Washington University in St. Louis
SCHOOL OF LAW

Civil Justice Clinic
Interdisciplinary Environmental Clinic

April 1, 2013

George Czerniak
Director, Air and Radiation Division
EPA Region 5
77 West Jackson Boulevard, 18th Floor
Chicago, IL 60604

Re: Comments on Draft Significant Modification to Title V Permit No. V-IL-1716300103-08-01
Veolia ES Technical Solutions, L.L.C.

Dear Director Czerniak:

On behalf of the American Bottom Conservancy (ABC), the Interdisciplinary Environmental Clinic at Washington University School of Law submits the following comments on the Draft Significant Modification to Title V Permit No. V-IL-1716300103-08-01 (Draft Permit) for Veolia ES Technical Solutions, L.L.C. (Veolia), owner and operator of a hazardous waste incineration facility in Sauget, St. Clair County, Illinois, pursuant to 40 C.F.R. § 71.11(e). ABC is a grassroots organization based in the Metro-East St. Louis region, with members residing and recreating in the communities surrounding Sauget, including St. Louis, Missouri and Cahokia and East St. Louis, Illinois. ABC's primary goal is to protect community members from air, water, and land pollution. This proves challenging in St. Clair County, which the Illinois EPA reports has relatively high levels of VOC, NO_x, NH_3 and $PM_{2.5}$ emissions, relatively high total population and population density, and a large percentage of urban land cover.[1] St. Clair County is also listed as an air pollution nonattainment region for fine particulate matter ($PM_{2.5}$)[2] and ground-level ozone.[3] In addition, Sauget is the location of two U.S. EPA Superfund sites, Sauget Area 1 and Sauget Area 2, and the Illinois Department of Public Health has documented elevated lead levels (above 400 ppm) in soil samples from a study area in East St. Louis.[4]

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[1] Illinois Environmental Protection Agency, *Technical Support Document for the Recommended Nonattainment Boundaries in Illinois for the 24-Hour PM2.5 National Ambient Air Quality Standard*, (Dec. 18, 2007), at 28, *available at* http://www.epa.state.il.us/public-notices/2007/pm25-standards/recommendations.pdf.
[2] USEPA Green Book, *Currently Designated Nonattainment Areas for All Criteria Pollutants*, (Dec. 14, 2012), *available at* http://www.epa.gov/oaqps001/greenbk/ancl.html#ILLINOIS.
[3] *Id.*
[4] *Preliminary Assessment of Uncontrolled Lead Releases in the Mississippi River Gateway Initiative Area.* IDPH Division of Environmental Health Toxicology Section, Sept. 27, 2002.

INTRODUCTION

The Veolia hazardous waste incineration facility is located in the greater St. Louis area, home to more than 2 million people. Many of the residents of this area, particularly those in the Metro-East region of Illinois, are exposed to emissions of hazardous air pollutants from Veolia and other industrial facilities in the same airshed, including terminals, municipal/ chemical wastewater treatment plants, and copper tubing and chemical and ethanol production facilities. According to Cooper Environmental Services' report titled *A Guide for Developing a Multi-Metals, Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors* (Cooper Report), "The EPAs Toxic Release Inventory lists over 1,099,641 lbs of total hazardous, on- or off-site disposal or other releases in this area."[5] This large concentration of industry gives rise to concerns over cumulative air quality impacts and, given the area's demographics, environmental justice concerns. Most of the residents who live within three miles of Veolia are low-income - a third live below the poverty line - and are predominantly African-American.[6] Disturbingly, several Cahokia and East St. Louis preschools and elementary schools, including the Jerome Early Childhood Center, Dunbar Elementary School and Maplewood Elementary School, are located within Veolia's airshed as well.[7] Because of the potential adverse public health impacts from exposure to the cumulative air emissions from Veolia and other industries in its airshed, it is very important for these facilities to strictly adhere to federal emissions limits for hazardous air pollutants and for state and federal regulators to consider cumulative emissions when issuing them air operating permits.

Veolia's air emissions contain toxic substances that can have significant health impacts on the community. The specific pollutants at issue in the Draft Permit are mercury and low- and semi-volatile metals, including arsenic, beryllium, cadmium, chromium, and lead. Although the Statement of Basis describes many of the adverse health effects resulting from exposure to these toxins, ABC wishes to elaborate on them by highlighting some communities that have already been affected by exposure to these dangerous substances.

- Short-term inhalation exposure to arsenic can lead to nausea, diarrhea, abdominal pain and nervous system disorders. Long-term inhalation exposure can cause irritation of the skin and mucous membranes, peripheral neuropathy and hyperpigmentation and lung cancer. A well-known example of the human health effects of long-term exposure to arsenic can be seen in Bangladesh. Bangladesh has experienced many deaths and diseases due to arsenic poisoning as a result of naturally occurring high levels of arsenic in its groundwater. A study conducted by Dr. Habibul Ahsan from the University of

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[5] John A. Cooper et al., *Guide for Developing a Multi-metals, Fence-line Monitoring Plan for Fugitive Emissions Using X-ray Based Monitors*, at H17-8 (2010).
[6] USEPA, *Statement of Basis,* at 27, *available at www.regulations.gov, Docket ID: EPA-R05-OAR-2012-0649-0002*
[7] Cooper Report at H13 (2010).

Chicago reported that almost half of the entire population of Bangladesh - around 77 million people - has been exposed to toxic amounts of arsenic. A follow-up study tracking 12,000 Bangladeshis over the course of 10 years found that 20% of all participant deaths were caused by arsenic.[8]

- Exposure to cadmium can lead to tubular dysfunction which can lead to chronic kidney disease. One significant instance of cadmium poisoning occurred in Toyama Prefecture, Japan. In this case, mass cadmium poisoning led to Itai-Itai disease, which is grouped among the four big pollution diseases of Japan.[9] This disease was known for its softening of the bones and kidney failure. The cadmium pollution was caused by mining companies releasing cadmium into rivers in the mountains. By 1955, over 200 patients had been diagnosed with Itai-Itai disease, 50% of whom later died.[10]

- Exposure to lead can cause declines in neurocognitive function and adversely affect kidney function and the immune, reproductive and cardiovascular systems. For infants and young children, low levels of lead can contribute to behavior problems, learning deficits and lowered IQ. In 2011, Mengxi Village in China experienced a case of massive lead poisoning, where residents experienced just these symptoms. A *New York Times* article on the incident reported 332 cases of lead poisoning, 99 of them occurring in children. The culprit: Zhejiang Haijiu battery factory, a producer of lead-acid batteries for motorcycles and electric bikes, which generated a significant amount of lead pollution.[11] Concerns over lead poisoning from automobile tailpipes was also behind the decision by 100 countries to reduce and remove the lead content from gasoline, which resulted in massive decreases in population blood lead levels.[12]

- Mercury can cause tremor, erethism, and renal proteinuria. It can affect the human nervous system and harm the brain, heart, kidneys, lungs and immune system. Mercury has been linked to Minamata disease, named after the first documented case in Minamata, Japan in 1956. Methyl mercury, generated as a byproduct to acetaldehyde and dumped by Chisso Corporation into Minamata Bay, was ingested by residents who ate fish and shellfish contaminated by the mercury pollution. Studies reported that at least 2,955 people in the area contracted Minamata disease. Of those affected, 100% experienced

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[8] Bryan Walsh, *Study Says Arsenic Poisons Millions in Bangladesh—But They're Not the Only Ones,* Time Magazine (June 19, 2010), http://science.time.com/2010/06/19/study-says-arsenic-poisons-millions-in-bangladesh%E2%80%94but-theyre-not-the-only-ones/.

[9] *The Four Big Pollution Diseases of Japan*, Student Network for Human Security Blog (Nov. 19, 2007), http://human-security.jp/blog/2007/11/the_four_big_pollution_disease.html.

[10] *Itai-Itai Disease*, Westox, http://westox.site.wesleyan.edu/itai-itai-disease/ (last visited March 28, 2013).

[11] Sharon La Franiere, *Lead Poisoning in China: The Hidden Scourge*, The New York Times (June 15, 2011), http://www.nytimes.com/2011/06/15/world/asia/15lead.html?pagewanted=all&_r=2&.

[12] Meyer, P.A., McGeehin, M.A., and Falk, H. *A Global Approach to Childhood Lead Poisoning Prevention*. International Journal of Hygiene and Environmental Health. 2003. 206,363-369.

visual disturbance, 93.5% experienced poor coordination, 88.2% experienced dysarthria, 85.3% experienced hearing disturbance, and 75.8% experienced tremor.[13]

These cases highlight the real and devastating toll that exposure to these toxins can exert on nearby communities. These same pollutants are emitted by Veolia and breathed by area residents. Furthermore, exposure to multiple pollutants at once can lead to synergistic effects, causing even greater health consequences. Strict regulations to control and limit these toxic pollutants, and to ensure that Veolia adheres to the proposed feedrate limits for mercury and the other low- and semi-volatile metals, are essential.

GENERAL COMMENTS ON THE DRAFT PERMIT

In this action to reopen Veolia's Title V permit, EPA is proposing to incorporate heavy metal feedrate limits based on historical feedrates and the feedrates from Veolia's 2008 performance testing. ABC agrees with this approach and believes EPA made the right decision when it denied Veolia's request to extrapolate to higher feedrate limits. Feedrate limits for low- and semi-volatile metals based on the highest 12-hour rolling average feedrate over a multi-year period should not hinder Veolia's routine operations in any way because this average represents the extreme range of normal operating conditions. Feedrate limits for mercury based on performance test feedrates, though more restrictive, are appropriate given the unpredictable nature of mercury emissions and thus the need to restrict feedrates to those that testing has demonstrated do not result in excess mercury emissions. ABC believes the proposed limits strike a reasonable balance between the company's need for operational flexibility and the importance of protecting the environment and human health in an overburdened environmental justice community.

In the current permitting action, EPA is also proposing to supplement monitoring requirements to verify compliance with the hazardous air pollutant (HAP) emissions limits by requiring a multi-metals continuous emissions monitoring system, or CEMS, on one of Veolia's three hazardous waste incinerators. This is unquestionably a step in the right direction as the CEMS will, for the first time in the life of the facility, provide accurate and reliable data regarding Veolia's HAP emissions on a continuous basis. However, ABC believes that EPA did not go far enough because the only way to verify full compliance with the HAP emissions limits is to permanently require multi-metals CEMS on all three of Veolia's incinerators.

Finally, ABC supports the Draft Permit's enhanced feedstream analysis procedures for mercury and low- and semi-volatile metals, which require Veolia to implement strict procedures for pre-acceptance waste screening, waste acceptance, batch sampling, and the treatment of

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[13] Masazumi Harada, *Minamata Disease and the Mercury Pollution of the Globe,* http://www.einap.org/envdis/Minamata.html (last visited March 28, 2013).

results below the detection limit in metal federate calculations. ABC believes that these enhanced procedures will give Veolia more accurate and detailed information about the waste it is burning, which will in turn help ensure compliance with the new feedrate limits.

SPECIFIC COMMENTS ON THE DRAFT PERMIT

I. EPA Correctly Denied Veolia's Request for Extrapolation

In its original significant modification permit application, Veolia requested feedrate limits for mercury and low- and semi-volatile metals that were extrapolated from the results of its 2008 performance testing. EPA denied Veolia's request to extrapolate these feedrate limits for three reasons. First, Veolia did not consistently conduct its performance tests at the extreme range of normal. As a result, EPA could not reliably conclude that Veolia would have equal system removal efficiencies at the requested feedrate limits. Second, EPA believed that extrapolation of mercury feedrates for Incinerator 4 was not appropriate because the tests did not provide sufficient data to understand the relationship between the amount of activated carbon needed to maintain the calculated system removal efficiency and different mercury feedrates. Third, EPA had a number of concerns with Veolia's 2008 comprehensive performance test procedures and the resulting data. For these and other reasons, ABC believes EPA was correct in denying Veolia's request to extrapolate to higher feedrate limits.

Higher feedrate limits would pose a significant health risk to the local community, especially with regard to mercury. There is special concern about mercury deposition in and around area lakes used for subsistence fishing based on EPA's own human health risk assessment, conducted for RCRA permitting.[14] This assessment identified significant mercury-related human health risks to the local community, which resulted in the Illinois EPA imposing stringent mercury controls and annual feed limits in Veolia's state-issued RCRA Part B permit. EPA's approach in the Draft Permit is to limit mercury feedrates to rates that performance testing has demonstrated do not result in excess mercury emissions. This is not an unreasonable approach, but EPA should consider further limiting mercury feedrates to decrease the risks identified in its human health risk assessment.

II. CEMS Should be Required on All Three Incinerators

The Draft Permit requires Veolia to install a multi-metals CEMS on just one of its three incinerators (Unit 3). ABC believes CEMS should be required on all three incinerators, as this is the only practical and effective way of assuring that Veolia's emissions of mercury and low- and

[14] *Illinois EPA and USEPA Response Summary,* Public Comments Offered on 2003 and 2008 Draft RCRA Permits for Veolia/Onyx Environmental Services/TWI Facility RCRA Part B Permit Renewal, *available at* http://www.epa.state.il.us/public-notices/2008/veolia/response-summary.pdf.

semi-volatile metals do not exceed federal HAP emissions limits given the heterogeneous nature of Veolia's feedstreams and Veolia's history of failing to accurately characterize the waste fed into its incinerators. EPA has this authority; Section 114 of the Clean Air Act, 42 U.S.C. § 7414, provides, in part, that the Administrator of the EPA may require any person who owns or operates any emission source to install, use, and maintain monitoring equipment to determine whether that source is in violation of Section 112 of the CAA, 42 U.S.C. § 7412.

A. CEMS are an Effective Means of Assuring Compliance with HAP Emissions Limits

ABC agrees with EPA that CEMS are the most direct means of ensuring compliance with emissions limits, which helps protect public health and the environment. CEMS monitor actual emissions, which is critical in the case of mercury given the special concerns about mercury identified in EPA's human health risk assessment and the unpredictable nature of Veolia's mercury emissions as described by Veolia's general manager, Doug Harris, and documented in EPA emails obtained through FOIA. According to one of these emails, Mr. Harris stated to EPA that there is no correlation between mercury feedrates and emissions from the stack.[15] Another email describes a meeting between Veolia and EPA at which Mr. Harris explained how unpredictable mercury emissions can be when performing stack tests.[16] According to the emails, Mr. Harris told EPA employees that, as an example, Veolia could feed in 10 lbs of mercury and get a result of 50 micrograms/cubic meter one time, feed in 20 lbs of mercury and get 25 micrograms/cubic meter the next time, and have no idea what happened in between the test runs to explain the difference.[17] Veolia's statements to EPA about the unpredictable nature of its mercury emissions is just one more reason why CEMS should be required on all three of its incinerators.

Multi-metals CEMS are a proven technology and have already been used successfully at another hazardous waste incinerator. Eli Lilly successfully installed, certified, and operated a multi-metals CEMS on a rotary kiln incinerator at its Tippecanoe Laboratory facility from 2005 until it sold the facility to Evonik in 2010.[18] During this time Eli Lilly realized several benefits from using the CEMS. First, using CEMS data for compliance reduced the need for sampling and analysis of individual containers to characterize the waste being fed to the incinerator.[19] This addressed some concerns Eli Lilly had regarding the costs and potential exposure required

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[15] Email from Sabrina Argentieri, Associate Regional Counsel, USEPA to Shannon Downey, USEPA (Sept. 2, 2010, 10:15 CST).
[16] Email from Shannon Downey, USEPA, to Sabrina Argentieri, Associate Regional Counsel, USEPA (May 26, 2010, 15:19 CST).
[17] *Id.*
[18] Keith Beach et al., *Execution of Comprehensive Performance Test Using Particulate, HCl and Metals Continuous Emissions Monitoring Systems*, at 1.
[19] Keith Beach et al., *Execution of Comprehensive Performance Test Using Particulate, HCl and Metals Continuous Emissions Monitoring Systems*, at 19.

by typical sampling activities. Reducing the typical sampling and analysis activities provided significant safety, operational, and economic benefits. Second, Eli Lilly benefited from the operational flexibility that could be realized by removing many of the prescribed HWC MACT operating parameter limits on the incinerator's air pollution control system.[20]

Veolia stands to realize these same benefits. With the use of CEMS on all of its incinerators, Veolia will have real-time access to actual emissions data, which will offer it more flexibility in feeding wastes and potentially allow it to increase feedrates. At the meeting referenced above Mr. Harris argued that one of the consequences of complying with a mercury feedrate OPL based on stack testing is that, due to the unpredictable nature of mercury emissions during stack tests, Veolia could end up "stuck" feeding mercury at a lower rate based on one test and have a subsequent test reveal that a higher feedrate would have been acceptable. With CEMS, Veolia would not be "stuck" with mercury or low- or semi-volatile metal feedrates and could adjust these feedrates in real time using the CEMS data.

With CEMS, Veolia could also realize substantial cost savings by eliminating certain feedstream analyses. By using CEMS on all of its incinerators, Veolia would be able to eliminate feedstream analysis for low- and semi-volatile metals, at a minimum.

