

APPENDIX F

Example Application: Primary Copper Smelter

DRAFT

**EPA Contract EP-D-05-096, Assignment 4-07
EPA Project Manager: Daniel G. Bivins**

**MACTEC Work Order No. 201001192
MACTEC Project No. 688009S509**

**Submitted To:
MACTEC Federal Programs
Research Triangle Park, NC**

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December 3, 2010

Summary

This hypothetical example is an illustration of how the Guide for Developing a Multi-Metals, Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors (Guide) might be applied to a large metals processing facility isolated in a rural setting with two adjoining “company towns”. In this particular example, controlled emissions are removed through a tall stack. Fugitive emissions represent the primary source of metal exposure to the community. Of primary concern are the high concentrations of arsenic to which the communities are exposed, and which are expected to exceed Occupations Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) ceilings over short averaging times. The primary objectives of this example are to: 1) illustrate how to develop a monitoring plan in an airshed with known intermittent, high concentration fugitive sources to support establishment of a not-to-exceed arsenic limit as well as an action concentration and goal concentration to protect the health of nearby communities; and 2) show how an ambient metals monitoring plan can provide timely exposure and fugitive source apportionment data to assist regulators and plant management with identification and mitigation of the problem.

ASARCO Incorporated operates a primary copper mine and smelter near Hayden and Winkelman, Arizona. Air quality concerns in the Hayden airshed are for particulate matter and toxic metal pollutants related to the smelter operations. Data from past studies show that Hayden has not yet attained the National Air Quality Standard (NAAQS) for particulate matter (PM), and elevated concentrations of arsenic (As), lead (Pb), cadmium (Cd), and copper (Cu) have been measured in both Hayden and Winkelman. There is a high probability that the general populations of these two communities have been exposed to hazardous metals concentrations from fugitive emissions that approach or surpass occupational standards that should not be exceeded in the workplace. This appendix provides a hypothetical example of how a Hazardous Ambient Metal Compliance Plan (Plan) might be developed to monitor short and long-term ambient metals concentrations in Hayden and Winkelman and develop a remedial plan to achieve local air quality limits. The Plan will provide the necessary data to assist the smelter in developing a control strategy jointly managed by the plant and the regulatory body to mitigate fugitive emissions.

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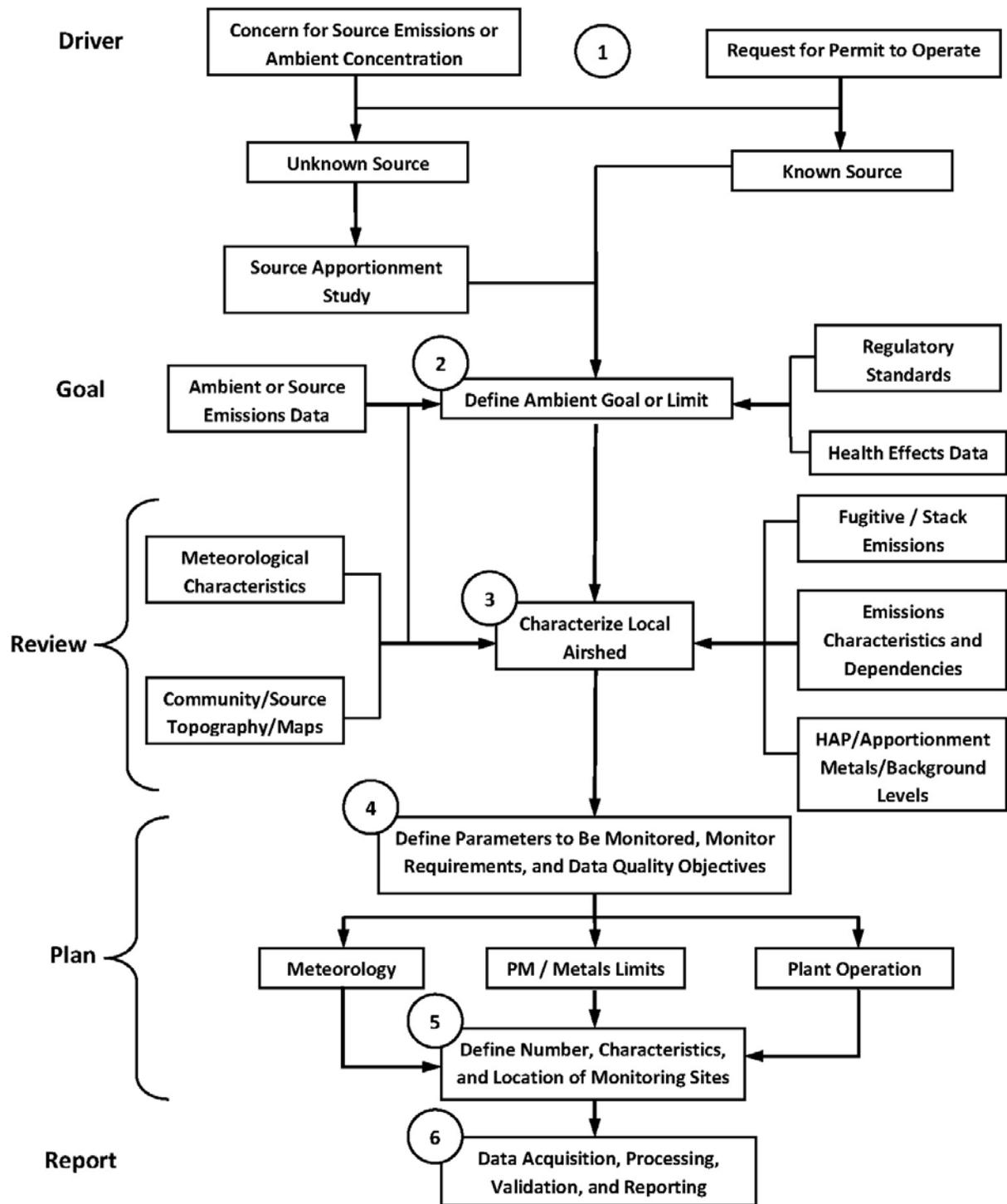


Figure 1. Procedure Flow Diagram

1.0 Driver – Arsenic and Lead from Fugitive Emissions

Hayden, Arizona, is a small rural town of about 900 people located 100 miles southeast of Phoenix and 50 miles southeast of Tucson. Less than one mile from Hayden is the town of Winkelman, population 444. The local economy is primarily driven by the ASARCO mine and the smelter located between the two towns. ASARCO Incorporated is a superfund copper mining operation that produces over 350 tons of copper a year from three local mines: Mission Mine, Silver Bell, and Ray Mine. Copper ore from ASARCO's mines arrives at the ASARCO smelter in Hayden to be refined and processed into high-grade commercial copper.

