. The samplers located on the up-sloping terrain at 300-m are surrounded by very sparse vegetation usually less than a meter in height with large barren patches of soil. On the other hand the samplers located in the down sloping region located at 379-m are
surrounded by significantly more vegetation including shrubs, bushes and trees that are typically 2-3 meters in height. The model however uses a constant surface roughness of 0.1-m. Large surface roughness and obstructing objects capture airborne dust in two ways, it removes momentum from the mean flow slowing transport of airborne particulates allowing them to gravitationally settle as well as directly capturing airborne dust through direct contact and impaction of the airborne dust. This severe change in surface roughness may explain the counter intuitive results from the samplers. Another possible reason might be the high natural variability in deposition may overwhelm the topographic effect.

C.3.3.3 Lead isotope analysis

The lead isotopes can be used to identify the sources of the lead collected in the inverted-disc samplers. Figures 11 and 12 shows the lead isotopic ratios for the dust collected for the May and June sampling periods, respectively. The Iron King tailings are characterized by lead isotopic ratios of 0.976 and 2.25. The background sample collected 5 km from the tailings has ratios of 0.863 and 2.09. Dust samples A and B located on the tailings themselves have same isotopic composition as the bulk tailings sample, implying the airborne lead captured in the samplers originated exclusively from the tailings, as expected.
Figure 11. A plot of lead isotopic ratios $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ for each inverted-disc sampler and a bulk sample of tailing material for the April 21 to May 22, 2014 sampling period. The letters represent the inverted-disc sample locations from Figure 1. Tailings represent “fingerprint” ratios of the source. Background sample was collected 5 km from the source and represent the natural Pb isotopic “fingerprint” of the region. Also included is the theoretical mixing line (black) that represents the age of the ore with lower ratios representing younger ore and higher ratios representing older ore.
Figure 12. A plot of lead isotopic ratios $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ for each inverted-disc sampler and a bulk sample of tailing material for the June 11 to July 9, 2014 sampling period. The letters represent the inverted-disc sample locations from Figure 1. Tailings represent “fingerprint” ratios of the source. Background sample was collected 5 km from the source and represent the natural Pb isotopic “fingerprint” of the region. Also included is the theoretical mixing line (black) that represents the age of the ore with lower ratios representing younger ore and higher ratios representing older ore.

Samples with lower isotopic ratios represent a regional background fingerprint and indicate that the airborne lead is not exclusively sourced from the tailings. For the May sampling period, the samples that have the lowest isotope ratio includes samples F and N. Sample F is the most southern sample located approximately 300-m from the southern edge of the tailings while N the eastern most sample is located approximately 500-m from the eastern-most edge of the tailings. The small contribution of tailings lead measured in these samplers matches the monthly wind patterns that predominantly transported dust northward, away from the samplers. Samples M and E also have a significantly lower isotopic ratios than the tailing samples. It is interesting to note that sample E which is located only about 200 meters from the southern edge of the tailings
has the same fractional contribution of tailings lead as the sampler located 1 km north, as expected from the prevailing winds. Also, the source of lead captured by the inverted-disc sampler N, located along AZ highway 69 which separates the Iron King tailings and the town of Dewey-Humboldt, had a smaller tailings contribution than the sampler located 1 km north of the tailings.

For the June sampling period the lead isotopic signatures were significantly closer to the tailings bulk sample when compared to the May sampling period. The samples with the lowest isotopic ratios included samples F, N and E. Sample F had the lowest lead contribution from the tailings, this matches the results from the May sampling period. However more of the lead measured in sample F was sourced from the tailings compared to May. For the eastern most sampler, N and southern sampler E, the isotopic ratios were closer to the tailings signature as well, while still maintaining the lowest isotopic ratios of all the June samplers.

It is interesting to note that the June samplers had significantly higher lead concentrations and isotopic ratios when compared to May. This was caused by a precipitation event that occurred on April 27. This precipitation event significantly increased the tailings moisture content minimizing wind erosion and reducing windblown lead deposition for the May sample period. In the June sample period the tailings had not received precipitation in over a month which significantly increasing the erosion potential, which resulted in more tailings sourced lead deposition causing the increase in lead concentrations and also shifting isotopic fingerprints closer to the tailings isotopic signature. This shows that local weather patterns including predominant wind directions
and precipitation have a significant effect on the deposition of windblown dust from the Iron King tailings impoundment.

C.4 Conclusions

The DFM is designed to utilize weather forecasts to predict the deposition of fugitive PM$_{2.7}$ dust originating from the Iron King tailings impoundment. By comparing the DFM predicted PM$_{2.7}$ deposition to arsenic and lead tracers collected by the inverted-disc samplers, it has been shown that the DFM performed very well with respect to capturing the spatial variations of the deposition patterns in the surrounding region up to 1 km distance from the tailings. The effects of topography on deposition still need adjustment due to the complex variations of surface roughness within the region. However, combining the deposition patterns generated by the DFM and the known concentrations of arsenic and lead in tailing dust we can provide quantitative estimates of arsenic and lead deposition rates near the tailings impoundment. These quantitative estimates of deposition should improve the characterization of potential health impacts caused by windblown transport from the tailings. Overall this model proved itself as a viable tool to forecast windblown deposition within close proximity of the Iron King Mine tailings impoundment and the surrounding region including the town of Dewey-Humboldt.

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C.5 References