B. Feedstream Analysis is Problematic

Feedstream analysis is Veolia's current procedure for ensuring compliance with the HAP emissions limits. However, feedstream analysis is problematic for several reasons. With feedstream analysis, there are uncertainties associated with the quantification of extremely low metals concentrations in the waste because results are less certain when at or near the quantitation limit. In addition, the heterogeneity of the waste may lead to a non-representative sample and hence inaccurate estimates of the rate at which metals are being fed to the incinerators. Finally, with feedstream analysis it is not possible to demonstrate continuous compliance with the HAP emissions limits since there is generally a considerable time lag time between sampling and analysis and incineration, and because only a small percentage of the waste fed to the incinerators is actually sampled. It would be necessary to sample 100% of the waste fed to the incinerators to ensure continuous compliance, which is simply not feasible.

1. *Veolia's Heterogeneous Feedstream is Problematic*

Feedstream analysis supplemented by periodic performance testing does not work because Veolia's feedstreams are heterogeneous, which makes accurate estimation of metals feedrates very difficult. Veolia's facility combusts halogenated solvents, acids, propellants,

[20] *Id.*

explosives, and other highly volatile and toxic chemicals.[21] This dynamic mix of wastes complicates feedstream analysis. Furthermore, EPA states that the performance testing conducted periodically by Veolia provides only a snapshot of its emissions. What is true one day, or even one hour, may not be true the next, and does not necessarily represent actual emissions performance with respect to all waste streams burned by Veolia throughout the year. Unless the EPA requires CEMS on all three incinerators, EPA cannot be certain that Veolia is in continuous compliance with the HAP emissions limits at the proposed feedrates.

2. *Veolia Inaccurately Characterizes its Waste*

Metals feedrates are designed and written into air operating permits to limit metals emissions. However, an increase in emissions could still occur through Veolia's stacks if it fails to adequately characterize its waste streams.[22]

Inaccurate waste characterization has a significant potential to result in increases in toxic metals emissions.[23] According to the Cooper Report, excess amounts of one low-volatile metal - arsenic - have been recorded near Sauget. On April 13, 2009, a multi-metals CEMS designed for fence-line ambient air quality monitoring located less than two miles from Veolia recorded an arsenic concentration of 2.34 $\mu g/m^3$.[24] This level is potentially dangerous to human health, exceeding the NIOSH 15-minute recommended occupational exposure limit, and it lasted approximately 8 hours.[25] Examination of public records and meteorological data from that day suggests that Veolia was the probable source of this arsenic.[26] The report stated "if it can be demonstrated that this, and other possible events like this, are the result of the hazardous waste stack fumigation, then the source should be required to place a multi-metals CEMS on its stack and limit its emissions of hazardous metals into the surrounding neighborhoods."[27] More comprehensive monitoring of Veolia's emissions is needed to detect similar releases in the future.

Veolia has incorrectly characterized its waste in the past because of its reliance on waste generator profiles. Some wastes burned by Veolia have unknown composition because their composition profiles have not been provided by the respective waste generator.[28] In many cases, Veolia relies on waste composition analyses supplied by individual waste generators but those

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[21] John A. Cooper et al., *Guide for Developing a Multi-metals, Fence-line Monitoring Plan for Fugitive Emissions Using X-ray Based Monitors*, at H5 (2010).
[22] John A. Cooper et al., *Guide for Developing a Multi-metals, Fence-line Monitoring Plan for Fugitive Emissions Using X-ray Based Monitors*, at H5 (2010).
[23] Id. at H16 (2010).
[24] Id.
[25] Id.
[26] Id.
[27] Id.
[28] USEPA, Statement of Basis, *available at* www.regulations.gov, Docket ID: EPA-R05-OAR-2012-0649-0002.

analyses are not always accurate. Without CEMS, Veolia will continue to monitor compliance with emissions limits by relying upon statements from generators who have no particular interest in knowing the exact composition of their waste.

Indeed, past experience demonstrates that Veolia has insufficient comprehension of the true characteristics of the waste it burns. Most recently, and most relevantly, EPA issued Veolia a Finding of Violation in August 2012 for violations of the Clean Air Act after an on-site compliance investigation conducted by EPA's National Enforcement Investigations Center (NEIC) in December 2011. The NEIC found significant problems with Veolia's feedstream analysis procedures and that a high percentage of its waste profiles were inaccurate. In some of the waste profiles, Veolia underestimated the actual metals concentration in the waste. In another profile, Veolia assigned metals concentrations based on the generic waste profile rather than analyzing for metals each time the waste was received. When using a particular generic profile, Veolia used a standard concentration value for chromium of 139 mg/kg, but when one of the loads was sampled and analyzed it had an actual chromium concentration of 99,780 mg/kg. It also appears that Veolia used several profiles that copied metals concentrations used in other profiles despite the fact that it is statistically unlikely that two different waste profiles would have identical metals concentrations. The NEIC stated that "by using generic waste profiles and assuming a constant metals concentration for variable wastes, rather than analyzing each waste stream, Veolia failed and continues to fail to obtain an analysis of each of the related feedstreams sufficient to document compliance."

NEIC also found that Veolia had failed to analyze ash at a frequency sufficient to document compliance with the applicable feedrate limits. The inspectors found that ash from Incinerators 2 and 3 was analyzed for metals only once in the last seven years. When NEIC inspectors analyzed six grab samples of ash from Incinerators 2 and 3, the results of the analysis showed that the metals composition of the ash was highly variable. Veolia had once again failed to correctly analyze what it was incinerating.

III. CEMS Are Needed on All Three Incinerators Because of the Differences Between the Three Units

Even if Veolia's feedstream analysis procedures were adequate to characterize its waste streams, there are additional reasons for requiring CEMS on all three incinerators. The Draft Permit currently requires Veolia to install a CEMS only on Incinerator 3. Although Incinerator 3 is nearly identical to Incinerator 2, Incinerator 4 is a different type of incinerator and has different emissions control equipment. Incinerators 2 and 3 are fixed-hearth, dual chamber,

multi-type feed incinerators and Incinerator 4 is a rotary kiln incinerator.[29] Incinerators 2 and 3 each use spray dry absorbers with lime slurry injection to control hydrogen chloride emissions and baghouses for particulate matter.[30] Incinerator 4 uses a spray dry absorber for HCl control, an activated carbon injection system for mercury control, and a baghouse for particulate matter control.[31]

In addition to differences in equipment, the incinerators are fed different types of waste. All three combustion units are fed liquid and solid waste streams; however, liquid containers and gas cylinders are charged to Incinerator 2, Incinerator 3 has a fume hood emission control system for wastes that require such handling, and bulk waste is fed to Incinerator 4. Because of the heterogeneous nature of Veolia's waste streams and the differences in feedstreams between the three incinerators, the materials fed to Incinerators 2, 3 and 4 are not identical. As a result, the CEMS data from Incinerator 3 cannot be used to document the emissions performance of Incinerators 2 and 4 without making unsupported assumptions.

IV. CEMS Should Be Required on All Three Units Permanently

Considering the substantial benefits of using CEMS, the Draft Permit should be strengthened by requiring permanent CEMS operation at Veolia, instead of for only one year as proposed. As noted, Veolia's feedstreams are heterogeneous, changing from day to day, month to month and year to year. Therefore, a one-year period of operation cannot guarantee Veolia's compliance with the HAP emissions limits in the future. Nor could any knowledge about the correlation between metals feedrates and emissions rates gained from using the CEMS for one year be applied to future years. Veolia's waste streams are just too variable.

Additionally, and as EPA knows well, CEMS are more accurate and reliable than feedstream analysis for monitoring HAP emissions. The people living near Veolia's facility deserve to live in an area where they know with certainty the amount of pollutants in the air they must breathe on a daily basis.

V. The Draft Permit Should Include a Detailed CEMS Implementation Schedule

The Draft Permit states that, "The Permittee shall install, calibrate, maintain and operate an x-ray fluorescence multi-metals CEMS on Incineration Unit #3 within 180 days after this permit becomes effective, unless the Administrator determines that a time extension is warranted based on the Permittee's documentation in writing of factors beyond its control that prevent the

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[29] USEPA, Statement of Basis, at 3, *available at* www.regulations.gov, Docket ID: EPA-R05-OAR-2012-0649-0002
[30] *Id.*
[31] *Id.*

Permittee from meeting the 180-day deadline."[32] ABC supports this provision, but believes the permit should include interim steps and deadlines to shepherd Veolia through the implementation process and enable EPA to ensure that the process moves along efficiently. The implementation schedule for Mercury CEMS provided in Appendix B to EPA's March 10, 2010 Request to Provide Information Pursuant to the Clean Air Act is a good model. This request provided the following interim steps and deadlines for the installation of the Mercury CEMS: "Veolia must submit Requests for Proposals (RFPs) to CEMS vendors for the purchase and installation of mercury CEMS within 10 days of receipt of this request; within 60 days of receiving responses to the RFPs, Veolia must submit an Alternative Monitoring Plan (AMP) covering the CEMS to be installed and operated on Incinerators 2, 3, and 4; the CEMS must be installed and operated in accordance with the EPA-approved AMP; the CEMS must be installed and commence operation on each of the incinerators within 60 days after approval of the AMP; CEMS must be evaluated and certified in accordance with an EPA-approved method for total mercury CEMS within 30 days after commencing operation." ABC believes that a similar schedule for implementation of the multi-metals CEMS would help ensure that Veolia installs and begins operating the CEMS in an efficient and timely manner.

VI. Activated Carbon Injection Systems Should be Required on Incinerators 2 and 3

ABC believes that Veolia should be required to install activated carbon injection systems on Incinerators 2 and 3. As documented in one of the EPA emails obtained through FOIA, Doug Harris stated to EPA personnel that carbon injection is becoming an industry standard.[33] If other incinerators are using carbon injection for mercury emissions control, Veolia should implement it as well. Furthermore, Veolia already has installed a carbon injection system on Incinerator 4, indicating that Veolia is familiar with the technology and understands its benefits. Carbon injection reduces the amount of mercury emitted into the air, and given the special concerns about mercury deposition in area lakes noted above, any control technology that reduces mercury emissions should be required on all of Veolia's incinerators. This is true regardless of whether or not CEMS are installed on all three of Veolia's incinerators.

VII. The Draft Permit's Beryllium-Containing Waste Prohibition Needs to be Clarified

Finally, ABC asks EPA to clarify the Draft Permit's prohibition of the burning of beryllium-containing waste. The original Title V permit stated on page 11, under Section C, Work Practice and Operational Requirements, that, "The Permittee shall not burn hospital medical infectious waste, municipal waste, or beryllium-NESHAP containing waste." In the

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[32] USEPA, Veolia Draft Permit, at 26-7, *available at* www.regulations.gov, Docket ID: EPA-R05-OAR-2012-0649-0001

[33] Email from Genevieve Damico, USEPA, to Charles Hall (Nov. 3, 2009, 13:00 CST).

Draft Permit, the word "NESHAP" has been deleted from the condition, presumably in an attempt to clarify the prohibition on burning beryllium-containing waste, but the condition is even more confusing now than before. The Draft Permit now states that Veolia cannot burn beryllium-containing waste while simultaneously specifying new feedrate limits for low-volatile metals, which specifically include beryllium.

Based on information in the record for the original Title V permit, it seems that the provision stating that Veolia may not burn "beryllium-containing waste" is related to 40 CFR Part 61 Subpart C, the national emission standard for beryllium for any incinerator which burns beryllium-containing wastes generated at a foundry, ceramic plant, propellant plant, or extraction plant. In a September 7, 2007 applicability determination requested by EPA, Veolia informed EPA that it has controls in place that prohibit the approval of wastes from these industries. ABC speculates that, based on these assurances, EPA accepted Veolia's non-applicability determination and the part of the Permit stating that Veolia may not burn any beryllium-containing waste refers only to beryllium wastes from the above mentioned types of industries, but not beryllium wastes generated by other industries. However, this is mere speculation and the meaning of the provision in question should be clarified.

CONCLUSION

Veolia's compliance history, the variability of its feedstreams, and its location in an area with significant environmental justice concerns underscore the need to permanently require multi-metals CEMS on all three of its incinerators to continuously monitor and confirm that its emissions do not exceed federal HAP emissions limits. Because of the inherent limitations of and specific problems with Veolia's feedstream analysis procedures, as well as the heterogeneity of Veolia's waste streams, operating a CEMS on just one incinerator would not demonstrate compliance with the HAP emissions limits by the other two incinerators. With the commercial availability of CEMS and their proven effectiveness, it is necessary and reasonable to require CEMS on all three incinerators. Veolia releases toxins with the potential to inflict a devastating toll on the local community. Strict regulation and monitoring is necessary to control and limit the release of these toxic pollutants and to ensure that Veolia adheres to the HAP emissions limits.

ABC appreciates the opportunity to comment on the Draft Permit for Veolia and urges EPA to make the revisions suggested above before issuing the final revised permit.

Sincerely yours,

Kristhy St. Hilaire
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St. Louis, MO 63130

cc: Kathy Andria, ABC

05-FOI-01384-12INT-51

Shannon Downey/R5/USEPA/US
05/13/2009 05:01 PM

To Cheryl Newton
cc Sarah Marshall, Brent Marable, Argentieri.Sabrina
bcc
Subject Summary of today's meeting with Veolia

Cheryl,
We met with Veolia today concerning the Section 114 issued to Veolia requiring the installation of Hg CEMS. Members of both the enforcement team, air permitting team and RCRA permitting team were present at the meeting. The problems that RCRA permitting and air permitting have with the August 2008 stack test were discussed. Veolia agreed to try to provide further information and explanation to the permitting teams regarding the discrepancies in the moisture percentages and the lab analysis. The team discussed the Hg CEMS. Both EPA experts and Veolia's expert agreed that the only technical issue with a Hg CEMS is the lack of NIST traceable calibration gases. Our EPA expert, Jeff Ryan, is currently working with NIST to develop NIST traceable calibration gases. EPA offered to extend the compliance deadline for the 114 to accommodate the time needed to work out the NIST traceable calibration gases. Veolia's main complaint is that they are the only commercial hazardous waste incinerator being required to install Hg CEMS. After a caucus, Veolia said that they might consider Hg CEMS in the future if it proved to be cost beneficial to them. Veolia understands that there would be possible cost savings as a result of being able to eliminate feed analysis for Hg.

The enforcement team

05-FOI-01384-12INT-92

Genevieve Damico/R5/USEPA/US
11/03/2009 01:00 PM

To Charles Hall
cc Christopher Lambesis, Todd Ramaly, Maria Gonzalez, Jane Woolums, Pamela Blakley, William Macdowell, Shannon Downey, Sarah Marshall, Sabrina Argentieri
bcc
Subject Notes from today's call with Veolia

Today Chris, Todd, Charlie and myself spoke with Doug Harris, Dave Klarich, and Dennis Warchol from Veolia about EPA's October 14 letter and Veolia's October 20 response.

Doug proposed that Veolia focus on the remaining MACT-required testing now but that we should set a date to discuss the possibility of another mercury test. We currently have February 23, 2010 pencilled in for that meeting.

Doug also mentioned that Veolia is in the beginning stages of considering carbon injection for units 2 and 3 since he is coming to realize that carbon injection is becoming an industry standard.

Doug's thoughts on the mercury OPLs are that we can use the most conservative moisture content from either PCS Republic or EPA's samples and a "small amount" of extrapolation. I mentioned that the current extrapolation request has been denied. Doug will be submitting another, "more conservative" extrapolation request.

The call ended with a summary of the information that both parties requested during the call.
- Veolia will submit to EPA the spike logs from the 2008 tests and PCS Republics moisture content SOP.
- EPA will send Veolia the moisture content results from RCRA's grab samples.

If I missed any information from the call, please send an e-mail to all with the updates.

05-FOI-01384-12INT-100

Genevieve Damico/R5/USEPA/US
02/12/2010 02:35 PM

To Charles Hall, Jane Woolums, Pamela Blakley
cc Todd Ramaly, Christopher Lambesis
bcc
Subject Conversation with Doug Harris at Veolia

I finally was able to get a hold of Doug to tell him that we weren't ready to meet on the 23rd and a few months from now would be a better time to meet with our respective attorneys present. He proceeded to go through the items he wanted to talk about on the 23rd. Doug expressed that he thinks Veolia's management doesn't think that EPA will accept any efforts on Veolia's part to resolve the disagreements between us, however, Doug wanted to use this meeting to come to an agreement. He was willing to install carbon injection on units 2 and 3 per the advice of Chris and Todd in the second quarter of this year and test for mercury in the 3rd quarter. According to Doug, he has got the funding to do these projects this year but the funding will dry up if we don't move forward soon. He is unwilling to do either of these things if it doesn't resolve the permitting (and maybe he was thinking the enforcement) issues, in particular, the moisture content.

As a side note, I spoke with Todd and Chris last week and they confirmed that they think they can justify using the PSC Republic moisture content as a conservative estimate and we can calculate some OPLs using the higher moisture content to determine the waste feed rate concentrations. Doug mentioned in our call this morning that he would be willing to accept OPLs based on the PSC Republic moisture content. So if Jane and Charlie agree then we might be able to issue a reopening with OPLs which won't be overly egregious to Veolia, extrapolation aside.

Doug only barely touched on the extrapolation. I think he is just going to send it in for us to evaluate. Doug pushed the request that EPA influence IEPA to issue construction permits for the carbon injection project citing that we want the project. (I don't know where he got the idea that we are just shy of insisting on carbon injection, nor did I give any indication that we would pressure IEPA into issuing construction permits on his behalf.) Doug was going to submit the application to IEPA but won't construct the carbon injection units unless we can work out our issues.

We ended the call with Doug's concern that he doesn't know what he should be doing at this point.