The ASARCO Smelter in Hayden consists of an inactive Kennecott smelter located to the north of Hayden, an active smelter located between Hayden and Winkelman, two tailings ponds south of Hayden, and a concentrator and crusher facility both located on the east side of Hayden. These facilities emit high levels of particulate matter (PM₁₀) and hazardous metals into the local airshed. The emissions of ASARCO have been measured since the closure of the Kennecott Plant in 1986. Fugitive emissions to the surrounding communities with elevated concentrations of arsenic, cadmium, and lead are of particular concern.

Previous studies and investigations focusing on the ASARCO smelter in Hayden have been performed by the Arizona Department of Environmental Quality (ADEQ) and the United States Environmental Protection Agency (U.S. EPA). A Source Apportionment Study in 1986 and 1987 characterized local pollutants and sources related to ASARCO operations. In a 1988 Preliminary Assessment (PA), the EPA determined that existence of hazardous substances at the site made the facility eligible for placement on the National Priorities List (NPL). Following the PA, a Site Inspection (SI) was recommended (ADEQ, 2003) and a source apportionment of suspended particles and toxic elements was conducted. In 2008, a Remedial Investigation at ASARCO examined impacts of environmental degradation and pollution within local groundwater, soil, air, and public health.

The results of these studies indicate that there is a significant risk in the Hayden and Winkelman communities of exposure to dangerous levels of arsenic, cadmium and lead due to fugitive emissions from smelter processes.

2.0 Goals: Characterizing the Source and Defining Ambient Goals and Compliance

Due to the ongoing exposure of Hayden and Winkelman residents to hazardous metals air pollutants at concentrations dangerous to human health, a Hazardous Ambient Metal Compliance Plan (Plan) to monitor local ambient air near the ASARCO smelter has been developed using the Procedure Flow Diagram. **(Figure 1)**

The goals of the continuous multi-metals ambient air monitoring program are to: 1) provide comprehensive, high quality ambient metals data within the local airshed to assess and protect public health, 2) identify and develop engineered controls to problematic fugitive emissions, and 3) to enforce compliance with applicable standards.

Continuous ambient metals monitoring is the appropriate air monitoring approach in the Hayden/Winkelman area for a number of reasons:

- 1) The primary receptors for air-borne hazardous metals particulate matter are the residents of Hayden and Winkelman, Arizona.
- 2) The majority of local air quality concerns is related to fugitive release of hazardous metals and therefore cannot be characterized through stack emissions monitoring.
- 3) Fugitive emissions are related to specific smelter operations. Human exposure is based on a confluence of meteorological conditions and temporal smelter processes. Near-real-time ambient metals monitoring characterizes short-term and long-term human exposures in order to assess health risks.

2.1.0 Primary Elements of Health/regulatory concern

Based on data collected during previous studies, the primary elements of concern are arsenic and lead. In the current range of emission values, both arsenic and lead have the potential to cause significant health impacts to the general population. Regulatory controls for ambient values of lead and arsenic include a National Ambient Air Quality Standard (NAAQS) for lead, EPA residential risk-based cancer screening value for arsenic, a California Residential Reference Exposure Level for arsenic, and a NIOSH 15 minute work-place ceiling value for arsenic. **(Table 1)**

Table 1. Lead and arsenic air quality standards and ASARCO/Hayden Investigation data summary

Element	Air Quality Standard	1986 Source Apportionment Avg.	2006-2008 Remedial Investigation Avg.	2006-2008 Remedial Investigation Hi
Lead (Pb)	NAAQS - 0.15 µg/m ³ /3month	0.2 µg/m ³	0.085 µg/m ³ /24hr	0.836 µg/m ³ /24hr
Arsenic (As)	Region IX RSL – 0.016 µg/m ³ California Acute REL 0.2 µg/m ³ /1 hr NIOSH 15 min. ceiling 2 µg/m ³	0.100 µg/m ³	0.024 µg/m ³ /24hr	0.189 µg/m ³ /24hr

Arsenic

In 1986-1987 NEA, Inc, performed a comprehensive source apportionment of suspended particles and toxic elements in Hayden, Arizona. The 24-hour average concentration of arsenic was found at 0.094 $\mu\text{g}/\text{m}^3$ at the Hayden Jail and 0.12 $\mu\text{g}/\text{m}^3$ at the Garfield sampling location. The highest recorded 24-hour average value for arsenic during the term of the study was recorded January 28, 1987, at 0.304 $\mu\text{g}/\text{m}^3$.

A Remedial Investigation (RI) was performed by CH2MHill in 2006-2008. During the RI, 24-hour PM_{10} samples were taken every six days over a two year period, during active and inactive smelter operations. For the period of the study, ambient arsenic concentrations at the Hayden sampling station averaged 0.004 $\mu\text{g}/\text{m}^3/24\text{hrs}$ during inactive smelter operations and as high as 0.024 $\mu\text{g}/\text{m}^3/24\text{hrs}$ during active smelter operations. However, concentrations of arsenic varied widely, with the highest value recorded September 11, 2007, at 0.189 $\mu\text{g}/\text{m}^3$, near the California Acute 1 hour Residential Reference Level of 0.2 $\mu\text{g}/\text{m}^3$, and an order of magnitude above EPA Region IX Residential Screening Level (RSL) for cancer set at 0.016 $\mu\text{g}/\text{m}^3$. At concentrations above the RSL, cancer risks increase in a given population. The RI found that 85% of all air samples had arsenic concentrations exceeding the defined arsenic ambient air Preliminary Remediation Goal (PRG) of 0.00045 $\mu\text{g}/\text{m}^3/24$ hours.

Short-term arsenic concentrations over a 4-hour or 1-hour sampling interval have not been characterized by historic studies. However, it is highly likely that short-term ambient arsenic spikes in the Hayden area surpass the California Acute Residential Reference Level and may approach the NIOSH 15-minute ceiling limit set at 2 $\mu\text{g}/\text{m}^3$.

Lead

The other major element of concern at ASARCO is lead. Health effects from lead are well-documented, and recent studies have determined that no blood level of lead is safe for humans. The EPA has established a NAAQS for lead at 0.15 $\mu\text{g}/\text{m}^3$, per 3 month rolling average. During the 1986 Source Apportionment Study, 24-hour lead averages exceeded the current NAAQS. During the Remedial Investigation, lead concentration averaged 0.016 $\mu\text{g}/\text{m}^3/24\text{hrs}$ during inactive smelter operations and 0.085 $\mu\text{g}/\text{m}^3/24\text{hrs}$ during active smelter operations at the Hayden sampling location. However, the highest lead concentration, based on samples collected in Hayden on September 11, 2007, was 0.836 $\mu\text{g}/\text{m}^3/24\text{hr}$, nearly six times the three month-rolling average of NAAQS and an order of magnitude larger than the Hayden daily lead averages.