DRAFT

Guide for Developing a Multi-Metals, Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors

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December 9, 2010

DRAFT

Guide for Developing a Multi-Metals, Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors

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December 9, 2010

Executive Summary

Airborne metals and metal compounds are of particular concern to human health. Not only are they included in the United States (U.S.) Environmental Protection Agency's (EPA) list of 187 hazardous air pollutants (HAPs), they represent 8 of the 33 urban pollutants identified by the EPA as posing the greatest potential health threat in urban areas. This is particularly significant since 80% of the U.S. population resides in urban areas. Premature deaths linked to particulate matter (PM), particularly PM in the respirable range, have been shown to be comparable to deaths from traffic accidents and second-hand smoke. Contemporary researchers in the field of airborne metals' health effects are finding that the metals components of PM are particularly toxic and cause a multitude of significant health effects from pulmonary inflammation, to increased heart rate variability, to decreased immune response. These effects are not only seen from chronic exposure, but also from short-term acute concentration spikes in ambient air.

A significant portion of the U.S. population lives in the vicinity of metals sources, such as waste incinerators, metal processors, metal fabricators, welding facilities, etc., where they may be exposed to airborne metals greatly in excess of typical ambient concentrations. With modern regulatory limits and controls on stack emissions at industrial facilities, many of the major regulatory and technological issues surrounding stack fumigation and pollution have been resolved. Alternately, fugitive emissions, also described as uncontrolled process emissions, occur at or near local elevations and can dominate local hazardous air pollutant exposure. In fact, recent modeling at secondary lead smelters indicates that at many facilities the majority of daily emissions are fugitive in nature. Additionally, at facilities such as primary and secondary lead smelters, short-term lead concentration spikes may comprise the majority of the mass of lead emissions and subsequent human exposure for a given month. Fugitive emissions typically occur intermittently and unpredictably throughout the course of a plant's daily operations. In addition, fugitive emission transport and exposure to human receptors may depend upon specific meteorological conditions, wind direction, and facility operations. Because these emissions are not measured by typical stack monitors, the specific source of the emission can be difficult to identify and control.

The objectives for a regulatory approach are to protect human health through continued reduction of hazardous air pollutant (HAP) exposure by measuring short-term peaks in concentration, identifying and apportioning sources, and providing feedback to plant operators. Historically, plant operators and regulators have not had the capability to measure short-term ambient metals concentrations, which is necessary to characterize the potential for acute exposure health effects and fulfill regulatory criteria. Commonly used ambient metals sampling devices generally collect 24-hour integrated average samples, which are then sent off to be analyzed in a lab, and as a result sampling data may take weeks to process. In addition, 24-hour average concentration samples do not fully account for shifts in the environment, such as short-term ambient metals spikes related to local fugitive emissions. In fact, during a short-term metals exposure event, 24-hour average sample concentrations for metals like arsenic and lead may be orders of magnitude lower than the 4-hour or 15-minute average concentration from the

same day. To achieve an accurate characterization of daily exposure, continuous monitoring is essential. Without the capacity to correctly characterize short-term exposure on a real-time scale, it has been difficult or impossible to either identify the source of the emission or to develop regulatory control strategies to reduce the impact of acute, high concentration exposures.

Presently, a newly proven technology exists that allows industrial operators, researchers, and regulators to monitor short-term variations in airborne metals concentrations in near-real-time (NRT) intervals. This tool, a mobile ambient air X-ray fluorescence metals monitor, has proven itself to be a reliable, precise, and accurate monitor that has been validated through comparisons with federal reference method (FRM) sampling and laboratory analysis. In addition, performance specifications and on-going quality assurance procedures have been developed and tested. This monitor provides a means to fulfill regulatory goals for implementing emission and ambient air maximum achievable technologies (MACT), as required by the Clean Air Act. The procedure, presented in this document, describes how this new monitoring tool might be used in permitting, monitoring, and compliance applications. It is based on well-established PM monitoring protocols covered extensively by the EPA and in published scientific literature. This guide covers key aspects unique to ambient air metals measurements, along with hypothetical examples of its application to selected real-world sources, such as a secondary lead smelter, a primary lead smelter, a primary copper smelter, a ferrous metal recycler, and a hazardous waste incinerator.

The procedure for measuring ambient air metals concentrations consists of six key steps:

Step 1. Define the Driver: It is assumed that the need to develop a fence-line metals monitoring plan is driven by either a source requesting a new or renewed permit to operate, a potential health concern based on previous ambient measurements, a need to monitor emissions at a remediation site, or to provide support for a state implementation plan (SIP).

Step 2. Define ambient goal or limit: This step requires the guide user to define an ambient limit or goal; i.e. metal and PM size fraction, concentration, averaging time, number of allowed exceedances.

Step 3. Review and Characterize the local Airshed features: Before the user can develop a monitoring plan, the relevant features of the local airshed, such as meteorological features, topography, and location of emissions sources, must be explicitly defined.

Step 4. Define parameters to be monitored: Once the problem has been defined and the airshed characterized, it is now possible to begin the planning step by defining the specific parameters to be measured.

Step 5. Define number, characteristics and location of monitoring sites: With the above information defined and available, it is now possible to define the number, purpose, characteristics and location for each monitoring site.

Step 6. Outline data processing and reporting channels: Reporting will be based around the specific monitoring and regulatory requirements of the program. Data reporting format, frequency, and extent will need to be defined considering the various public and private stakeholders involved in the ambient metals monitoring plan.

These tools, i.e. NRT monitoring, performance specifications, quality assurance procedures, and procedure guide, provide the data and feedback to regulators, facility operators, the public, and other stakeholders necessary to develop and enforce established not-to-be-exceeded health limits, action levels, and goals for ambient air metals concentrations. The multi-metals FLM has the ability to characterize short-term exposure to hazardous metals during a time when a growing body of evidence points to the significance of ambient air metals in contributing to adverse human health effects. Accurate, NRT data not only helps to identify source contributions to key emissions events, it provides an early warning system to protect public health, improve controls, and reduce future emissions. The capability to relate short-term airborne metals variability to wind conditions and plant operating processes provides a tool of unprecedented power for source apportionment, regulation, improved air quality, and protection of human health and the environment.

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1.0 Introduction

This guide introduces near-real-time (NRT) multi-metals ambient air monitors and describes how to develop a monitoring plan for fugitive metal emissions based on these new monitors located at or near a fence-line of an industrial facility or in a sensitive residential area. It is generally based on the U.S. Environmental Protection Agency's (EPA) dynamic air quality management framework including goal setting, defining required emission reductions, control strategies, implementation, evaluation of results and trends, and adjusting plans to more effectively meet established goals. Much has been written over past decades regarding establishing air pollution monitoring networks with a wide range of objectives and measured pollutants. Although this guide relies on this previous work, it focuses primarily on those aspects pertaining to particulate matter (PM) as it applies to fugitive emissions and multi-metals fence-line monitors (FLM). The guide thus provides the user with a summary of the general approach to establishing these monitoring systems, highlighted with the unique requirements of the FLM, and illustrated with examples. For more details on the general approach to establishing PM monitoring networks, the reader is directed to the vast collection of EPA and other published literature, some of which is noted in the "General Air Pollution Monitoring System Design Bibliography" in Section 13.

The guide assumes an initial driver exists, such as meeting the National Ambient Air Quality Standard (NAAQS) for lead, previous measurements suggesting potential health concerns, or a new permit/permit renewal request. It provides steps to follow in defining compliance limits and/or goals, including setting indicators, averaging times, concentration levels, and chemical form. It then provides steps to define a monitoring plan to demonstrate compliance and/or progress towards meeting goals. The guide includes suggestions for establishing number, location, and characteristics of monitoring sites, as well as operational parameters. In addition, this guide provides suggestions for data processing, quality assurance, and reporting. Procedures for demonstrating that a metals monitor meets initial performance specifications and on-going quality assurance procedures are provided by following steps described in Performance Specification AA: *Specifications and Test procedures for X-ray Fluorescence Based Metals Fence-line Monitors* (PS-AA) and Procedure BB: *On-going Quality Assurance Requirements and Procedures for X-ray Fluorescence Based Metals Fence-line Monitors* (P-BB). These specifications and procedures are provided in Appendices A and B of this guide.

The following section provides a background for this new multi-metals monitoring technology, summary of airborne metals health effects, and a brief description of the recommended regulatory approach. Contemporary multi-metals FLM and their unique characteristics are described in Sections 3 and 4. The steps in the guide are summarized in Section 5, and Sections 6 through 12 provide a more detailed description of the 6-step procedure. Sections 6 through 8 describe steps for building a foundation on which to develop a monitoring plan. Sections 9 and 10 describe specific monitoring plans and procedures for developing data processing. Quality assurance and reporting are described in Sections 11 and 12. A key component to developing a monitoring plan is defining limits and/or goals for key hazardous metals; Appendix C: *Overview of Metals Regulations, Exposure Limits, Health Effects, and*

Contemporary Research is provided to assist the user in defining the importance of airborne metals as they relate to human health effects and how these effects influence setting appropriate limits and/or goals. Representative examples of applying this process to secondary and primary lead smelters, a primary copper smelter, a ferrous metal recycler, and a waste incinerator are provided in Appendices D through H, respectively.

2.0 Background

2.1 Regulation of Metals

The U.S. Congress amended the federal Clean Air Act (CAA) in 1990 to address a large number of hazardous air pollutants (HAPs) that are known to cause adverse effects to human health. Section 112 of the Clean Air Act Amendments (CAAA) governs the federal control program for HAPs. National Emissions Standards for HAPs (NESHAPs) are issued to limit the release of specified HAPs. These standards are "technology-based" meaning that they represent the maximum achievable control technology (MACT). The CAAA require EPA to review and revise MACT standards as necessary every eight years, and they direct the EPA to assess the risk remaining (residual risk) after the application of the MACT standards. The EPA is further directed to issue additional standards, if required, to provide an ample margin of safety to protect public health. This ongoing process is comprehensively evaluated through National Air Toxics Assessments (NATA). Thus far, EPA has completed three assessments that characterize the nationwide chronic cancer risk estimates and noncancer hazards from inhaling air toxics. The latest NATA in 2002 was made available to the public in June of 2009.[1] The EPA is in the process of reviewing residual risk standards for HAPs as part of the subsequent 8-year cycle.

Permitting, monitoring, and enforcement of fugitive metal emissions for HAPs (MACT or residual risk related) are an integral part of managing and improving air quality to protect human health and the environment. Stack emissions are relatively easy to regulate, they can be accurately monitored with continuous emissions monitoring systems (CEMS), and limits enforced based on these measurements. However, it is difficult to permit and enforce fugitive metal emission limits under MACT because 1) there are frequently numerous points for fugitive metal emissions within a single plant; 2) they can cover large areas and change locations; 3) fugitive emissions are likely to be intermittent and can depend on variable processes, such as wind direction, and meteorology; 4) they are frequently unique to a specific plant or site such that it would be difficult to define an industry MACT base; and 5) fugitive emissions monitors and the necessary models for estimating their emissions are not available, except for a few organic vapor species.

Even in the case of fugitive organic vapors, where technologies such as open-path, path-integrated optical remote sensing are available to monitor emissions passing through the plane of a fence-line and models are available to estimate the fugitive emissions, they are not being routinely used, in part, because of the remaining high uncertainties in the model-estimated emissions. Instead, permitting is based on compliance with ambient measurements and progress towards meeting established goals. On the other hand, contemporary permitting and enforcement of fugitive metal emission sources are still based on decades-old, crude estimates of emissions and assumed good management practices. This uncertainty and management

difficulty is of particular concern because fugitive emissions are often highly variable and may be responsible for the dominate exposure to HAP metals for nearby residents.

Metals and metal compounds are of particular concern to human health. Not only are they included in EPA's list of 187 HAPs, they represent 8 of the 33 urban pollutants identified by the EPA as posing the greatest potential health threat in urban areas, with arsenic (As) being the third highest priority. Table 1 below lists these HAP metals as well as those with California reference exposure level (REL), and those exhibiting human health effects at ambient PM concentrations (based on contemporary human health research and standards). Detailed information regarding human health effects of the metals listed in Table 1 is presented in Appendix C.

Hazardous metals are unique in that they will not biodegrade; once released into the environment, they will always be potentially available for re-introduction into the air, water, and food chain. This persistence is particularly important in the context of environmental justice and areas where hand-to-mouth type pathways can represent significant exposure. In local airsheds, fugitive metal HAP emissions can make a significant contribution to total HAP exposures. Perimeter or nearby ambient air monitoring programs to evaluate these contributions have become increasingly valuable. Fence-line or nearby ambient monitoring offers the potential to not only reduce exposure to HAP metals, but also greatly increase the accuracy of exposure estimates and enforcement, as well as potentially eliminate the need for costly monitoring of poorly defined emissions from many possible area/fugitive compliance sources within a facility. This NRT monitoring can also provide timely feedback to plant operators to identify sources, minimize their emissions before they become a more serious problem, and improve their management and control procedures.

Table 1. List of Metals of Potential Health Concern

Name - Symbol (Atomic No.)	187 HAP	33 Urban HAP	CA REL	Ambient PM
Antimony - Sb (51)	X			
Arsenic - As (33)	X	X	X	
Beryllium - Be (4)	X	X	X	
Cadmium - Cd (48)	X	X	X	
Chromium - Cr (24)	X	X	X	X
Cobalt - Co (27)	X			
Copper - Cu (29)			X	X
Iron - Fe (26)				X
Lead - Pb (82)	X	X		X
Manganese - Mn (25)	X	X	X	X
Mercury - Hg (80)	X	X	X	
Molybdenum - Mo (42)				
Nickel - Ni (28)	X	X	X	X
Selenium - Se (34)	X		X	
Vanadium -V (23)			X	X
Zinc - Zn (30)				X

2.2 Fugitive Emissions

The EPA defines "fugitive emissions" as "those emissions which could not reasonably pass through a stack, chimney, vent, or other functionally-equivalent opening." Furthermore, EPA has clearly defined that emissions which *are actually collected* are not fugitive emissions. Fugitive emissions are air emissions that are not released through a stack, vent or other confined air stream. For example, non-stack emissions that escape during material transfer, from buildings that contain a process, or directly from process equipment are fugitive emissions. Some additional examples include fumes from welding; dust from unpaved roads; dust from grinding, crushing, and sandblasting operations; and dry material loading or unloading.

It is important to note that the above definition and examples are based on a source's perspective. This distinction is not necessarily relevant from a monitor's or local community's perspective, which may be impacted by both fugitive and non-fugitive sources, as well as background sources. In the case of the lead NAAQS, short-term fugitive emissions have been shown to comprise a significant portion of lead emissions contributing to the NAAQS non-attainment (see Section 10.7). This typically isn't a problem in the case of emissions ducted through tall stacks (500 to 1,000 feet) that have a low probability of impacting a fence-line monitor or local community. On the other hand, ducted HAP metals emitted from short stacks may have the potential to fumigate a possible fence-line or local community monitor. Although, as noted above, CEMS are available for stack emissions, it may be impractical to install CEMS on any but the largest of stacks. As such, there may be a number of short stacks, which have not yet been routed to tall stacks that must be considered as possible sources impacting fence-line and local community monitors.

2.3 Fence-Line Monitoring

When establishing community air quality monitoring sites, locations that might be directly impacted by specific sources are typically avoided. The objective in such applications is to obtain a sample representative of the average exposure of a typical community resident. In contrast, with fence-line or near fence-line monitoring, the source and its impact are the subjects, and as such the monitoring site might be located at or near the source or at a point of maximum source impact. In this case, the range of concentrations is expected to be substantially greater for a fence-line monitor, since there will be times when the source will be up wind or down wind, or the source may be emitting at its maximum emission rate or not emitting at all. As such, longer term average measured concentrations are not expected to be good representations of shorter term peak concentrations. For example, a 15-fold lead concentration differences has been observed between 24-hour average lead concentrations and 1-hour peak average concentrations measured with a fence-line monitor in Herculaneum, MO. A 22-fold arsenic concentration difference has been observed between a 24 hour average arsenic concentration and 2-hour average peak arsenic concentration measured with a fence-line monitor in East St. Louis, IL.[2] Averaging times are particularly important when using 24-hour measurements to estimate potential short-term exposures and potential health risks, or defining short-term ambient concentration limits or goals. Short-term peak concentrations are

often responsible for the largest portion of overall exposure; therefore, knowledge and subsequent elimination of the responsible events causing these short-term peak concentrations can greatly reduce the longer-term average exposures, measured concentrations, and potential adverse health effects.

2.4 Health Effects

Protection of community health is a key component of a perimeter air monitoring system. As such, one objective of a monitoring program should be to alert the public to short-term exposure levels of target compounds that might be hazardous. These warnings should be designed so that acceptable risks for acute exposures are not exceeded. However, acceptable risk for some metals has become somewhat blurred, as discussed below and in more detail in Appendix C.

Regulatory bodies such as federal, state, and local environmental protection agencies are responsible for assuring the public that the air is safe to breathe. These agencies are required to set standards, levels, and/or goals that will protect public health with an adequate margin of safety. These standards are established not only to protect healthy individuals, but also to protect sensitive population subgroups, such as children, asthmatics, the elderly, and individuals with emphysema, chronic obstructive pulmonary disease, or other conditions that render the group particularly vulnerable to air pollution. Although there is only one metal NAAQS (lead), there are numerous other workplace and community-based screening levels, exposure limits, reference concentrations, etc. for airborne metals that can be used as guidelines for concern over exposure to metals and to set acceptable levels of exposure.

A more detailed listing and discussion of regulations, health effects, exposure limits, and contemporary research on the health effects of metals, including metals as components of PM, at ambient concentrations is provided in Appendix C. A review of contemporary literature and available regulations suggests that our understanding of the health effects associated with inhalation of metals is severely limited, but has improved dramatically, even in the past five years. This improved understanding is due in part to a growing body of evidence that suggests metals may be responsible for the dominant portion of observed PM health effects. For example, in the recent revision of the NAAQS for lead, the EPA noted that there was no apparent threshold for lead in blood below which no health effects would be observed. In addition, premature deaths linked to PM have been shown to be comparable to deaths from traffic accidents and second-hand smoke[3]; and there is an increasing number of epidemiological and toxicological studies suggesting these PM health effects are predominantly caused by trace concentrations (ng/m^3) of metals such as vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), zinc (Zn), and lead (Pb). In addition, recent studies have shown that the metals component in fine and ultrafine PM is particularly toxic and are the primary contributors to negative human health effects.[4]

Below is a summary of conclusions from the works of recent investigators in this field. A complete table and references are provided in Appendix C.

- 1996, Ghio et al[5].: "Transition metals have the capacity to support electron exchange and catalyze free radical production."

- 1997, Costa and Dreher[6]: "The lung dose of bioavailable transition metal, not instilled PM mass, was the primary determinant of the acute inflammatory response for both the combustion source and ambient PM samples."
- 1997, Costa and Dreher[5]: "...Soluble metals from PM mediate the array of PM-associated injuries to the cardiopulmonary system of the healthy and at-risk compromised host."
- 2002, Magari et al.[4]: "The metals components in fine and ultrafine PM are particularly toxic and are the primary contributors to negative human health."
- 2002, Magari et al.[4]: "…Results of this study suggest an association between exposure to airborne metals (vanadium, nickel, chromium, lead, copper, and manganese) and significant alterations in cardiac autonomic function."
- 2002, Ghio et al.[7]: "…Transition metals present in ROFA (especially vanadium) participate in Fenton-like chemical reactions to produce reactive oxygen species (ROS)."
- 2002, Zelikoff et al.[8]: "…Both iron and nickel (inhaled) reduced pulmonary bacterial clearance in previously infected rats."
- 2002, Molinelli et al.[9]: "…Ambient air particles in the Utah Valley induce their health effects in part by delivering transition metals to the airway epithelium in a catalytically-active form."
- 2002, Molinelli et al.[8]: "Results (in vivo and in vitro) support a role for transition metal involvement in PM-associated increases in morbidity and mortality."
- 2006, Lippmann et al.[10]: "Nickel appears to be the component (of fine particulate matter) most likely to cause acute cardiac responses."
- 2009, Konkel (Environmental Health Article)[11]: "(There is)…evidence linking nickel, vanadium, and elemental carbon in the air to wheeze and cough in inner city children."
- 2009, Chen and Lippmann[12]: "…Concentrations of nickel and vanadium in ambient air PM were associated with significant differences in mortality rates, while other measured PM components were not."
- 2009, Chen and Lippmann[12]: "...Reduction of metals in PM associated with a year-long closure of a steel mill was associated with improved health conditions in the local population. The role of metals was further confirmed by later studies using human clinical as well as animal toxicology studies."
- 2010, Maciejczyk et al.[13]: "Three metals (nickel, barium, and manganese)… appear to be much more influential on lung cell responses than black carbon and sulfate ions that are present at much higher mass concentrations."
- 2010, Sangani et al.[14]: "Metals in the water-soluble fraction of air pollution particles decrease whole-blood coagulation time."

It is clear from these statements that momentum is building towards a consensus that certain metals at ambient concentrations are responsible for a large part of PM health effects. These recent findings are of particular interest because of the implications they have for short-term exposures to these metals at much higher concentrations near their source as well as the implications for future limits, goals and/or regulations.

Typical urban air concentrations of metals with associated concentrations for acute, chronic, and cancer health effects are provided in Table 2. The urban air concentrations are not absolute; rather they are presented as a typical level found in urban centers. Likewise, the typical health effects concentrations are representative values of regulatory limits set by such agencies as the EPA, Agency for Toxic Substances and Disease Registry (ATSDR), and

California EPA and are not absolute; rather they depict a general level of concern for differing effect levels. Concentrations found in more industrialized urban areas should expect to be higher than those shown here. Table 3 provides a summary of Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) exposure limits and ceilings. These tables are provided to illustrate a number of points regarding protection of human health. First, it is clear from the typical urban ambient air concentrations that metal concentrations in urban centers of the U.S. may be in excess of the toxicity and dose-response based human health effects concentrations developed by scientific and regulatory agencies. According to the most recently published data by the U.S. Bureau of the Census (2000), approximately 80% of the U.S. population lives in urban areas, which makes urban air a priority for protection of human health. In addition, urban areas with a high proportion of industrial activity would expect to see significantly higher ambient air metals; rural or remote areas typically do not observe equally elevated levels of ambient metals, unless they are near a specific source (see levels presented in Appendix C, Table 1).

An important element of certain urban air ambient metals is that concentrations tend to be anthropogenic in origin. Crustal elements tend to be introduced into the air through mechanisms such as suspension of soil by wind, volcanic activity, and weathering of ores and minerals; these particles are typically larger (i.e. greater than 10 μm), fall quickly from the air column, and do not typically reside in the respirable fraction of particulate matter.[15] In contrast, metals introduced to the air through anthropogenic activities tend to reside in the smallest particles (i.e. less than 10 μm). These particles pose increased risk to human health. Not only do these small particles have the potential to remain airborne for longer (around 100 days),[16] this size of particle can deposit deeper in the lungs eliciting a stronger inflammatory response.[5]

When comparing the levels considered to adversely affect human health at a community level versus levels permissible in an occupational setting, it is clear that a large discrepancy exists. Although the occupational scenario considers a shorter duration of exposure (i.e. an 8- to 10-hour work day), occupational exposure levels (OELs) are not necessarily keeping pace with current scientific knowledge. The advantage of OELs is that they are produced through a very strict process that provides checks and balances, which makes these limits legally enforceable.[17] However, when looking at exposure limits for Nickel, the most relevant medical and toxicological literature lists an acute (1-hour) average of 6 $\mu g/m^3$ (as reported in California EPA's reference exposure level (REL)), whereas the 8-hour permissible exposure limit (PEL) is 1,000 $\mu g/m^3$ (which equals 125 $\mu g/m^3$ for 1 hour). Even more recent data, such as research being performed by Lippmann and Chen at New York University's School of Environmental Medicine, suggests that nickel at even the lowest ambient levels has the potential to cause adverse health effects.[12] In an article presented in Environmental Health and Safety Today, John F. Meagher states, "Most environmental, health and safety professionals will admit that strict adherence by employers to OSHA's PELs, especially older ones or those that have not kept pace with scientific health risk knowledge, will not protect a company from liability or be able to be argued as a gold standard of occupational health care for its workers."[16] Further discussion on contemporary health effects of metals in ambient air is presented in Appendix C.

Table 2. Community Metals Concentrations of Concern (µg/m^3)

Metal	Typical U.S. Urban Air Concentration[c]	Typical Health Effects Concentration[e]		
		Acute	Chronic	Cancer
Antimony[a]	0.032	-	0.2	-
Arsenic[a]	0.02[d]	0.2	0.015	0.0002
Beryllium[a]	0.002[d]	-	0.02	0.0004
Cadmium[a]	0.008[d]	0.03	0.01	0.0006
Chromium[a]	0.02[d]	-	0.01	-
Chromium VI[a]	0.0016[d]	0.3	0.1[f]	0.00008
Cobalt[a]	0.0005[d]	-	0.0063	0.00027
Copper	0.29	100	-	-
Iron	1.6	-	-	-
Lead [a,b]	0.04[d]	-	0.15[b]	0.03
Manganese[a]	0.02	-	0.05	-
Mercury[a]	0.014	0.6	0.3	-
Nickel[a]	0.02[d]	6	0.05	0.004
Selenium[a]	0.015	-	21	-
Silver	0.004	5	20	-
Vanadium	0.065[d]	0.8	0.1	0.00029[g]
Zinc	0.103	-	-	-

[a] Metals designated as Hazardous Air Pollutants by the EPA.

[b] National Ambient Air Quality Standard for lead is 0.15 µg/m^3 as a rolling three month average

[c] Typical urban ambient air concentrations procured from the EPA, the Association for Toxic Substances and Disease Registry (ATSDR), the Hazardous Substances Database (HSDB), and/or the World Health Organization (WHO). The majority of the values are based on PM_{10} measurements taken in the 1980's and 1990's, but may include TSP or $PM_{2.5}$ measurements. These values are not absolute; they are intended to represent typical concentrations found in urban environments.

[d] Ambient air values exceed one or more of the regulatory health limits for that metal.

[e] Typical health effects concentrations (acute, chronic, and cancer) are set by EPA, ATSDR, and California EPA. These levels, where available, represent concentrations at or above which health effects might occur.

[f] Typical chronic concentration for Chromium VI is for particulate matter, a typical chronic level for aerosols and mists is approximately 0.008 µg/m^3

[g] Typical cancer concentration is for vanadium pentoxide

Table 3. Occupational/Industrial Limits for Metals of Concern (µg/m^3)

Metal	Carcinogen?	IDLH	NIOSH REL (10-hr TWA)	OSHA PEL (8-hr TWA)
Antimony [a]	No	50,000	500	500
Arsenic [a,b]	Yes	500	2[b]	10
Beryllium [a,c]	Yes	400	0.5	2
Bismuth [d]	No	N.D.	5	5
Cadmium [a]	Yes	900	N.E.	0.005
Chromium [a]	No	250,000	0.5	1
Chromium III [a]	No	2,500	0.5	0.5
Chromium VI [a]	Yes	-	0.001	0.005
Cobalt [a]	No	20,000	0.05	0.1
Copper [e]	No	100,000	1	1
Lead [a,f]	No	100,000	50	50
Manganese [a,g]	No	500,000	1000	5,000
Mercury [a,h]	No	10,000	0.1	100
Nickel [a,i]	Yes	10,000	15	1000
Selenium [a,j]	No	100	200	200
Silver	No	10,000	10	10
Vanadium [k]	No	35,000	50	50

IDLH = Immediately Detrimental to Life and Health

NIOSH = National Institute of Occupational Safety and Health

REL = Recommended Exposure Limit

OSHA = Occupational Safety and Health Administration

PEL = Permissible Exposure Limit

[a] Metals designated as Hazardous Air Pollutants by the EPA.

[b] NIOSH REL for arsenic is a 15-minute ceiling

[c] OSHA PEL for beryllium has a 30-minute ceiling of 5 µg/m^3

[d] REL and PEL for bismuth is a respiratory limit, the total REL is 10 µg/m^3 and total PEL is 15 µg/m^3

[e] Additional REL of 0.1 and PEL of 0.1 for copper fume

[f] NIOSH REL for lead is an 8-hour TWA standard

[g] NIOSH short term exposure limit (STEL) for manganese is 3,000 µg/m^3 and the PEL is a ceiling limit

[h] NIOSH REL for mercury for skin is 50 µg/m3 and the REL is a ceiling

[i] Nickel as $Ni(CO)_4$ has an IDLH of 14,000 µg/m^3 and an REL and PEL of 7 µg/m^3

[j] Selenium as SeF_6 has an IDLH of 2000 µg/m^3 and an REL and PEL of 400 µg/m^3

[k] NIOSH REL for vanadium is a 15-minute limit

2.5 Regulatory Approach

Three regulatory approaches were considered for development of fugitive metal emissions monitoring based on this new continuous multi-metals fence-line technology including: 1) Source-oriented MACT; 2) Ambient-oriented MACT; and 3) Ambient concentration limit or goal.

The first approach was rejected in part because the uncertainties in model estimated emissions are expected to be unacceptably high; it is unlikely that an industry MACT base could be established for each fugitive emission category; and it doesn't appear to be used in other regulatory applications. The second option was excluded on similar grounds, as well as the fact that it has not been used before and would require considerable development with little likelihood that an ambient MACT base could be established. The third regulatory approach was selected because of the following advantages:

1) It is currently being used for fugitive organic vapor emissions;
2) It can be implemented immediately;
3) It is expected to be both precise and accurate (~10 to 20%);
4) The modeling tools and enforcement experience (NAAQS, SIP) are available;
5) It allows for maximum source flexibility;
6) It is relevant to health, residual risk, environmental justice and right to know; and
7) It can be implemented in a single airshed independent of other airsheds.

A more in depth discussion of current regulatory approaches, suggested exposure limits, and general health effects resulting from exposure to metals is provided in Appendix C.

3.0 Overview of Multi-Metals FLM Technology

This subsection provides a brief overview of contemporary multi-metals FLM technology and its measurement capabilities. Appendices A and B provide the performance specifications and on-going quality assurance procedures to assure the reliability of the metals concentration data reported by the FLM. This brief technology overview is intended to provide the user with the background needed to develop a monitoring plan using a multi-metals FLM. For more details, you are directed to your specific FLM user's manual.

Contemporary multi-metals FLMs are based on a reel-to-reel filter tape sampling with simultaneous metals determination using X-ray fluorescence (XRF). This analytical technology for metals determination in PM deposits on filters has been routinely used in laboratories for decades and procedures for its use are described in EPA's Compendium of Inorganic Methods (IO 3.3). This XRF technology is combined with reel-to-reel filter sampling to provide continuous in-field measurements of metals with one-hour detection limits equal to or better than samples collected over 24 hours and analyzed in the laboratory.

In XRF, high energy X-rays from an X-ray tube irradiate a filter deposit as illustrated in Figure 1. These X-rays eject inner shell electrons from analyte atoms in the filter deposit creating vacancies that are filled by electrons from outer shells. The binding energy difference between

these two electron shells is given off in the form of X-rays characteristic of the element. These new characteristic X-rays plus scattered X-rays when measured with an energy dispersive X-ray detector form an X-ray energy spectrum that can be used to qualitatively identify the elements present by the peak energy and the amount of the element based on peak intensity. The elements that can be measured by laboratory XRF are illustrated with the periodic table shown in Figure 2. The multi-metals FLM is only able to quantify elements with atomic number 19 and above.

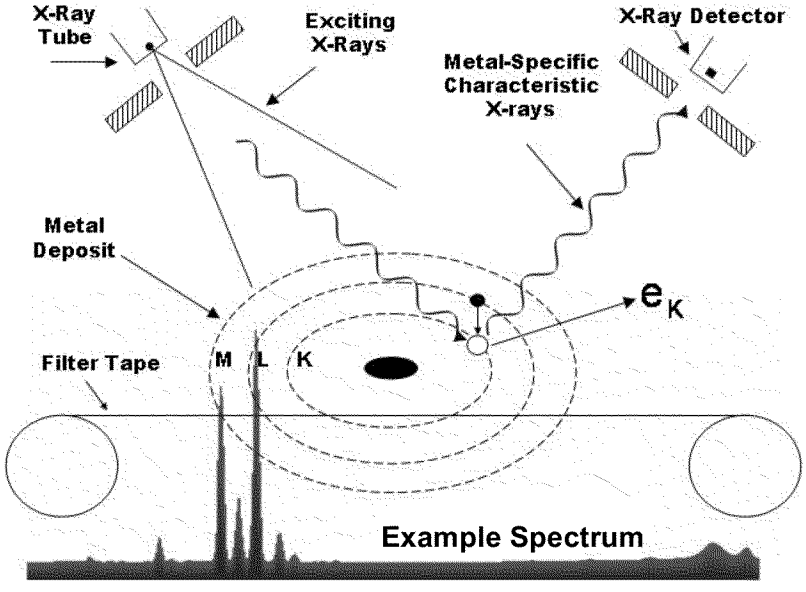

Figure 1: Diagram showing the main features of the multi-metals FLM technology

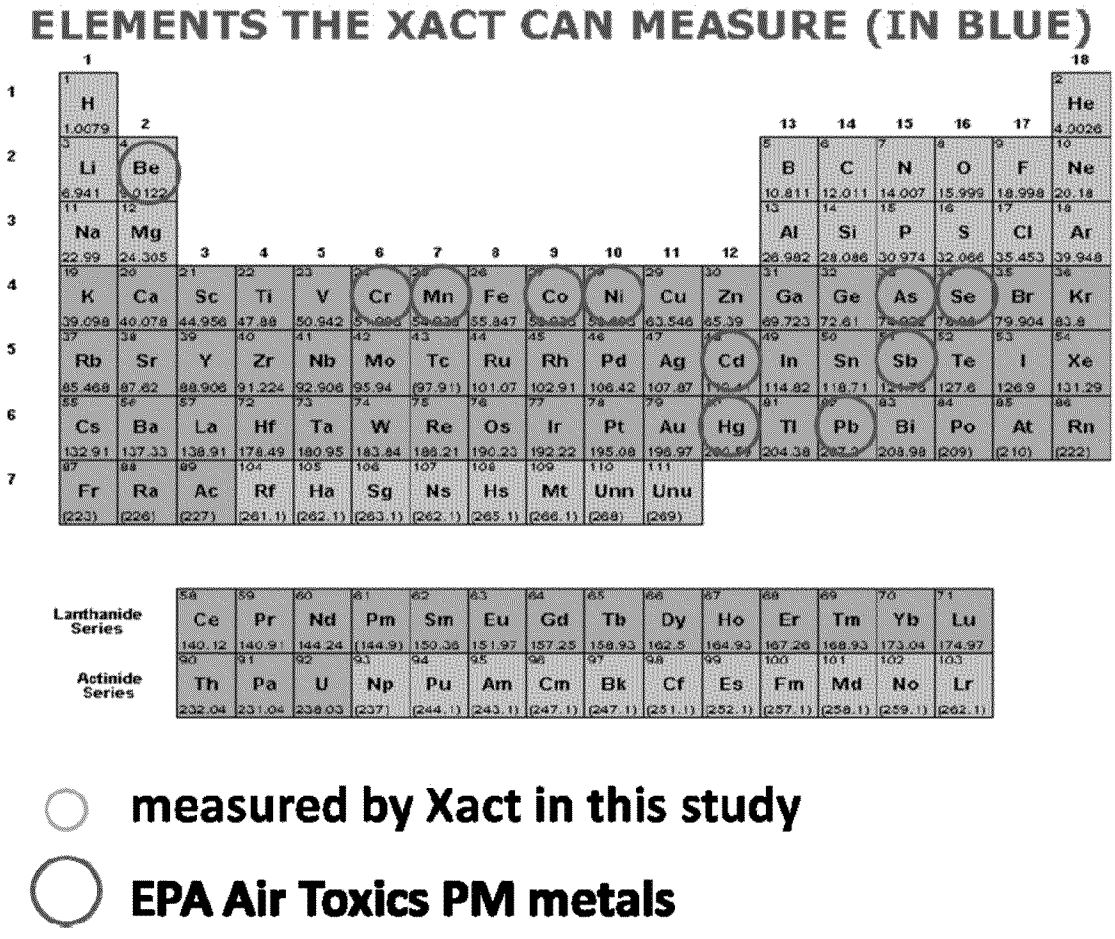

Figure 2: Elements that can be measured by XRF (blue)