Examining the Remedial Investigation's hazardous ambient pollutant data, arsenic and lead follow similar concentration patterns. The order of magnitude degree of variation between 24-hour average values and maximum recorded concentrations supports the importance of continuous multi-metals monitoring to protect human health near high-risk areas like the ASARCO smelter.

2.1.1 Secondary Elements of Concern

Cadmium, chromium, and copper are emitted from the ASARCO smelter and also pose a potential health risk. At certain concentrations exposure to these metals is dangerous to human health and the environment. Data from ASARCO indicates that cadmium, chromium, and copper are generally found in concentrations well below their respective health limits, however there still is potential for acute concentrations that reach or exceed limits. Regulatory controls and limits include California screening levels for acute copper exposure, EPA Region IX residential risk-based cancer screening values for cadmium and chromium, and Agency for Toxic Substance and Disease Registry (ATSDR) acute and chronic values for cadmium.

2.1.2 Source Apportionment Elements

A comprehensive Source Apportionment using chemical mass balance receptor modeling was conducted at the ASARCO site and nearby communities by NEA, Inc., in 1986. Silicon was the most abundant element detected in the study in both the coarse and fine size fraction, at about 20% of the mass. Calcium, iron, and aluminum were the next most abundant elements in the coarse fraction, and sulfur and aluminum were the second and third most abundant elements found in the fine fraction. Concentration of hazardous air pollutants arsenic, cadmium, and lead were also detected. Average PM₁₀ arsenic concentration was measured at 0.100 µg/m³, average cadmium concentration was 0.005 µg/m³, and average lead concentration was 0.2 µg/m³.

Sources for the various hazardous and non-hazardous particulate matter were determined. The main contributors to PM₁₀ mass were ore dust and road dust, which accounted for nearly 80% of the mass at both monitoring sites. However, ore and road dust contributed less than 10% of the PM₁₀ lead and less than 6% of the PM₁₀ arsenic. The large majority of hazardous metals air pollutant sources were from fugitive emissions associated with slag skimming and pouring, matte tapping and secondary converter operations

Source profile data is available from the study which will be utilized to determine fugitive emission sources and enforce corrective action. As data emerges from ambient metals monitors, it will be compared to source profile chemical fingerprint data to determine the fugitive source of metals emissions. **(Table 2)**

2.2 Regulatory Standards

Ambient air quality standards are limited in scope, and lead is currently the only metal covered by national NAAQS at 0.15 µg/m³ over a 3 month rolling average period. During the 1986 source apportionment the average lead value exceeded the current lead NAAQS, and during the more recent Remedial Investigation lead values often exceeded the national ambient air quality standard.

Region 9 EPA has promulgated Regional Screening Levels (RSL) for arsenic, cadmium and chromium. Concentrations above RSLs indicate increasing cancer risks in a general population.

The RSL is 0.016 µg/m³ for arsenic, 0.01 µg/m³ for cadmium, and 0.01 µg/m³ for chromium. The California residential acute standard for arsenic is set at 0.2 µg/m³, and for this example will be utilized as the Action Level for arsenic near Hayden. **(Table 3)**

Comprehensive ambient metals standards and continuous monitoring can protect residences near the Hayden ASARCO smelter from adverse health effects. The continuous ambient multi-metals monitoring plan will provide the monitoring capability to record continuous ambient metals data and work to fully characterize and limit the amount of pollutants being emitted by ASARCO into the neighboring communities.

**Table 2. Source composition Profiles for Representative Key Sources and Species
Fine Fraction (< 2.5 µm), Percent**

Element	Kennecott Road Dust	Plant Road Dust	Ore Crusher Dust	Slag Skim	Matte Tap	Scndry Cnvrtr Duct
K	0.79	0.70	3.06	0.40	0.33	0.20
Ca	12.95	1.84	1.40	0.00	0.00	0.00
Ti	0.25	0.14	0.61	0.00	0.00	0.00
Mn	0.09	0.05	0.08	0.02	0.01	0.00
Fe	3.10	9.88	4.97	0.96	2.69	0.04
Ni	0.01	0.08	0.01	0.00	0.00	0.05
Cu	0.74	14.58	0.07	0.20	3.35	0.57
Zn	0.02	1.52	0.03	25.42	9.77	6.93
As	0.00	0.54	0.01	16.50	32.78	7.65
Br	0.00	0.04	0.00	0.00	0.00	0.00
Cd	0.00	0.08	0.00	2.19	1.68	0.87
Sb	0.00	0.00	0.00	1.39	1.99	1.15
Pb	0.04	3.1	0.01	21.16	12.46	25.49

Table 3. Primary and Secondary Elements of Concern Standards and Limits: Cr, Cd, and Cu (Not-To-Be-Exceeded Levels in *bold italics*)

Element	NAAQS ($\mu\text{g}/\text{m}^3$)	California ($\mu\text{g}/\text{m}^3$)	Region IX EPA ($\mu\text{g}/\text{m}^3$)	ATSDR
As	n/a	<i>Acute - 0.2/1 hr</i> Chronic – 0.015	Non cancer Hi -0.016	n/a
Pb	<i>0.15 rolling 3 month avg.</i>	n/a	n/a	n/a
Cr	n/a	Chronic – 0.2	<i>Non cancer Hi - 0.01</i>	n/a
Cd	n/a	n/a	<i>Non cancer Hi – 0.01</i>	Acute – 0.03 Chronic – 0.01
Cu	n/a	<i>Acute – 100/1 hr</i>	n/a	n/a

2.3 Health Effects Data: Risks from Hazardous Ambient Metals Exposure Air Monitoring Sampling Frequency

Recent evaluation of monitoring data and meteorological conditions, along with basic mathematical modeling, suggests arsenic and lead concentrations over 24-hour averages may be significantly lower than 12-hour averages, 4-hour averages or discrete 15-minute averages. Due to the nature of fugitive emissions, which are tied to specific plant processes, the majority of an arsenic or lead release might occur over a very brief period of time. Dynamic wind conditions also result in varying concentrations recorded in an ambient metals air sampler. During a 2009 ambient air metals sampling event near a hazardous waste incinerator in East St. Louis, Missouri, arsenic was detected over a 12-hour period in a range from 0.65 ng/m³/2hr to 2345 ng/m³/2hr. The range of concentrations is hypothesized to be related to the highly dynamic wind conditions in the area. Considering the range of values, the 12-hour averaged concentration at the monitor is around 362 ng/m³. In fact the 12-hour average and the 2-hour average are different by a factor of about 6.5. (**Table 4**)

Table 4. Recorded As concentration averages in East St. Louis, IL, 4/13/2009, demonstrating time averages and metals concentration

	As 12 hr Avg	Time/Conc Factor	As 2 hr Avg.
East St. Louis, IL 4/13/2009	0.362 $\mu\text{g}/\text{m}^3$	6/6.5	2.34 $\mu\text{g}/\text{m}^3$

While no specific data comparing 24-hour averages or 12-hour averages to 15-minute averages exists at Hayden, there are justifiable concerns that 24-hour averaged arsenic and lead concentration data provided in the historic reports does not fully characterize or quantify hazardous air pollutants and risks to human health and the environment that occur over a shorter period.