A schematic of an ambient multi-metals monitor is illustrated in Figure 3[18]. Figure 4 depicts a real-world example of an air-conditioned monitoring shed that houses a multi-metals FLM. The FLM consists of a PM_{10} inlet and temperature sensor, a sampling and analysis module and a flow control module. It operates by drawing 16.7 liters per minute through a PM_{10} size-selective inlet and a filter tape located in the sampling and analysis module. At the end of a sampling interval that can last from 15 minutes to 4 hours (operator defined), the resulting filter tape deposit is advanced approximately 2 inches for analysis. While this sample is being analyzed for metal content, the next sample is being collected. The only dead time in the sampling and analysis system is about 20 seconds required to advance the tape and prepare for the next sample. The average metal concentration for each sampling interval is calculated by dividing the XRF-determined metal mass by the sampled volume. The resulting concentration (ng/m^3) is automatically stored in a computer and/or reported to a central monitoring location. Table 4 provides a detection limit summary for various metals measured by the Xact 620 monitor. In general the Xact one-hour detection limits are 2 to 20 times lower than the detection limits achieved using 24-hour FRM sampling followed by laboratory XRF analysis (FRM/IO3.3).

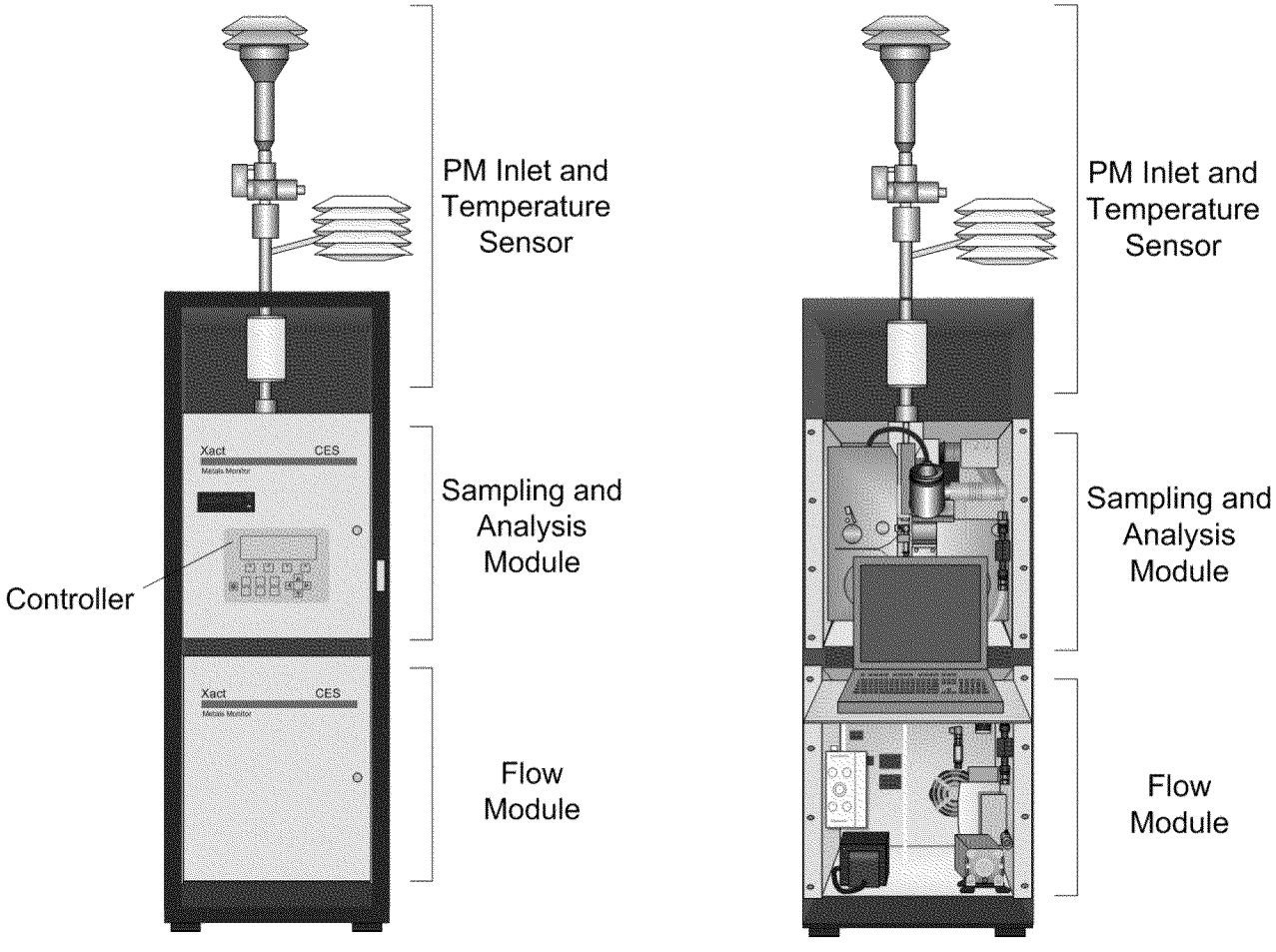

Figure 3. Schematic of the Cooper Environmental Services Xact 620

Figure 4. Photograph showing air conditioned monitoring sheds used to house an Xact FLM in Herculaneum, MO.

Table 4. Ambient Xact 620 Detection Limits Summary (EPA I03.3; 1 Sigma; Interference Free; ng/m^3)

Element	Atomic Number	4-hour	3-hour	2-hour	1-hour	30 min.	15 min.	FRM/I0 3.3 24-hour[a]
K	19	0.101	0.156	0.029	0.811	2.294	6.489	1.91
ca	20	0.040	0.062	0.113	0.321	0.907	2.565	2.74
Ti	22	0.022	0.034	0.063	0.177	0.501	1.416	5.13
V	23	0.019	0.026	0.048	0.137	0.388	1.097	1.61
Cr	24	0.014	0.021	0.039	0.109	0.309	0.873	0.91
Mn	25	0.008	0.013	0.024	0.067	0.190	0.536	0.24
Fe	26	0.010	0.015	0.028	0.080	0.225	0.637	0.21
Co	27	0.006	0.009	0.017	0.047	0.132	0.374	0.12
Ni	28	0.004	0.007	0.013	0.035	0.100	0.283	0.18
Cu	29	0.008	0.012	0.023	0.064	0.181	0.512	0.21
Zn	30	0.005	0.008	0.015	0.043	0.122	0.346	0.30
Ga	31	0.003	0.005	0.008	0.024	0.067	0.190	0.49
As	33	0.003	0.005	0.010	0.027	0.078	0.220	0.24
Se	34	0.004	0.006	0.011	0.032	0.091	0.257	0.21
Ag	47	0.103	0.158	0.290	0.821	2.321	6.565	6.09
Cd	48	0.169	0.260	0.479	1.353	3.828	10.827	6.70
Sn	50	0.318	0.489	0.899	2.543	7.194	20.347	9.30
Sb	51	0.083	0.128	0.235	0.665	1.880	5.318	9.57
Ba	56	0.050	0.076	0.140	0.397	1.124	3.179	15.78
Hg	80	0.005	0.008	0.015	0.043	0.122	0.346	0.46
Tl	81	0.006	0.009	0.016	0.046	0.131	0.369	0.46
Pb	82	0.007	0.010	0.019	0.053	0.151	0.426	0.46

[a] Federal reference method sampling for 24 hours and laboratory X-ray fluorescence analysis using EPA Compendium Method IO 3.3

4.0 Unique Aspects of Contemporary Multi-Metals Fence Line Monitors

Advances in measurement technology provide reliable and practical instruments for PM and multi-metals quantification over averaging times ranging from minutes to hours. Commonly used continuous PM monitors measure inertial mass, mobility, electron attenuation, light absorption, and light scattering properties of fine particles. While our increasing knowledge of coarse and fine PM has contributed significantly toward our understanding of PM health effects, the uncertainty of PM composition prevents us from understanding what causes PM toxicity. PM is not an entity in itself, rather it is a collection of compounds, aerosols, elements, etc, with widely varying toxicities. PM component species such as sulfate, nitrate, marine aerosols (sodium chloride), bound and adsorbed water, etc, which make up the most significant fraction of PM mass, are considered either benign or are thought to be relatively harmless. On the other hand,

trace PM component species such as vanadium, arsenic, nickel, lead, mercury, and organic compounds such as dioxins, furans, and polycyclic aromatic hydrocarbons may be highly toxic, hazardous, or potent even at relatively low concentrations. Multi-metals NRT monitors are designed to detect some of the most toxic components of PM and report the data in near-real-time.

PM and multi-metals FLM differ in their respective analytical range and sensitivity. However, in general, requirements for ambient air monitoring, including such aspects as sampling location, number of monitoring sites, and concern for local obstructions, are similar for both PM and multi-metals. While PM and multi-metals monitors are similar in some ways, such as their ability to make sensitive and accurate short time interval measurements and in their site selection criteria, a multi-metals monitor is unique in that it measures the individual metal components of PM. This component-specific quality of multi-metals FLMs has the capacity to provide invaluable tools towards defining the true toxic risk of PM and for characterizing specific metals emission concentrations and sources. Unlike PM, SO_2, CO, and other single parameter monitors, multi-metals FLMs can measure up to 30 analytes (see Figure 2), each with unique physical, chemical and toxic features (see Appendix C for a discussion on the individual human health effects and properties of certain metals). The analytical range of the multi-metals FLM data can be invaluable for assessing health risks and identifying specific sources.

In any monitoring scenario, a sampling regime begins with a pollution hypothesis, permit application, and/or an environmental concentration standard or limit. A multi-metals sampling plan will be designed specifically for the metals fraction of total PM, and therefore will need to consider particle size, detection limits and metals associated with a given source. One point of divergence therefore between a multi-metals and PM monitor pertains to source apportionment and begins at optimizing the particle size inlet to the specific metals source. The detection limits may also change depending on the element(s) the study hopes to characterize. In general, detection limits for PM monitors are several orders of magnitude higher than what is necessary to gauge the levels of multi-metals in ambient air, and detection limits for multi-metal FLMs can be in the low picogram range for some metals. Multi-metals occupy a small fraction of total PM, and multi-metals monitoring should be designed to accurately characterize ambient metals based on the given source(s).

In summary, multi-metals NRT monitors provide a more sensitive, detailed characterization of airborne PM by measuring the contribution and speciation of metals in near-real-time, 15-minute to four-hour intervals. With up to 30 elements measured with each sample, it is possible to conduct chemical mass balance receptor modeling with data from each measurement. Unlike 24-hour PM samples, multi-metal FLM data, with averaging times as short as 15 minutes, can be precisely related to wind speed and direction for improved source apportionment. The unique attributes of the multi-metals monitor have special relevance in assessing short and mid-term metals exposure and subsequent human health impacts, as well as apportioning metals emissions within a dynamic airshed.

5.0 Process Summary

Air quality is a dynamic and complex environmental parameter exhibiting large temporal and spatial variations due to changes in meteorological conditions, local topography, and source

emission rates, that in-turn contribute to changes in dilution, chemical reactions and removal rate of pollutants. The EPA recognizes that monitoring air quality is an integral part of the control and minimization of source emissions and the protection of human health and the environment. Although protection of human health represents the ultimate goal, monitoring objectives other than compliance demonstration such as source apportionment, evaluation of risks and control effectiveness, defining background levels, documenting air quality during site activities, etc. can represent primary objectives that might drive specific multi-metals monitoring plans. As such, when designing monitoring programs, it is important to define overall program objectives and systematically address key components to make the program technically defensible and cost-effective. It should be clear that each step is interdependent and that a properly designed plan will consider each step in terms of the effect on the other parts of the plan. Core components of these programs include such topics as identifying target parameters and action levels, monitoring instrumentation, data/telemetry, data processing, archiving, quality control, etc. With these component considerations, a viable and cost-effective air monitoring plan can be developed.

This guide for using a multi-metals FLM in a metals monitoring program consists of several general steps requiring the user to define the problem consisting of establishing the driver and goal; define the airshed and resources; and develop a plan to achieve the goal based on the airshed boundary conditions and available resources. The detailed steps in this general process are outlined in Figure 5.

Step 1. Define the Driver: It is assumed that the need to develop a metals monitoring plan is driven by either a source requesting a new or renewed permit to operate, a potential health concern based on previous ambient measurements, a need to monitor emissions at a remediation site, or to provide support for a lead state implementation plan (SIP). In the case of a permit request, the source is clear, while in the case of a measured ambient concentration of concern or providing SIP support, the impacting source may not be as certain. In these latter two cases, it may be necessary to first conduct a source apportionment study to define the source(s).

Step 2. Define ambient goal or limit: This step requires the guide user define an ambient limit or goal; i.e. define the:

- Indicator – metal and PM size fraction
- Level – concentration
- Period – averaging time
- Form – number of allowed exceedances

In the case of lead for which there is a NAAQS, these are already defined. However, for all other metals the guide user will need to define these parameters based on available ambient measurements and health effects data such as that summarized in Appendix C.

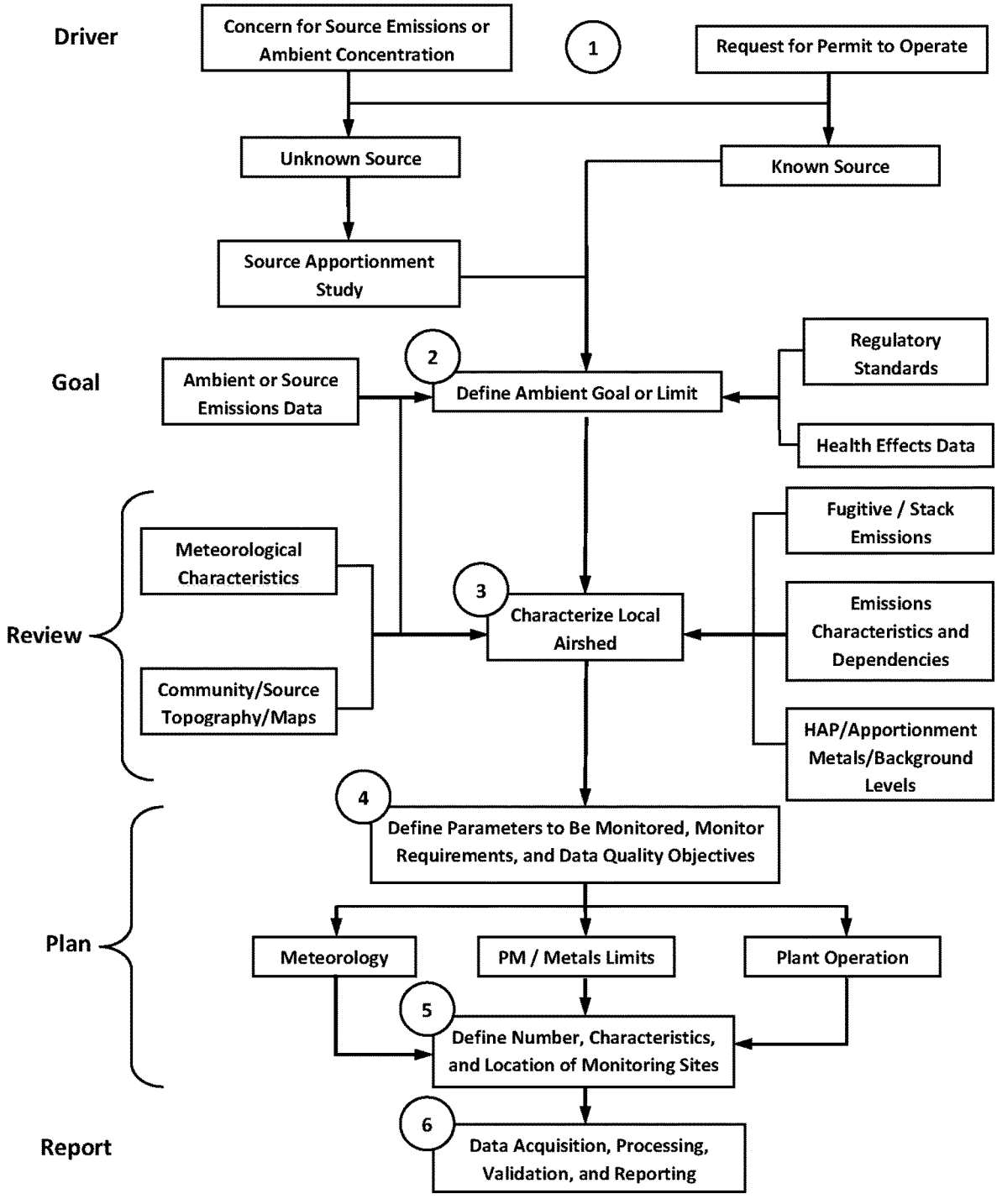

Figure 5. Flow diagram illustrating key steps in developing a fence-line monitoring plan for fugitive metals emissions

Step 3. Review and Characterize the local Airshed features: Before the user can develop a monitoring plan, the relevant features of the local airshed must be explicitly defined. Meteorological features, such as wind roses and meteorological regimes responsible for varying levels of PM and metals, etc. must be characterized. The topography and location of other sources, existing monitors, and meteorological stations also should be described. Regional emissions inventories need to be established for key species that might require goals or limits. Emission inventories might also be used to estimate source contributions, as well as to establish expected background concentrations.