Using the data from East St. Louis as a general reference, and extrapolating the numerical relationships between 24-hour averages and 2-hour averages, arsenic concentrations of 0.3 $\mu\text{g}/\text{m}^3$ measured at Hayden during the 1986 source apportionment study could result in 15-minute averages in the range of 7.5 $\mu\text{g}/\text{m}^3$. Lead concentrations of 0.836 $\mu\text{g}/\text{m}^3/24$ hour from the Remedial Investigation may have 15-minute averages as high as 20.9 $\mu\text{g}/\text{m}^3$. While this is just a rough estimation and needs more data to verify, concerns that long-term averages do not represent real-time ambient metals concentrations in fugitive air emissions are substantiated by the available concentration data, general knowledge of plant operations and fugitive emissions sources, as well as a consideration of the basic meteorological data.

Not To Be Exceeded Limits for Arsenic and Lead

Arsenic and lead have well-documented toxic and carcinogenic health effects on humans. It is reasonable to assume that the population of Hayden and Winkelman may have frequently been exposed to 15-minute arsenic concentrations that approach or surpass the National Institute for Occupational Safety and Health (NIOSH) standard for acute adult exposure in the workplace set at 2 $\mu\text{g}/\text{m}^3$. This example proposes an ASARCO Hazardous Ambient Metal Compliance Plan with Not To Be Exceeded Levels and Action Levels for short-term fugitive arsenic and lead emissions that are designed to assess risks to local human health and prompt corrective action. The California acute Reference Exposure Limit for arsenic is 200 $\text{ng}/\text{m}^3/1$ hour sampling average, which will be utilized as the Not to Be Exceeded (NTBE) value for the Arsenic Compliance Plan at Hayden, AZ. See **Table 3** for other Compliance Plan Levels.

2.4 Action Levels and Demonstrating Compliance

There is currently no data that characterizes short term 15-minute to 1-hour arsenic and lead concentrations near Hayden and Winkelman. This hypothetical near-real-time ambient multi-metals monitoring plan is designed to assess short and long-term metals exposures to the local population. An effective plan should have Action Level set below the NTBE level. This

concentration represents a value at which the plant will gather data and develop an effective corrective action approach. For this example, the NTBE level is set at 200 ng/m³/1 hour. An appropriate Action Level will therefore be 80 ng/m³/1 hour. If data emerging from the ambient monitors results in ambient metals concentrations that exceed the Action Level, the facility would take immediate action to identify sources and develop controls. If concentrations continue to increase and exceed NTBE levels, corrective action would proceed including a temporary shut-down of operations until an effective mitigation is implemented.

Since the majority of elevated arsenic and lead concentrations found in Hayden’s residential areas are due to fugitive emissions, ASARCO should develop a feasibility study and remedial plan to address fugitive metals emissions at the facility using the source profiles from the 1986 NEA study. **(Table 2)** Compliance at the ASARCO plant will be based on yearly progress to meet the 10-year Plan goals to lower short-term arsenic and lead levels to acceptable levels. **(Figure 2 and 3)** As a long-term goal, the plant will strive to reach concentrations 10 times the background, determined by the average annual values recorded at the background monitoring site. The multi-metals continuous ambient air monitoring devices will provide comprehensive data to monitor the threats that fugitive metals pose to human health and the environment of Hayden, and also detail the success and progress with the facility’s remedial plan.

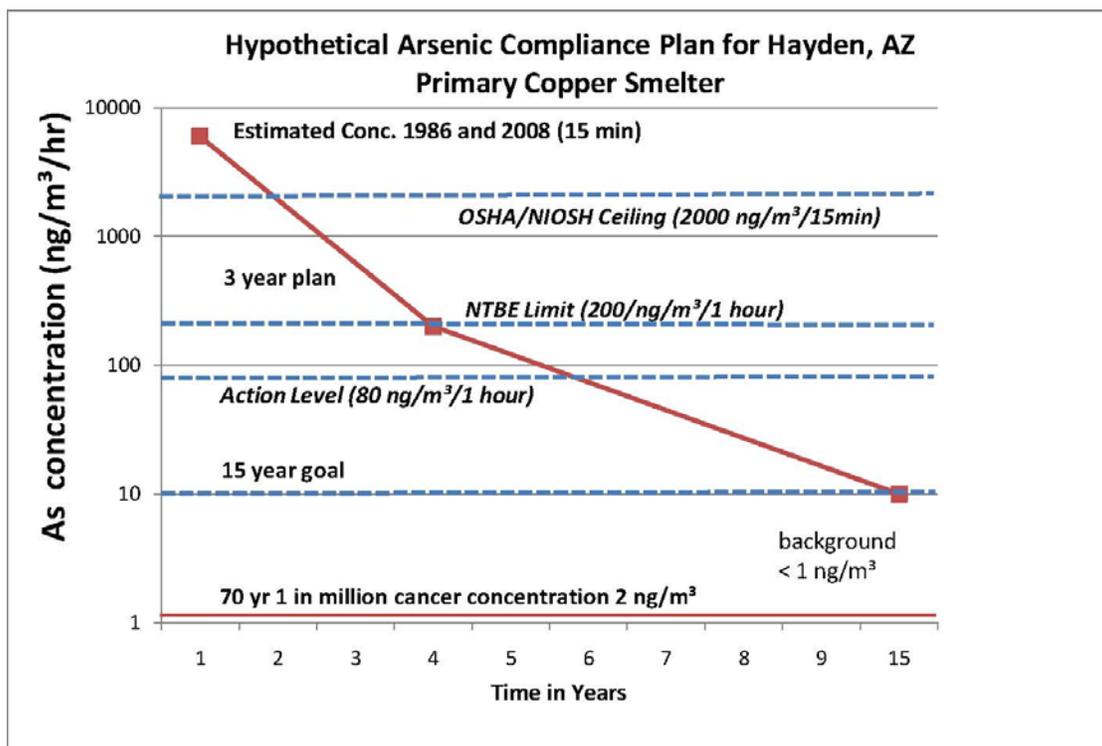


Figure 2. Potential Hazardous Ambient Metal Compliance Plan for Residential Arsenic at Hayden, AZ

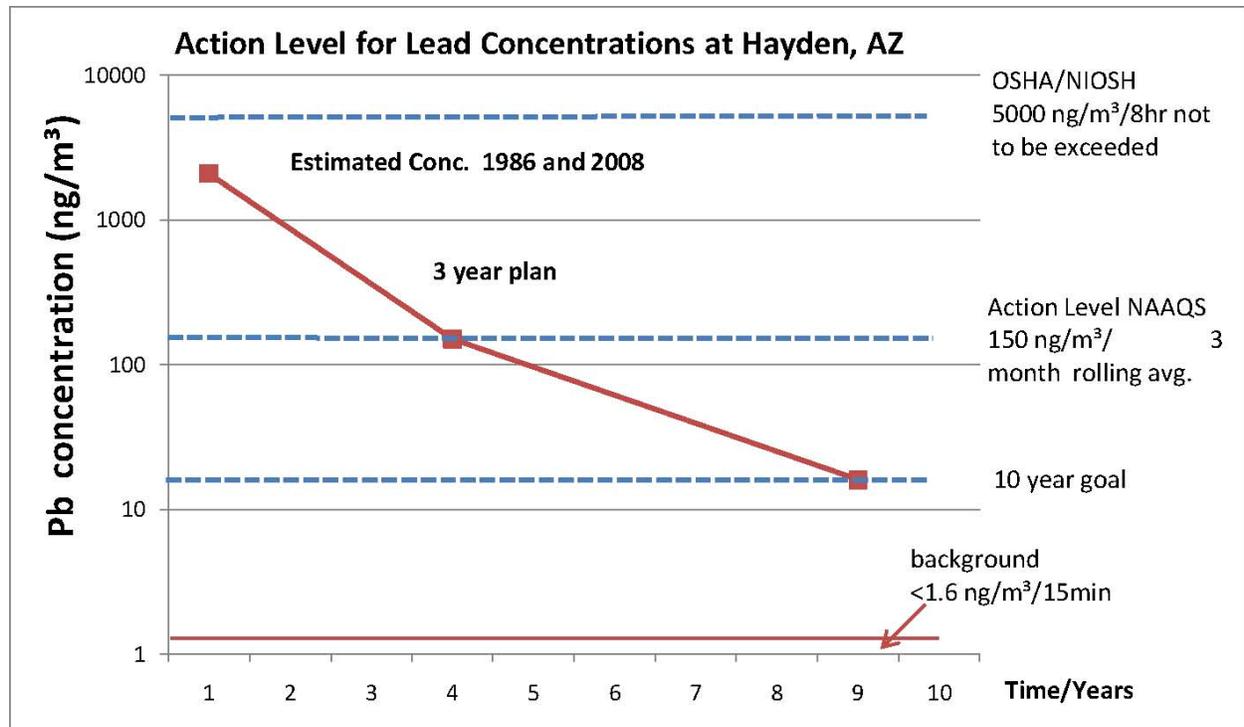


Figure 3. Potential Hazardous Ambient Metal Compliance Plan for Residential Lead at Hayden, AZ

3.0 Local Airshed Characteristics

3.1 Physical Features

The ASARCO smelter and the neighboring towns of Hayden and Winkelman, Arizona, are located in south central Arizona in Gila and Pinal County. The Dripping Spring Mountains, near the confluence of the Gila and San Pedro Rivers, lie to the northwest of Hayden. The Tortilla Mountains, which form the western border of the Gila River Valley, are located several miles to the west of Hayden. Relief is moderately gentle on the west side of the study area, transitioning to moderately steep slopes further west in the Tortilla Mountains. Elevation ranges from 3,947 feet above mean sea level (msl) at Horse Hills in the Tortilla Mountains to approximately 1,900 feet msl along the Gila River in the northwestern corner of the site. The highest point in the area is Tornado Peak (located approximately three miles north of Hayden) at 4,484 feet msl.

The town of Winkelman is located southeast of Hayden and is bounded to the north by the ASARCO active smelter operations and to the south and east by the Gila River. The Winkelman School Complex is located approximately 1,300 feet directly south from the slag dump and oxygen plant areas of the active ASARCO smelter. The topography of Winkelman is relatively flat, with a gradual decrease in elevation toward the Gila River flood plain. The southernmost part of Winkelman is located within the flood plain of the Gila River.