Step 4. Define parameters to be monitored: Once the problem has been defined and the airshed characterized, it is now possible to begin the planning steps by defining the specific parameters to be measured. This includes, but is not limited to, meteorological parameters like wind speed and direction, metals and PM concentrations, plant operations, etc.

Step 5. Define number, characteristics and location of monitoring sites: With the above information defined and available, it is now possible to define the number, purpose, characteristics, and location for each monitoring site.

Step 6. Outline data processing and reporting channels: The metals FLM monitor will likely have built-in data processing and storage components, which can be accessed remotely. Data reporting will be based around the specific monitoring and regulatory requirements of the program. Data reporting format, frequency, and extent will need to be defined considering the various public and private stakeholders involved in the ambient metals monitoring plan.

6.0 Define Driver (Step 1)

The driver(s) is (are) expected to be different for each airshed, but as indicated in Figure 5 will likely be initiated by either a new or renewal permit request, concern for ambient concentration, previous measurements suggesting potential health concerns, or a lead NAAQS State Implementation Plan (SIP). Illustrative examples of process applications are presented in Appendices D through H. Although the airsheds and conditions in these examples are based on actual airsheds and sources, the process application is hypothetical and used to illustrate how the process might be applied in a real-world situation. For example, the procedure applications described in Appendices D and E are based on lead smelters; one a secondary lead smelter in an industrial area of Los Angeles (Appendix D) and the other an integrated primary lead smelter in a rural area of Missouri (Appendix E). Although these are quite different applications of the procedure, the primary driver is the same in both cases; i.e. monitoring to demonstrate compliance with the lead NAAQS, to assist with source apportionment, and/or concern for potential health impacts from other elements such as antimony and cadmium. Although lead is the primary driver in both these examples, secondary drivers might be quite different because of the more complex processes and materials used in a primary lead smelter compared to a secondary lead smelter.

Applying the procedure to a primary copper smelter is illustrated in Appendix F. In this case, the driver is concern for community health due to exposure to fugitive arsenic emissions from a known source. Contemporary and historical 24-hour PM_{10} arsenic measurements suggest that NIOSH health limits, set at 2 $\mu g/m^3$, which is a ceiling level never to be exceeded over 15

minutes, may have been exceeded in the local communities of Hayden and Winkelman, Arizona, on numerous occasions over the past two decades. The key goals in this particular example are to measure short-term average arsenic concentrations in the community to characterize actual acute exposures, develop a monitoring and control plan to eliminate these possible NIOSH exceedance events, and reduce the community's general exposure to arsenic and other HAP metals.

Appendix G illustrates the application of the procedure to an airshed with a ferrous metal foundry and recycling facility. The driver in this example is assumed to be a permit renewal and community concern for metal emissions. The situation in this example is substantially more complicated, in part because of the emerging health concerns for exposure to transition metals, such as iron, nickel, and vanadium. Although previous metals measurements have not indicated exceedances of any health standards, short-term exposures to elements such as manganese, iron, nickel, zinc, and lead are of concern in light of these newly emerging PM health findings. In contrast to the other applications, there are also potentially significant metals contributions to daily exposures from background and other sources in the area. As such, there is an additional driver to apportion the metals to possible contributing sources.

The last appendix (H) illustrates another example where there is some uncertainty in the source contribution and, therefore, will also have a source attribution driver component. The primary driver is similar to the copper smelter; i.e. concerns for public health due to measured community exposure to arsenic concentrations exceeding the 15-minute NIOSH ceiling limit. In this case, a two hour average concentration was recorded (2.3 $\mu g/m^3$) that exceeded the 15 minute ceiling (2 $\mu g/m^3$) in the airshed of East St. Louis, Missouri. This particular example is further complicated because the source has not been unequivocally identified, but the functioning hypotheses is that the high community exposure is due to plume fumigation from a hazardous waste incinerator. Thus, the primary driver is health concern for the community with a source attribution and environmental stewardship component.

Clearly, the goals of these applications and resulting monitoring plans will be significantly different for each of these illustrated examples based in part on differences in their primary drivers. For example, the arsenic exposure drivers are more urgent than the health concerns of the ferrous metal recycler, and require more extensive efforts to identify the fugitive and/or stack emission sources, prevent future exposures of similar magnitude, and develop plans to control and enforce emissions reductions on the responsible sources.

7.0 Define Limits and Goals (Step 2)

Except for the lead NAAQS, there are no enforceable ambient standards or clearly defined limits for the other HAP metals. California and Region IX EPA list RELs and regional screening levels (RSLs) (Table 2), but they appear to provide general guidelines for community exposure and risk assessment, as opposed to permitted and enforceable limits. OSHA and NIOSH list exposure limits enforceable in the workplace (Table 3) just inside a fence-line but are not enforceable outside a fence-line. However, it is essential that a goal or permitted limit be established before a meaningful monitoring plan can be established. As such, the guide user will need to define these limits or goals. In some cases, this may not be difficult. For example,

in the case of the two arsenic exposure cases, it is clear that no community should be exposed to concentrations that workers are not allowed to be exposed as a short term limit. In addition, one could reasonably argue that the community, which includes the "at risk" sub-population, should not be exposed to even one-tenth the allowable worker exposure. Appendix C is provided to assist the guide user in defining these limits and/or goals.

Any limit or goal will need to define an indicator (metal and particle size), concentration limit or goal, averaging times and form (allowed exceedances and/or a progress schedule). As such, the starting point is to review ambient metal concentrations and dispersion model screening estimates to determine likely metals of concern based on their measured or modeled concentrations relative to regulatory standards, limits, guidelines, or other known health effect levels. Based on these comparisons, it should be possible to define limits that should not be exceeded, action levels (concentrations that if exceeded trigger an action to reduce emissions by the likely source), and/or longer term goals to work towards. Figure 6 illustrates a hypothetical example for Hayden and Winkelman, AZ, two communities near a large primary copper smelter, as discussed in Appendix F. In this example, a limit never to be exceeded is set at one tenth the 15-minute NIOSH ceiling limit averaged over one hour. The California acute REL for arsenic is also set at this specific concentration.

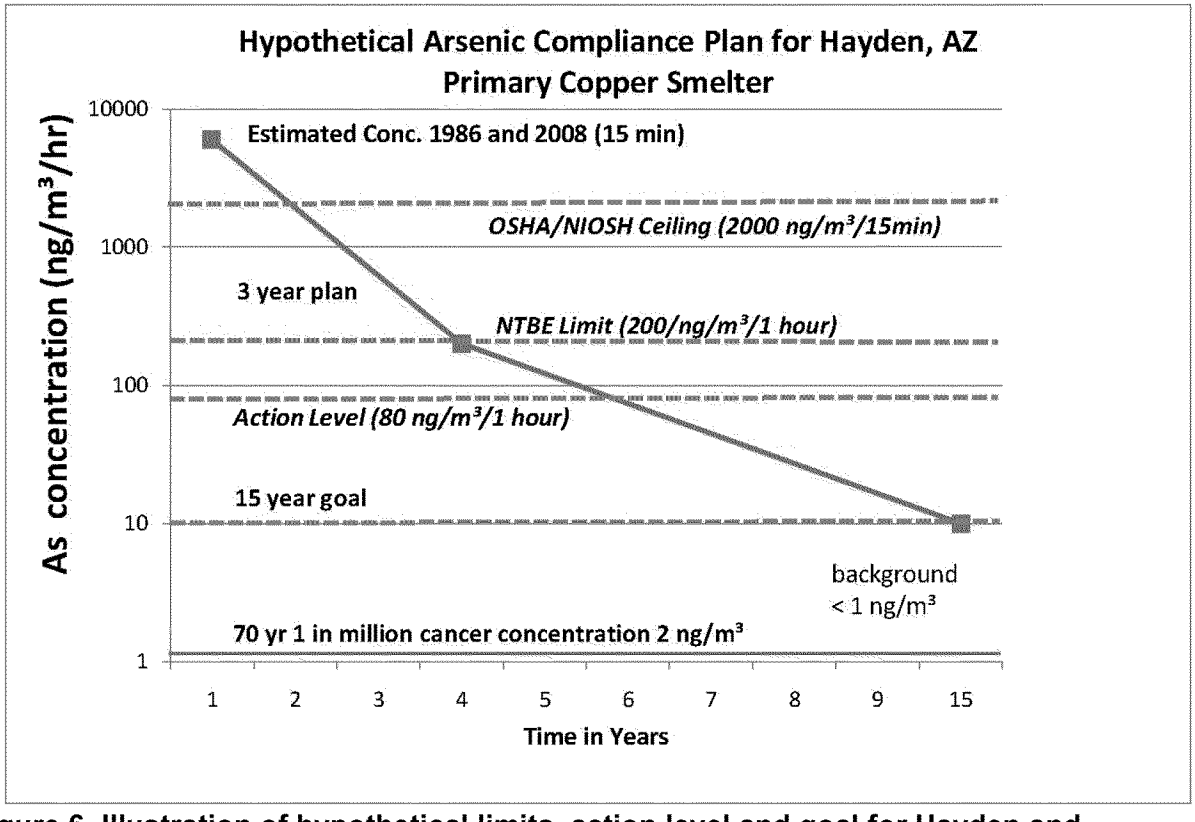

Figure 6. Illustration of hypothetical limits, action level and goal for Hayden and Winkelman, AZ as discussed in Appendix F

The Action Level concentration is set lower than the "never-to-be-exceeded" community or fence-line concentration limit, and represents a level of heightened concern above which the

facility should gather data and develop a plan to reduce emissions. If this concentration is exceeded, the smelter will need to take immediate action to mitigate emissions through correction of any plant upsets or shut the process down to prevent the limit from being exceeded. The third concentration shown in Figure 6 is a goal the facility needs to progress towards through improved understanding of the causes of high concentration events, improvements in controls, and process management.

A similar set of limits and goals might be set for the hazardous waste incinerator example in Appendix H. The limits and goals for the two lead smelter examples will be determined primarily by the lead NAAQS requirements and as determined from federal reference method monitors. The use of FLM in these two applications would be 1) to improve understanding of those processes and events that are responsible for the short-term high concentration events; and 2) evaluate short-term exposure levels to other HAP metals and their sources.

Other FLM applications will need to develop risk-based ambient action levels and goals based on receptor models and potential risks to human health. For instance, it is more difficult to set goals and limits for the ferrous metal recycler example described in Appendix G because there is no clear imminent danger or standard involved. On the other hand, contemporary research into PM health effects summarized in Appendix C is strongly suggestive that exposure to metals like manganese, iron, zinc, and lead, as emitted from the source, is likely to represent a health risk that could be minimized through improved process management and controls. In this hypothetical example, it is assumed that the plant's permit is up for renewal. Historical measurements and anecdotal information from the surrounding community in the form of complaints of occasional "metal odors" is suggestive of fugitive emission events that could be potentially hazardous, and could be reduced with FLM and NRT feedback to plant management.

Action levels are toxic air concentrations which trigger remediation activities and/or shut-down of site activities to help reduce the possibility of adverse health impacts near a project site. Action levels for targeted parameters should be developed as risk-based, consistent with EPA guidelines[19] to protect human health and the environment for short-term acute and long-term chronic exposures. The approach and methodology used to calculate the various action levels should be described in detail. As noted earlier, this is becoming more of a challenge as the community learns more about the role metals contribute to PM health effects.

Determining parameter-specific action levels during the initial monitoring program design will help determine what monitoring instruments should be used. The first step in a risk-based action level calculation is to determine the specific metals of interest at a site. Note that target parameters will likely change from site to site. It is critical to evaluate human exposure potential at each monitoring site. Human receptors include residents, workers at nearby businesses, schools, hospitals, day care centers, etc. Wind direction and other meteorological data can be used to identify receptors that are likely to receive the highest air concentrations.

The main airborne metals exposure pathway for humans is inhalation of particulates. Depending on the receptor and location, the length and type of exposure will vary. For example, if a residential location was maximally affected, adult and child receptors should be evaluated. For a business location, only an adult receptor would be evaluated.

The average length of exposure time for residential versus worker receptors also varies. For example, residential receptors have longer exposure times and are generally calculated over a lifetime (i.e. 70-years), whereas occupationally exposed workers have exposure times calculated based on an average work week (i.e. 8-hours per day, 40-hours per week). In addition, the distance of a receptor from a site should be factored into developing action levels. Lower action levels are appropriate when the receptors are a further distant from a pollution source.

Toxicity assessments for action levels involve identifying toxicity values for the chemicals of interest. In human health risk assessment, chemicals should be evaluated for noncarcinogenic and carcinogenic properties. Toxicity values are available from EPA databases and from some states (see lists in Appendix C and in Tables 2 and 3 for examples). In addition to identifying toxicity values, state or federal ambient air quality guidelines should also be identified. It may be necessary to base the action levels on these guidelines.

Once the exposure and toxicity information is collected, action levels should be calculated following EPA risk assessment guidelines at receptor locations. Action levels should generally be derived using human health-based criteria for different averaging times and subjected to normal variations in atmospheric dispersion. The results of air modeling should then be used to calculate action levels at the fence-line. The fence-line action levels can then be used to design the final perimeter monitoring program.

8.0 Characterize Local Airshed and Emission Sources (Step 3)

The type of information required to characterize the airshed and contributing emissions sources is expected to be generally available to the local or regional air quality management group, as well as community residents. However, it may not be explicitly defined and readily available for the monitoring plan development process. The task here is to explicitly define the relevant details of the airshed and sources that will be required to make decisions such as where to locate monitoring sites, averaging times, metals to measure, and other characteristics of monitoring sites. This database should include all the normal information that will be needed to locate monitoring sites and should include such items as:

- Local, regional, plants and community topography and maps showing the location of major topographical features, sources, major structures, current monitoring sites, government buildings, etc.
- A list of local sources with their specific emissions inventories, defined emissions characteristics and dependent variables such as wind speed and direction dependencies, process events, etc.
- Meteorological characteristics such as wind speed and direction, wind roses, regime categorization, dependences of emissions on meteorology, etc.
- Historical ambient and source measurements, and results of source attribution studies.
- Survey modeling results indicating points of maximum likely impact.

With this information in hand, the guide user can move on to Step 4, where decisions can be made with regards to the characteristics of monitoring sites and parameters to be measured at each monitoring site.

9.0 Define Parameters to be Monitored (Step 4)

Step 4 is the first step in developing your metals monitoring plan. Key components of the monitoring plan are developed through completing Steps 4 through 6 of the procedure. There are many references available that describe procedures that can be used to design monitoring programs, establish sites, assure data quality, etc. As noted earlier, a representative selection of these references are provided for the guide user in Section 13 (General Air Monitoring System Design Bibliography). The objective here and in the following sections is to assist the guide user in defining and selecting optimal multi-metals FLM operating parameters, monitoring locations and other conditions unique to this type of monitor to achieve the user's objectives in the most cost effective manner.

In Step 4, the guide user is required to define the parameters that must be measured to achieve the monitoring plan's goals, measure and apportion key species, and relate these measurements to specific plant operations. This will typically include meteorological parameters like temperature, humidity, wind speed and direction; PM mass; key metals required to assess health issues and apportion contributions to sources; and plant operations. Plant operation logs will be helpful in this process of assigning contributions and providing support for continual improvement in reducing emissions.