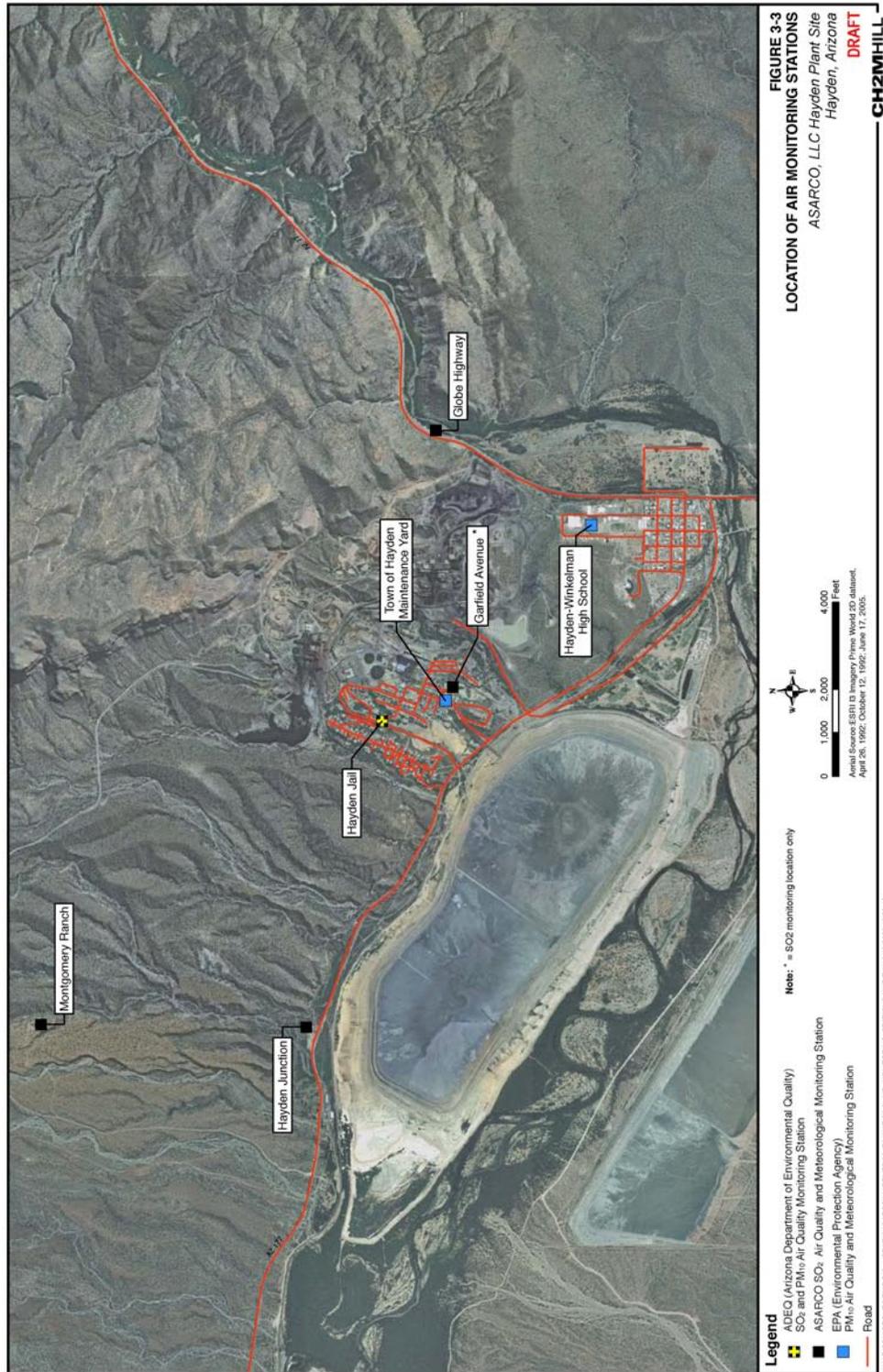


Figure 4. Local Airshed Map
 Cooper Environmental Services

3.2 Meteorological Characteristics

Hayden and Winkelman are located in the Sonoran Desert, one of the largest and hottest deserts in North America, and characterized by low precipitation and extreme temperatures. The south central Arizona landscape has no large bodies of water, but is interspersed with several mountainous zones. There is relatively consistent and predictable meteorology for the Hayden/Winkelman area. Wind data taken by the meteorological stations in Hayden (Montgomery Ranch, Hayden Junction, and Globe Highway) show wind patterns that contour to the flow of the Gila River. In Hayden, the wind flows primarily east-to-west, while in Winkelman, wind flows northeast-to-southwest. **(Figure 5)** Temperatures vary from low 50's in winter to high 80's in summer, and temperatures can change over 20°F between day and night. Hayden has an annual average precipitation of 13.9 inches, which occurs primarily during winter, summer and fall.

3.3 Source Characteristics

ASARCO operations including the crusher, concentrator, smelter, and tailings impoundments, surround the Hayden community on the northern, southern, and eastern edges of town. Residential areas are located on the west and southeast edge of town. Public areas, including a library, playground, and swimming pool area are located adjacent to and west of ASARCO's concentrator facilities

Based on past studies by ADEQ and EPA, the chemicals of concern near the ASARCO plant are particulate matter and hazardous air pollutants such as arsenic, cadmium, copper, and lead. The sources responsible for toxic elements are fugitive emission processes which include slag skimming, matte tapping, converter operations, and slag pouring. (NEA, 1987) PM size is generally less than 10 µg. **(Table 3) (Figure 6)**

4.0 Monitoring Plan

4.1 Parameters to Monitor

4.1.1 Meteorology

Real time, comprehensive meteorological data will be gathered in conjunction with the metals data to fully characterize source emissions and assess risks to the local population. In the Hayden area, there are three ASARCO meteorological monitors and two EPA meteorological stations. The three ASARCO stations are located at Montgomery Ranch, Hayden Junction, and Globe Highway. Montgomery Ranch is positioned one mile to the Northwest of Hayden, Hayden junction is one mile to the west of Hayden and Globe Junction lies on the Gila River half a mile to the Northeast. **(Local Airshed Map Figure 4)** The EPA monitoring stations lie in the Hayden Maintenance yard on Garfield Ave. and on top of the Winkelman High school. All of the stations record precipitation, wind speed/direction, relative humidity and temperature and could provide concurrent meteorological data of the Hayden/Winkelman airshed to accompany data recorded by the multi-metals ambient air monitors.

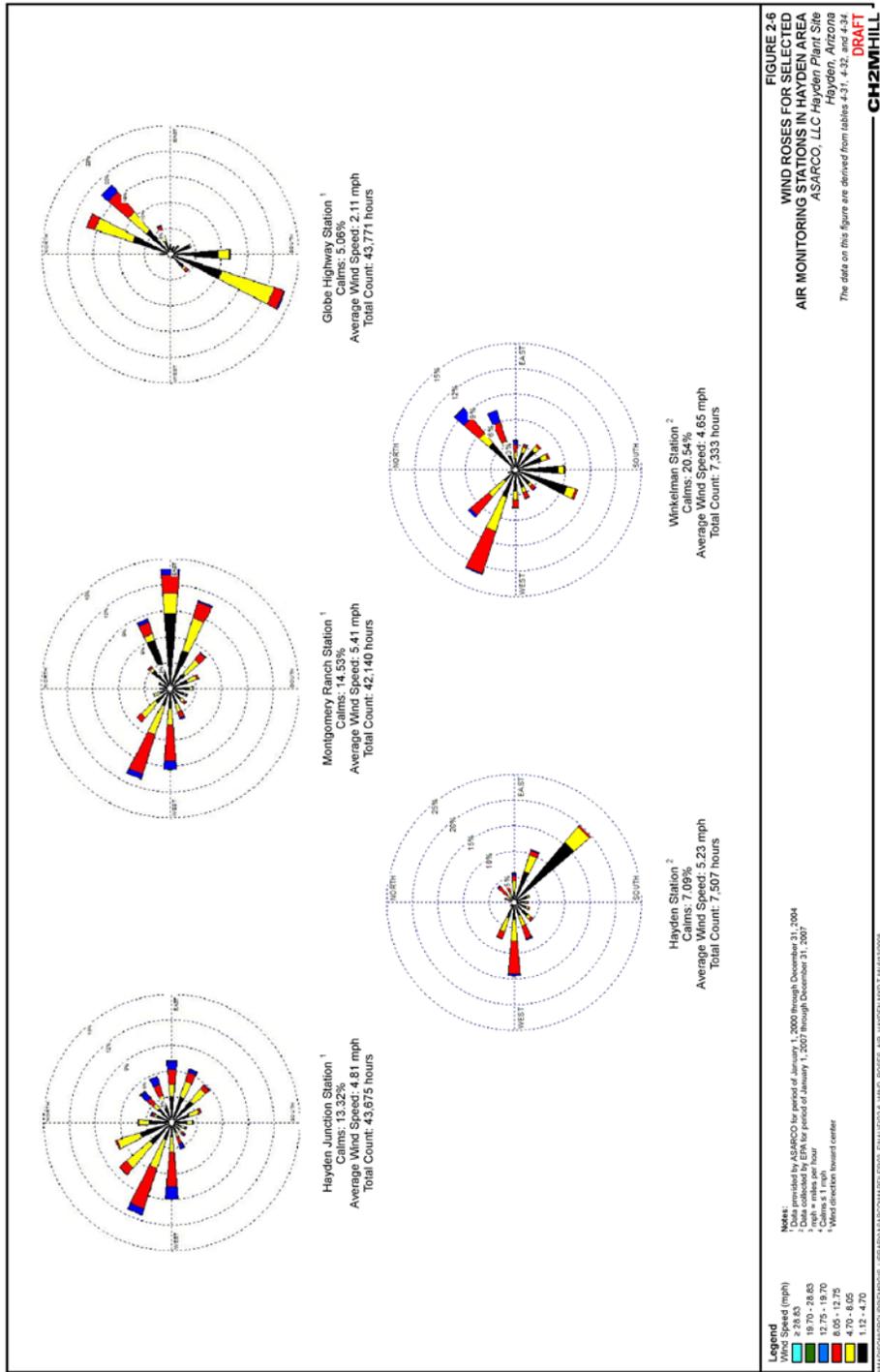


Figure 5. Wind Rose Data, Hayden/Wickelman Airshed

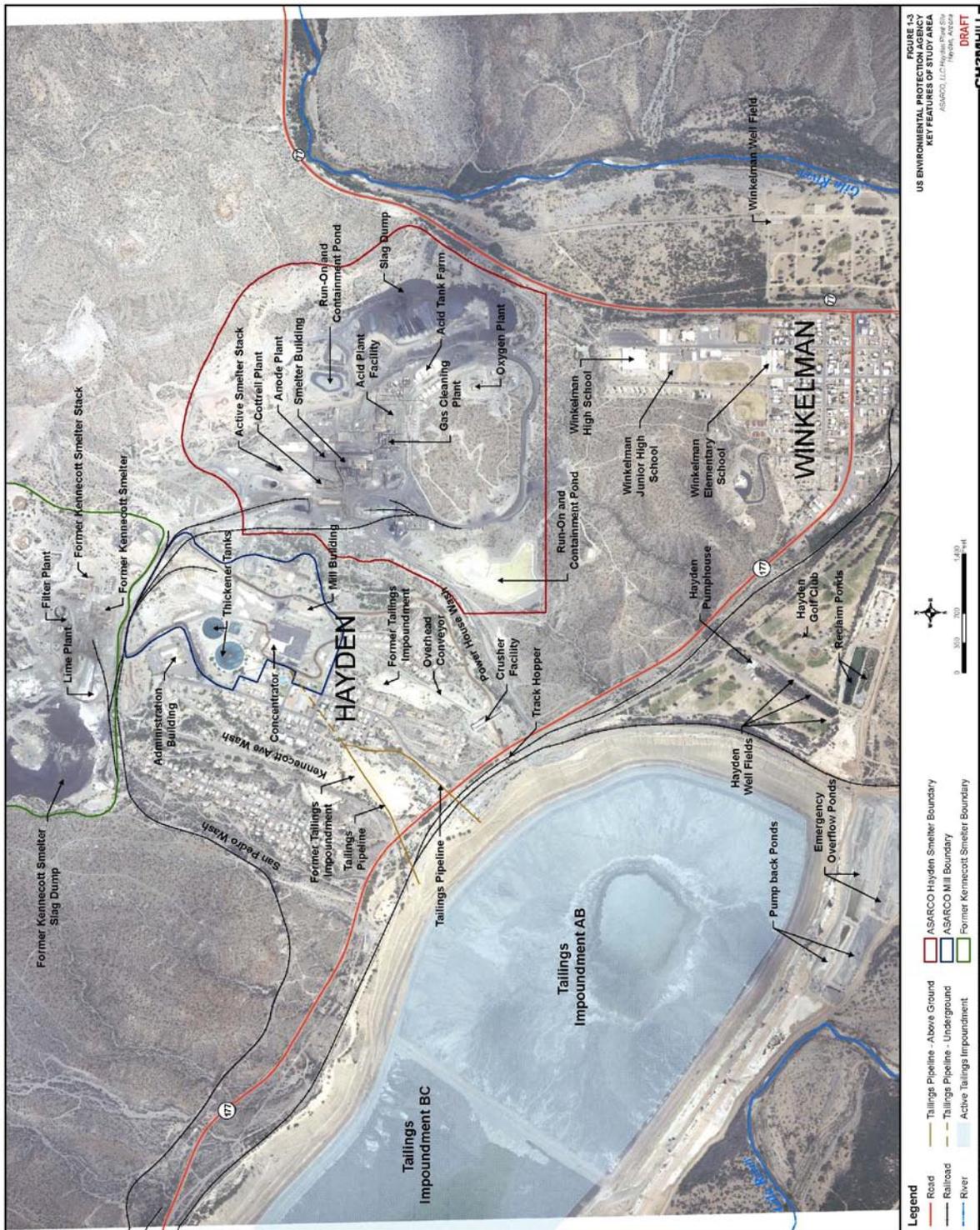


Figure 6. Hayden/Winkelman Detail

4.1.2 Elements and PM

Elements to be monitored in this hypothetical plan are primarily hazardous metals that pose health risks to individuals. These metals are **arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), and copper (Cu)**. These metals are known to be emitted from ASARCO operations in potentially dangerous amounts from the stack and fugitive emissions. Monitoring for these metals will require a PM_{2.5} inlet. Historic data shows that 85% of arsenic is in the PM_{2.5} fraction. The smaller particle size is associated with high heat fugitive smelter emissions. A smaller particle size will improve the source apportionment study by eliminating coarse particle interference.

Accompanying metals detected by the continuous multi-metals ambient air sampling device include calcium (Ca), scandium (Sc), titanium (Ti), vanadium (V), iron (Fe), cobalt (Co), nickel (Ni), bromine (Br), tin (Sn), and antimony (Sb).

4.1.3 Plant Processes and Events

Plant processes along with hazardous ambient metals and meteorology will be monitored to provide a comprehensive set of information to characterize and reduce fugitive emissions. The operations of ASARCO are primarily associated with copper smelting. The copper concentrates ignite, melt, and partition to produce matte (approximately 55% copper) and slag. During this process, sulfur from the ore is oxidized to form SO₂ gas. The matte from the flash furnace is subsequently processed in converter furnaces to remove additional impurities (arsenic/lead) and produce blister copper (approximately 98.5% copper). The blister copper is further processed in anode furnaces to produce copper anodes that are 99% pure. The anodes are shipped offsite for final processing (ADEQ, 2003). The melting and refining of the copper ore results in the majority of fugitive metal emissions at the facility.