The parameters to be monitored generally fall into the following categories:

- Parameters related to the primary metal(s) of concern
    - Indicator – TSP lead, PM_{10} arsenic, PM_{10} manganese, etc.
    - Averaging time – three month average for lead NAAQS; one hour average for arsenic; to be determined for other metals, but may be as short as one hour even for lead if source apportionment is a primary objective
    - Concentration level – 150 ng/m^3 for TSP lead, 200 ng/m^3 for PM_{10} arsenic, to be determined for other metals
    - Form – not-to-be-exceeded, action level, goals

- Parameters related to source apportionment, emissions reduction and/or potential health effects
    - Wind speed and direction – Continuous and high enough to avoid perturbations of general air flow direction from local surroundings. A ten-meter tower is preferred to minimize impact of local turbulence caused by nearby structures and to provide a better estimate of the general air flow representative of the source and monitor.
    - PM mass – A measure of continuous PM mass is preferred so it can be directly related to the metals measurements. This will prove useful for source apportionment and correlations with other PM monitoring locations where metals FLM may not be available.

- Other metals – Selected on the basis of potential health effects and emission characteristics. Metals such as potassium, calcium, transition metals, copper, zinc, arsenic, selenium, cadmium, tin, antimony, mercury and lead have proven to be useful in past monitoring and apportionment programs.
- Organic and elemental carbon – Continuous monitoring of these two parameters can, like PM, be useful both for source apportionment, as well as in relating continuous metals measurements with a FLM at one monitoring site to similar measurements at other secondary monitoring sites.
- Gas and vapor indicating species such as CO, CO_2, SO_2, HCl, Cl_2, etc. – Continuous monitoring of these species, although perhaps not required for the basic monitoring plan, can, like the organic and elemental carbon measurements, prove useful in source apportionment. For example, measurements of HCl and/or Cl_2 can be useful in identifying impacts from thermal decomposition of plastic materials that are commonly associated with stack emissions from secondary lead smelters and municipal or hazardous waste incinerators. Of course, SO_2 would also be useful in identifying impacts from fossil fuel combustion, ore roasting/smelting, coke reducing procedures, etc.
- Log of source operations – Although this may be routine for major plant operations, it is less common for processes that can contribute to fugitive emissions. However, with the improved time resolution of metals measurements available with contemporary multi-metals FLM, keeping detailed records of these fugitive emissions will greatly aid the apportionment process and as a result improve the plant's emissions management and control efficiencies.

Of the above parameters that might possibly be measured, the three parameters that are generally most important are the metals speciation, wind speed and direction, and PM mass.

In the case of the two lead smelter examples (Appendices D and E), it would clearly be necessary to measure the parameters defined by the lead NAAQS. In addition, depending on if the areas are in attainment or not, measurement of wind direction and speed along with source apportionment metals would be helpful. In the case of the primary lead smelter, measurement of cadmium is important because of its potential health effects, expected high concentrations and utility in apportioning lead to its potential fugitive sources within the smelter. Arsenic would not be essential in either of these airsheds because, historically, its concentration has been relatively low. Even if the local airshed is in attainment of the lead NAAQS, there should be an interest in continuing to reduce lead concentrations because of the growing body of evidence that it is detrimental to human health at any concentration. Short-term high concentration episodes can frequently be responsible for a substantial portion of a longer-term average concentration. If the cause of the short-term event can be identified, it might be eliminated and thus contribute to reaching still lower ambient concentration goals.

Arsenic is obviously an essential parameter to measure at the copper smelter, along with other species that might help identify the responsible fugitive emission within the smelter. Since historical measurements of arsenic have indicated that over 85% of the measured arsenic mass was less than 2.5 microns, the appropriate indicator would probably be $PM_{2.5}$ arsenic. This size

limitation would also help in the source apportionment, since it eliminates some of the interference from other possible sources. In addition, since there is the potential that a significant fraction of the arsenic could exist in the vapor phase, a special study should be conducted to determine the vapor-phase arsenic fraction. Continuous wind speed and direction should also be included in the list of measured parameters and would be especially helpful in determining whether the arsenic is coming primarily from activities such as slag pouring or kettle tapping.

Arsenic would also be an essential parameter to measure in East St. Louis; however, measurement of other metals may also be useful in identifying a source or narrowing down the list of potential sources of the high arsenic episode. This is due to the fact that there were no other significantly measurable elements associated with the previous arsenic episode, and because of the unique, arsenic-intensive chemical fingerprint of the recent release, other metals may be useful in indentifying what sources are *not likely* candidates for the release. In addition, whereas there have been repeated measurements of elevated arsenic episodes in Hayden, there has only been the single (known) measured episode in East St. Louis. As such, one of the primary objectives in East St. Louis would be to establish the frequency of these episodes. Concern for the presence of vapor phase arsenic would take place after establishing that this episode was not an isolated event. In addition, since the only historical measurement available is PM_{10} arsenic, the indicator in this case should remain as PM_{10} arsenic. In this case, continuous measurement of PM_{10} as well as wind speed and direction are essential parameters to monitor. In the absence of other major elements associated with the high arsenic episode, continuous PM_{10} measurements would provide an indication of other, non-measured elements like oxygen or carbon being associated with the episode while wind direction would apply geographical boundaries to the source location. If the measured episode was the result of plume fumigation, the probability of repeating a similar measurement might be quite low, but fumigation could be taking place in other regions of the airshed. As such, the use of either a mobile metals monitor or additional secondary monitoring sites might be appropriate. As the study progresses, measurement of the fine particles (i.e., $PM_{2.5}$ or less) may need to be considered in order to assess human health risk.

In the case of the ferrous metal recycler example, there is also a major source apportionment component. As such, wind direction and speed are important parameters to measure in addition to a full complement of metals, including those of potential health concern (Cr, Mn, Fe, Ni, Zn and Pb) and those useful in source apportionment.

10.0 Develop Monitoring Plan (Step 5)

A formal monitoring plan should include sections such as:

- Monitoring objectives
- Monitoring site locations and parameters measured at each location
- Monitoring protocols, frequency of sampling, data reporting, etc.
- Instrumentation to be used at each monitoring site
- Action limits for key parameters
- Routine operational procedures

- Data telemetry approach
- Data reporting formats and frequency
- Monitoring system calibration and
- QC protocols.

In addition, each potential site needs to be evaluated for the following factors to determine the optimum number and location of fence-line air monitoring locations:

- Availability of electrical services
- Security of site perimeter
- Extent and length of perimeter boundaries
- Proximity of site activities to local residents and other sensitive receptors
- Risk analysis for nearby sensitive receptors
- Predominant wind directions, based on climatological analyses
- Ability to mobilize monitors from one site to another
- Time schedule for installation
- Budget considerations.

Although formal plans need to include the above components and discussions, only those aspects relevant to a multi-metals FLM network will be discussed here.

10.1 Network Specifications

The total of all air monitoring stations, meteorological monitors, calibration equipment, and data acquisition equipment required to meet the total objectives of a multi-metals air quality program represent the air monitoring network. To understand the interrelationships between the component parts of the network, allow decisions to be made about the number and type of each piece of equipment, and the interdependence of the equipment in meeting the study objectives, a set of specifications for the network must be developed early in the planning process.

Air monitoring network specifications should include the number of sites to be monitored, species to be measured, meteorological measurements at each site, duration of the monitoring program, including any special studies such as special measurements for source apportionment, manpower requirements, etc. These network specifications should be determined in light of known limitations of physical, engineering, economic and human factors as well as limitations due to equipment availability and completion deadlines.

Considering all of the stated sampling requirements and available resources, the types of air quality and meteorological monitoring equipment can be identified, including the number of samplers and analyzers for each type of measurement to be performed. Next the calibration systems can be defined for each analyzer and specified, which is then followed by specifying the data acquisition system. At this point, air monitoring specifications can be developed for each monitoring site in the network. Station specifications include the setting of sampling objectives for each station and the selecting of compatible hardware for each station.

There are typically eight discrete elements or components of a typical monitoring station that might be used in a PM and/or multi-metals program:

- Sampling inlet (TSP, PM_{10}, $PM_{2.5}$) and tubing to transport air sample

- Sample conditioning component to maintain integrity of air sample under a wide range of temperature and humidity conditions
- Sample collection
- Metal and/or other parameter analyzer such as PM, meteorological conditions
- Flow control and measurement component
- Calibration components
- Data recorder
- Equipment shelter and air conditioner

10.2 General Network Station Siting Criteria

Design of an air monitoring network involves trade-offs between what is considered desirable from a strictly technical point of view and what is feasible with the available resources. An ideal network will usually require more resources than are available. The objective is to design the least cost monitoring network still capable of meeting the major surveillance requirements. As noted earlier, choice of monitoring site depends on the objective of the monitoring program. Historically, these objectives or goals might include:

- Determine compliance with and/or progress made toward meeting air quality standards, limits, goals, etc.
- Activate emergency control procedures to prevent high metal concentration episodes.
- Document pollution trends
- Provide data to evaluate effects of pollution

Most of the criteria regarding the siting of individual samplers or continuous monitors are aimed at insuring the collection of a representative sample without undue influence from immediate surroundings. Some of these criteria include:

- Uniformity in height above ground level for the entire network of monitor inlets.
- Avoid constraints to airflow from any direction by placing inlets at least three meters from buildings or other obstructions.
- Surrounding area should be free from stacks, chimneys or other local emission points
- Elevation of inlets should be three to six meters above surfaces, which could contribute to reintrainment of surface deposited particles.

Some sites in your network may need to follow the above recommendations, but the location of the multi-metals FLM will need to be located at sensitive areas, such as modeled points of maximum impact from a fugitive emission source or short stack.

10.3 Site Selection for Metals FLM

The objective in this case is to locate your multi-metals FLM in the immediate area of a source, either at or near a fence-line or in a community in the immediate area of the source. The most important site criterion is to locate the monitor at a point estimated to represent the maximum concentration impact that is realistic from a community human health perspective. Identification of this point can be based on historical measurements or a dispersion screening model estimate. In the case of fugitive emissions, it is particularly difficult to estimate this point with dispersion models because emission characteristics are highly uncertain and are typically released close to the ground where local obstructions and turbulence can significantly influence the plume behavior. As such, monitor site location to capture fugitive emissions can be done on the basis of simple meteorological data, such as a wind rose, and locating the monitor near the fugitive source in the most probable wind direction. On the other hand, locations for low emitting stacks and elevated fugitive emissions should be based on dispersion survey model estimates of point of maximum impact.

Additional guidance details for preparing such monitoring plans are provided in the many references listed in **Section 13**. All monitoring plans represent a compromise between the ideal and the practical, guided by the reality of limited resources; this is the assumed condition in the examples discussed in this guide. A more detailed discussion is provided in the appendices. Only selected aspects of a plan are discussed and highlighted here to illustrate key points.

Sampling frequency can be separated into three categories depending on the field study.

If **continuous analyzers** are used, data should be available and averaged on a short-term basis (5, 10 or 15 minutes), depending on the program requirements. This frequency provides detailed and continuous information to help control emissions and protect sensitive receptors. Continuous monitoring instrumentation requires rigorous calibration and maintenance protocols which often limit data availability. Due to the relative immobility of continuous monitoring sites, it is often necessary to install enclosures at a number of locations.

Portable instrumentation provides more flexibility for fence-line monitoring and can be brought down wind of site activities to ensure that measurements are taken where emissions are impacting a site. The mobility of portable instrumentation also allows for periodic site surveys of the fence-line. A disadvantage of using portable instruments is that it is usually only possible to measure at a single location at a time. If a site is large, a survey may be impractical due to the time required for a single trip around the fence-line.

Integrated samplers collect a sample over a designated period and can be set up at multiple locations around the fence-line. Integrated samplers may be relocated easily without disruption of site activities. Analytical results of integrated samplers (usually provided by an off-site laboratory) will usually provide more speciated data than from continuous or portable instrumentation. Only one sample is collected per day and the data are generally not available from the analytical laboratories for up to 4 weeks.

Independent of the equipment used and the sampling frequency, perimeter sampling should be performed daily during all site activities. In addition, background perimeter monitoring should

also be conducted prior to site activities to help establish background levels for the target parameters and potential local offsite sources of the various analytes.

10.4 Primary Copper Smelter (Appendix F)

This copper smelter is located in the foothills of the Tortilla Mountain range about 50 miles northeast of Phoenix, AZ. Hayden, a community of about 400 residents, is located west of the smelter fence-line and Winkelman, a community of about 700 residents is located south of the smelter fence-line. The next closest community is about 10 miles west of Hayden and does not have a history of high metal readings. Contemporary and historical measurements of arsenic in Hayden suggest concentrations of arsenic have likely exceeded the NIOSH ceiling of 2,000 ng/m^3 on numerous occasions over the past two decades. The smelter and its associated operations are the accepted source of these high arsenic episodes and are assumed to be associated with fugitive emissions since ducted air pollutants are emitted from a 1,000 foot stack.

Driver: Concerns for community health resulting from exposure to high concentrations of arsenic is the primary driver, with a secondary driver focused on source apportionment and fugitive emission controls.

Limits and goals: Hypothetical limits and long-term goals for arsenic were noted earlier in Section 6.2 and illustrated in Figure 6. The primary indicator would be $PM_{2.5}$ arsenic. Historic data shows that 85% of arsenic is in the $PM_{2.5}$ fraction. This smaller particle size should improve the source apportionment study by eliminating course particle interference.

Specific plan limits include an Action Level set at 80 ng/m^3/1 hour. This concentration represents a value at which the plant should gather data and develop an effective corrective action approach. The concentration not-to-be exceeded (NTBE) is set at the California REL at 200 ng/m^3/1 hour. If ambient levels surpass the NTBE value, the facility should immediately suspend plant operations. The corrective action plan should be implemented to mitigate dangerous ambient arsenic concentrations in the community.

The long-term goal of the fugitive emissions study and FLM plan should be to reduce the concentrations in nearby communities to levels at or near background, or less than 2 ng/m^3/1 hour.

Existing monitoring sites: Current monitoring sites exist in the two communities. Two $PM_{2.5}$ monitoring sites with meteorological stations exist in Hayden: one at the Jail and the other closer to the smelter on Garfield Street. There is also a 24-hour $PM_{2.5}$ monitoring site on the top of the Winkelman School that abuts the southern smelter fence-line.

New FLM sites: Because these two communities are small, yet they receive different air flows from the smelter depending on the wind direction, it is recommended that two multi-metal FLM sites be established: One on the Winkelman School and one at the Hayden Jail site. These two multi-metals FLMs would be the primary supplement to its general monitoring programs. Two monitors are warranted because of the potential severity of the problem and the need to reach more acceptable limits and goals in the shortest possible time. These two multi-metals sites along with wind direction and smelter operational logs should provide adequate data to 1) identify the source(s) and; 2) take corrective action to mitigate the problem before the health

limit is exceeded. Additional monitoring sites in this case are not required because there are no other significant sources of metals up-wind of the smelter nor are there nearby significant population centers other than Hayden and Winkelman.

10.5 Hazardous Waste Incinerator (Appendix H)

East St. Louis is an industrialized urban center on the Illinois side of the Mississippi River. Recently, a multi-metals FLM operating in East St. Louis at an established monitoring site recorded a high arsenic episode that lasted for about eight hours. The episode's peak two-hour average concentration was 2.3 $\mu g/m^3$. This measured arsenic concentration exceeded the NIOSH 15-minute ceiling; i.e. a 15 minute average arsenic concentration that should never be exceeded in the workplace, yet several schools are located in the vicinity of the monitor. Based on wind direction during the peak concentration period and toxic release emission inventories for industries in the area, the source of arsenic was most probably a hazardous waste incinerator located less than two miles from the monitor. Furthermore, based also on the meteorology for the day, it is likely that the hazardous waste incinerator emissions from a short stack not only fumigated the monitor for an hour or two, but also fumigated regions of St. Louis on the west side of the river for six hours or more. This episode and the possible sources in the area are discussed in more detail in Appendix H.

Driver: The driver in this case is concern for community health resulting from exposure to high concentrations of arsenic. Although this was a single recorded event in East St. Louis and fumigation of this particular location may be relatively infrequent, further investigation into ambient air quality in the region is necessary. If it can be demonstrated that this, and other possible events like this, are the result of the hazardous waste incinerator stack fumigation, then the source should be required to place a multi-metals CEMS on its stack and limit its emissions of hazardous metals into the surrounding neighborhoods.

Although the primary driver for further monitoring is the concern for residents' health in the surrounding communities, the immediate driver is the need to substantiate the potential arsenic impact and identify its source.

Limits and goals: Hypothetical limits and goals for this airshed would be similar to those suggested for the copper smelter communities with the exception that the indicator should be PM_{10} arsenic since the recorded episode was a PM_{10} episode. However, because the stack emissions from the hazardous waste incinerator may contain other hazardous metals that could reach concentrations of concern during fumigation episodes, a full range of HAP metals need to be monitored during this initial source apportionment and fumigation substantiation period.

Local airshed characteristics: The airshed surrounding the possible source is characterized by relatively flat terrain accentuated with the Mississippi River depression. There is a substantial meteorological database for the area and extensive regional air pollution models dating back to the early 1970s that should make predicting potential fumigation events relatively precise.

Parameters to be monitored: This early stage of a monitoring program in this airshed should be defined by the objective to capture additional fumigation events from a clearly hypothesized source and unequivocally identify it as the source of arsenic and other possible hazardous metal pollutants. As such, a complete compliment of hazardous and source apportionment metals

need to be measured, as well as wind speed and direction. Key to this phase of the program will be defining meteorological regimes and locations for possible stack fumigation events.