The smelter facility includes several waste management activities. The active smelter building is approximately 110 feet tall, and a portion of the air emissions are released to the atmosphere through a 1,000-foot-tall stack. During the smelting process, sulfur from the ore is oxidized to form SO₂ gas, which is converted to sulfuric acid in the sulfuric acid plant. Slag from the smelter operations is transferred to open waste stockpiles located immediately southeast of the smelter operations area where arsenic, lead, cadmium, and chromium are released. Treated wastewater and other process waters are discharged to containment pond CP-1, located east of the smelter. Decant water from the tailings impoundment is discharged to retention ponds located east of Tailings Impoundment AB/BC, where it is reclaimed into the process operations (ADEQ, 2003).

4.2 Monitoring Sites

4.2.1 Primary Monitoring Sites

Considering the size of both Hayden and Winkelman and the meteorological regime of the area, only two multi-metals ambient air monitors are required to measure the toxic metals in the air. With the focus of the study being the relation of toxic metals to inhabitants and high priority victims, these monitors should be located in the residential areas. For this application, two NRT multi-metals ambient air monitors will be obtained for the ambient concentration samples. The first monitor (**FLM #1**) will be placed on the rooftop of the Hayden Jail. The monitor will be protected from weather conditions with a shelter and rain guard. A $PM_{2.5}$ inlet protruding from the shelter will funnel particulate to the sampler. Electrical lines and data acquisition cables will run from the shelter to the nearest phone/internet connection. The second monitor (**FLM #2**) will be placed at the Winkelman High School, in the corner of a field. The shelter will be positioned at least ten meters from any obstruction or drip line and provide ample spacing for the $PM_{2.5}$ inlet. Data and electricity lines will run from the nearby school. (**Figure 7**)



Figure 7. Multi-metals ambient air sampling locations

4.3 Monitoring Protocol

Multi-metals ambient air continuous sampling devices can be programmed to sample at a range of intervals from high resolution data such as sampling every fifteen minutes, to lower resolution data like a four-hour sampling period. Higher data resolution provides more information to regulators to assess and protect worker and public health, and to further characterize local air quality and industrial operations on emissions. In order to ensure that hazardous ambient

metals concentrations near the ASARCO smelter will be fully characterized and the risks to human health adequately assessed, the NRT multi-metals ambient air sampling devices will initially be programmed to sample every 30 minutes. After three months of ambient air sampling, data can be analyzed to determine if a decrease in sampling frequency would maximize project cost efficiency while maintaining data quality standards.

Data will be available within two hours of the sampling event, streamed via wireless or cabled connection, and stored on the on-board computer system. Sampling tape will be changed out periodically as necessary by trained technicians. Samples will be collected, labeled with location, time interval and sampler identification information, and stored and preserved.

4.4 Data Processing and Reporting

4.4.1 Quality Assurance

Multi-metals ambient air sampling devices are initially calibrated by the manufacturer using thin film standards which are inserted into the monitor and analyzed to provide a control metals concentration from which calibrations can be based. Periodic audits of the monitors are conducted using a Quantitative Reference Aerosol Generator (QAG) to test the machines X-ray Fluorescence and sample analysis components. The QAG is an effective quality assurance tool and can be utilized to ensure accurate data is provided by the device. The QAG disperses a control metals aerosol sample to the device, which is then compared against the recorded value analyzed by the monitor. The QAG individually tests a wide range of metal concentrations against the monitoring unit, and the accuracy is determined by testing the relative bias of the monitor. The multi-metals ambient air sampling devices will be audited and serviced by trained technicians consistent with the device manufacturer's recommendations (See Appendix B).

4.4.2 Regulators

When data has passed all QA/QC procedures, regulators will examine the concentration levels to determine if an exceedence dangerous to human health and the environment has occurred, as well as to gauge how ASARCO is progressing in the Hazardous Ambient Metal Compliance Plan goals. Regulators will utilize historical meteorological data such as wind speed, wind directions, humidity and time of day as well as ASARCO plant records to determine the nature and extent of the hazardous metals release and assess risks to the general public. If concentrations exceed Action Levels, source identification using historic source profiles would proceed and a fugitive emissions Corrective Action Plan would be developed by ASARCO. Regulators would summarize their results in a quarterly report and confer with ASARCO to determine how to mitigate their fugitive emissions.

4.4.3 Plant

ASARCO will work in good faith with the regulators to protect local residents' health and the environment. All multi-metals ambient air data will be shared between regulators and ASARCO, and the two entities will work together to achieve the long-term Hazardous Ambient Metal Compliance Plan goals. If ambient metals concentrations exceed Action Levels, ASARCO would develop and implement a Corrective Action Plan to limit fugitive emissions in order to achieve the long-term Plan goals. An Annual Hazardous Ambient Metal Compliance Plan Report will be submitted by ASARCO to regulators to document the Plan progress.

4.4.4 Internet and Public

All data gathered at the ASARCO plant by NRT multi-metals ambient air monitors, as well as all documents and reports associated with ASARCO's Hazardous Ambient Metals Compliance Plan will be public record and will be made available by state and local authorities. The near-real-time hazardous ambient metals data gathered by the project will be made available on the internet to the citizens of Hayden and Winkelman, AZ. All data will be public domain and can be used by organizations and individuals to study effects of ASARCO metals emissions on local or regional air quality.

In the event a multi-metals ambient air monitoring Action Level is exceeded, regulators would notify sensitive receptors such as schools and hospitals. Recommendations would be given for those at elevated risk like children and pregnant women to remain indoors until the issue is addressed or the concentrations dissipate. A full report of the incident would be written and forwarded to ASARCO and state, local and federal authorities.

5.0 References

- 1) NEA, Inc. *Source Apportionment of Suspended Particles and Toxic Elements in Hayden, Arizona*. Rep. Beaverton, OR: 1987. Print.
- 2) Hillenbrand, John. *Preliminary Evaluation of PM10 and Metals Concentrations from October 2007 to December 2008 in Ambient Air at the Hayden and Winkelman Monitoring Stations*. Tech. no. 381679. CH2MHill, 2008. Print.
- 3) U.S.EPA (1987) *PM10 State Implementation Plan Development Guideline*. Report No. EPA 450/2-86-001, U.S. Environmental Protection Agency, Research Triangle Park, NC.
- 4) U.S. EPA (1984) *Optimum Sampling Site Exposure Criteria For Lead*. Report No. EPA 450/4-84-012, U.S. Environmental Protection Agency, Research Triangle Park, NC.
- 5) U.S. EPA (1982) *Basic Air Pollution Meteorology*. Report No. EPA 450/2-82-009, U.S. Environmental Protection Agency, Research Triangle Park, NC.