Because the probability of a possible fumigation event occurring anywhere in the surrounding communities may be only about 10 to 20% throughout the year, it will be important to be able to predict the areas where and when this will most likely happen to maximize the probability of capturing such an event. Thus, not only will the local meteorological component of this program be substantial, but so will the dispersion model component be essential.

Monitoring Sites: In this particular example, monitoring sites need to be located based on model predictions where fumigation might happen. It is probable that in this case, four or five fixed, secondary monitoring sites would be established covering both sides of the river having both a meteorological station and PM_{10} sampler. Each fixed secondary site should consist of 24-hour sequential PM samplers using 47 mm diameter PTFE filters for subsequent XRF analysis to determine metals content. Because the subject is plume fumigation, the concentrations of hazardous metals are expected to be adequate for this sampling and analysis process. In addition, to keep monitoring costs to a minimum, only samples collected during possible fumigation periods as determined retrospectively would be analyzed.

Also in the interest of cost minimization, only one multi-metals FLM would be used in this initial monitoring program. This monitor should be reasonably mobile and located at a site predicted to have the highest probability of experiencing a fumigation event based on predicted meteorological regimes occurring that might contribute to an event at that particular location.

Data processing and reporting: Also to keep costs for maintaining this network to a minimum, it would be advantageous if the monitor(s) at each site have a degree of remote operation capabilities such that the sampler(s) can be turned on and off, and the data emerging from the device be monitored remotely, especially at the meteorological stations and the multi-metals FLM.

10.6 Ferrous Metal Recycler (Appendix G)

The ferrous metal recycler example does not necessarily represent an immediate health concern based on conventional exposure standards. However, the emerging body of evidence on the role of metals such as vanadium, manganese, iron, nickel, copper, zinc and lead in explaining the dominant portion of health effects of PM at typical ambient concentrations suggests that there should be concern for cases where possible exposure to these metals might be substantially greater than typical ambient concentrations.

This particular ferrous metal recycler and specialty steel manufacturer is located in a northwest industrial section of Portland, OR, near a transition to residential/commercial land use. A school is located in the nearby residential area about a mile from the recycler. Anecdotal information from local residents suggests that odors from the plant's fugitive emissions occasionally are detected in the neighborhood and concern for the possible health effects have been noted. An early prototype of a FLM was evaluated in the area and detected elevated concentrations of metals such as manganese, iron, lead and zinc coming from the direction of the facility.

Driver: The driver in this case is a combination of concern for the health of local residents and corresponding pressure from these residents. Thus, the driver here is a need to characterize

the short-term exposure conditions and in so doing, create a database that can be used to evaluate the potential health hazards in light of the emerging concerns for exposure to metals even at typical ambient concentrations.

Limits and Goals: There are no goals or limits in this particular example.

Airshed characteristics: This industrial section of Portland is located in a broad river valley running from southeast to northwest. During the summer months, the prevailing winds are out of the northwest putting the school and residential area downwind of the plant a majority of the time. The summer months of June through August would be the best time to conduct a brief study to evaluate the impact of the plant on the residential community.

Monitoring plan: There is currently an on-going monitoring program by the state in the area. The monitoring site is located in the residential area near the school. For this brief study lasting several months, it is recommended that the existing monitoring site be supplemented with a multi-metals FLM and operated during the summer months to develop an adequate database to evaluate potential health effects from short-term exposure to plant emissions. Impacts from plant emissions would be determined by wind direction, chemical mass balance and co-variance modeling.

10.7 Primary Lead Smelter (Appendix E)

Primary lead smelters are large industrial operations that incorporate three major steps: sintering, reduction and refining. The first step involves converting lead sulfide ore concentrates to lead oxide and lead sulfate sinter. This sinter is then converted to lead bullion in a reduction process using coke. The third step involves melting the relatively impure lead bullion and refining it to produce high purity lead with controlled impurities such as silver, copper, arsenic, zinc, iron and or bismuth. Emissions from most of these processes are controlled, but there are still leaks from buildings, upsets, emissions from materials handling, road dust, wind-blown dust, etc. The vast majority of process emissions are ducted to and emitted from a tall stack that typically does not impact the local or nearby surrounding communities.

Over the past several decades, a primary lead smelter located in Herculaneum, MO, has struggled first to meet the historic lead NAAQS at 1.5 $\mu g/m^3$ and now is struggling to meet the new lead NAAQS at 0.15 $\mu g/m^3$. In this process it has worked hard to enclose more of its operation and to improve its emission controls. However, it is still expected to be a challenge to meet the new standard.

A number of studies have been conducted over the past couple of decades to determine the distribution of lead in Herculaneum and in surrounding communities as well as to understand the particular operational processes within the plant responsible for the remaining lead measured in the community. A recent accuracy and precision demonstration study involving a multi-metals FLM during the summer of 2009 found that 16% of the samples collected represent 87% of the total measured lead mass during the study period. Even more surprising was that a single one hour average sample represented more than 11% of the lead mass collected over a period of almost one month. The one-hour average concentration was 43 $\mu g/m^3$, which

averaged over a month is 0.060 µg/m^3 representing 40% of the NAAQS of 0.150 µg/m^3. Clearly, identification and mitigation of the responsible source for this single event as well as those responsible for the 16% highest lead measurements would go a long way towards reducing lead exposure and attaining the NAAQS for lead.

Driver: The primary driver in this case is the need to meet the new NAAQS for lead and reduce the community's exposure to short-term high lead concentrations. It is clear from the above data that eliminating the few high concentration episodes will go a long way towards meeting the NAAQS. Thus, the key driver for a multi-metals FLM is to assist the state and plant management in identifying and controlling the source and plant processes responsible for these few high concentration events that contribute almost 90% of the lead in the community.

Standards, Limits and Goals: Although the current NAAQS for lead is set at 0.15 µg/m^3, there is increasing data suggesting that short-term exposures to lower concentrations can be harmful, and if so, short-term exposure to significantly higher concentrations is likely to also be harmful. Thus, a long-term goal is set to eliminate all high concentration events (one-hour average) greater than 1 µg/m^3 by the year 2020.

Local airshed characteristics: The primary lead smelter in this example is located in Herculaneum, MO, along the west side of the Mississippi River about 50 miles south of St. Louis, MO. Lead smelting in the area has been ongoing for nearly one hundred years. To the east of the plant on the other side of the river is mostly agricultural land use. The area is flat, Mississippi River bottoms flood plain. Wind speed averages around 10 mph from the southwest but can vary substantially.

Parameters to be monitored: TSP lead is currently monitored as part of the NAAQS attainment plan. Additionally there is an ongoing study at the site utilizing continuous FLM monitors recording PM lead associated with fugitive emissions. Cadmium is emitted with primary lead smelting and additional data on ambient cadmium is helpful to assess risks to the local population. Meteorological data and plant operational data is also monitored to further characterize fugitive sources and threats to the local airshed.

Monitoring sites: The monitoring sites at the primary lead smelter would be based on established TSP lead NAAQS point of compliance sampling locations, as well as continuous multi-metals FLM monitor locations at fugitive emissions points of maximum impact.

Data processing and reporting: Data will be reported to state regulators and plant managers to assess attainment with the lead NAAQS. Continuous multi-metals data will also be reported to regulators and plant managers to aid in developing a fugitive emissions lead NAAQS attainment plan.

10.8 Secondary Lead Smelter (Appendix D)

Secondary lead smelters are relatively small, about one square block, compared to a primary lead smelter, which may be more than a mile long. Primary smelters are located in relatively rural settings and secondary smelters are typically located in urban/industrial land use areas.

Driver: The primary driver in this case is to meet the new NAAQS for lead and reduce the community's exposure to short-term high lead concentrations. It is hypothesized that

eliminating the few highest concentration lead episodes will significantly help in meeting the NAAQS. Thus, the key driver for a multi-metals FLM is to assist the state and plant management in identifying and controlling the source and plant processes responsible for these few high concentration events that contribute almost 90% of the lead in the community.

Standards, limits and goals: Although the current NAAQS for lead is set at 0.15 µg/m^3, there is increasing data suggesting that short-term exposures to lower concentrations can be harmful, and if so, short-term exposure to significantly higher concentrations is likely to also be harmful. Thus, a long-term goal is set to eliminate all high concentration events (one-hour average) greater than 1 µg/m^3 by the year 2020.

Local airshed characteristics: For a hypothetical application of the procedure, we used a secondary lead smelter located near downtown Los Angeles, California, as an example. The Los Angeles basin is known for its general air pollution concerns including air particulate matter. Winds are consistently around 8 mph from the west.

Parameters to be monitored: TSP lead and PM lead should be monitored in order to assess attainment with the lead NAAQS and identify potential fugitive sources near the site. Samples will be taken once per hour. Meteorology and plant records would also be monitored.

Monitoring sites: Four (4) established sampling sites to the north, east and west of the secondary lead smelter would be utilized. The California Air Quality Management District and the smelter facility have historic ambient lead concentration data from each site. One FLM would be utilized and stationed initially at the location of highest lead TSP concentration to study fugitive lead impacts on non-attainment status and develop a corrective action plan.

Data processing and reporting: Data would be reported to state regulators and plant managers to assess attainment with the lead NAAQS. Continuous multi-metals data would also be reported to regulators and plant managers to aid in developing a fugitive emissions control plan to attain the lead NAAQS.

11.0 Data Processing/Quality Assurance and Control (Step 6 A)

Typical multi-metal FLMs have built-in data processing components included in the on-board computer. The operational protocol for providing defensible data relates directly to calibration and periodic audits. Calibration initially occurs at the manufacturer with thin-film test strips serving as metals concentration control values. Periodic audits can then be conducted using a Quantitative Aerosol Generator (QAG) which compares a control metals ambient concentration in the form of a reference aerosol (traceable to NIST standards) to the value recorded by the FLM. Adjustments are made based on these audit results. *Validation of Three New Methods for Determination of Metal Emissions Using a Modified Environmental Protection Agency Method 301* by Yanca, et al of Cooper Environmental Services details the validation of the QAG calibration method.

Records of instrument maintenance, documented in operator checklists, are necessary to demonstrate that proper quality control measures have been applied to the monitoring equipment. Appendix A and B detail quality assurance protocol and schedules, including

calibration, calculating sample analysis drift, and on-board quality assurance; for further information on these aspects of the monitoring procedure, please refer to these appendices.

12.0 Reporting Procedures (Step 6 B)

Ambient metals samples are analyzed by the FLM and data is stored in the onboard computer and/or offsite database through the data telemetry system. FLM devices would be serviced routinely by trained technicians. Sampling tape would be changed and the device would be calibrated as necessary. It is usually prudent to prepare operator check sheets that can be used to remind site operators to address the various routine maintenance tasks.

Data reporting procedures will depend upon the specific goals and requirements of the monitoring program. For example, monitoring programs based on compliance with the lead NAAQS will have a significant regulatory and public data reporting component due to the specific requirements of attainment status with the Clean Air Act and general public interest. However, public involvement and reporting procedures for continuous multi-metals monitoring not associated with specific regulatory mandates, such as the ferrous metals recycler example, will have to be developed based upon the level of public health risk and interest. At a minimum, all data recorded by a FLM should be made available to the public and to the applicable state or federal environmental regulatory agency. In the final analysis, public health is the primary concern of all ambient metals monitoring, and data reporting procedures associated with a monitoring program should take into account that priority. The local community should be fully aware of the goals of the monitoring program, and the data emerging from the monitors should be made available to the public through a well-managed internet site.

The role of the facility, as well as state and federal agencies in reporting procedures, will also depend upon the specific nature of the monitoring program. A NRT multi-metals monitoring plan might be implemented voluntarily, as a part of a corrective action plan, a lead NAAQS State Implementation Plan, or a consent order. Regulators from state and federal agencies would be involved to varying degrees with each of these scenarios, as would their involvement with data reporting. Alternately, the facility itself may be primarily responsible for data collection and reporting. Regardless, it is the role of the state agencies to implement environmental regulations and represent the interests of the public in environmental issues. All data emerging from the ambient monitors should be made available to state and federal regulators. Facilitating ambient metals data reporting as it pertains to specific regulations and public health will be one of the primary responsibilities of the state or federal agency within the continuous multi-metals monitoring program. If ambient metals exceedances occur that pose significant risks to human health, regulators should notify local media and government of the concern and proceed with established shut-down or other corrective action plans to mitigate the emissions.

Perimeter monitoring programs monitor and document the air quality during site activities and at sensitive receptors. No matter what instruments or sampling frequency is used, all data should be archived and reported systematically. Real-time data telemetry or a manual data archiving system should be employed. Whether the system provides a continuous real-time telemetry or requires manual archiving, all data should ultimately be archived in a central computerized database. The sophistication of the data telemetry system should be based upon the data quality objectives and the need for real-time action level exceedance alarms. To determine the

type of data telemetry collection and archiving system required, evaluate the installation schedule, target parameters, instrumentation and mobility requirements, site size, sampling frequency, costs, and the need for real-time exceedance alarms.

AutoMet+ Recorder Report
25-AUG-08 07:47:51
ID XACT
SN D0000
Units ng/m^3

Time	AT(°C)	SAMPLE(°C)	ZINC	GALLIUM	**ARSENIC**
4/12/2009 6:00	4.4	22.2	24.458	0.15	**1.381**
4/12/2009 8:00	6.5	22.8	18.43	0.154	**1.69**
4/12/2009 10:00	10.6	24.2	14.5	0.265	**1.323**
4/12/2009 12:00	12.4	26.9	11.794	0.253	**1.152**
4/12/2009 14:00	13	26.6	10.642	0.157	**0.723**
4/12/2009 16:00	12.6	26.4	10.288	0.153	**0.856**
4/12/2009 18:00	12.2	25.8	11.726	0.159	**1.658**
4/12/2009 20:00	10.9	24.4	12.383	0.174	**0.9**
4/12/2009 22:00	10.2	23.2	7.539	0.18	**0.64**
4/13/2009 0:15	10.2	23.2	7.539	0.18	**0.64**
4/13/2009 0:00	8.3	22.5	6.883	0.139	**0.712**
4/13/2009 2:00	8.2	23.3	6.15	0.158	**0.981**
4/13/2009 4:00	8.2	23.2	7.347	0.17	**0.707**
4/13/2009 6:00	8.3	23.4	8.712	0.162	**0.646**
4/13/2009 8:00	8.8	22.9	9.733	0.139	**0.582**
4/13/2009 10:00	10.2	23.8	9.347	0.163	**0.758**
4/13/2009 12:00	11.4	25.4	21.291	3.439	**2345**
4/13/2009 14:00	12.1	26.6	19.772	0.412	**173.38**
4/13/2009 16:00	11.4	26	14.592	0.174	**10.73**
4/13/2009 18:00	10.7	24.5	9.619	0.103	**2.441**
4/13/2009 20:00	9.9	23.1	6.688	0.076	**0.54**
4/13/2009 22:00	8.5	22.5	4.895	0.086	**0.336**

Figure 7. Example of Xact 620 data report example

13.0 General Air Monitoring System Design Bibliography

1. Pelton, D.J. and R.C. Koch, GEOMET Technologies, Inc. *Optimum Sampling Site Exposure Criteria for Lead*. EPA-450/4-84-12. OAQPS, EPA. Feb 1984.

   Describes sampling site criteria for ambient monitoring of lead. Good description of meteorological and topographical effects on samplers. Some discussion of fence-line monitor placement, a flow chart page 45 of pdf.

2. Monitoring and Data analysis division, OAQPS, *Office of R&D Environmental Monitoring Systems Lab. Ambient Monitoring Guidelines for Prevention of Significant Deterioration*. EPA-450/4-87-007. May 1987

   Presents a guide for probe siting for specific analytes, including Pb, PM and non-NAASQ Particulates. The location guide doesn't apply to fence-line monitoring specifically. However the criteria are still good. Good info on Meteorological measuring, quality assurance, and quality control as well.

3. Office of Air and Radiation, OFAQPS, EPA. *Meteorological Monitoring Guidance for Regulatory Modeling Applications*. EPA-454/R-99-005. Feb 2000

   Describes proper meteorological monitoring protocol. This includes location criteria, types of monitors, as well as quality assurance and control. Will be a great asset to user since meteorological data is necessary in conjunction with fence-line monitoring.

4. Carney John, American EcoTech . *Planning for Fence-Line Monitoring. Pollution Engineering*, March 2010.

   This article describes the basic goals of a fence-line monitoring system, as well as questions that need to be considered for the user. Followed up Article with a call to author. Said that there basically is no standard protocol for implementation, all depends on what the client wants to know and who is impacted by industry's operations.

5. EPA Office of Air Quality Planning and Standards. *Quality Assurance Handbook for Air Quality Measurement Systems, Vol II, Ambient Air Quality Monitoring Program* EPA-454/B-08-003. Dec 2008.

   Detailed information regarding site placement criteria. Also probe placement criteria, detailed meteorological impact descriptions. Good information on data quality objectives and quality assurance, as well as on ambient air pollution regulation.

6. Watson, J.G. et al. *Guidance for using Continuous Monitors in PM 2.5 Monitoring Network*. OAQPS EPA-454/R-98-012. May 29, 1998

   Discusses the advantages of including continuous monitors in conjunction with filter monitors (Section 5). Also discusses PM variability with the wind in continuous monitoring.

7. Aggarwal, L. et al. *Draft Conceptual Guidelines and Common Methodology for Air Quality Monitoring, Emission Inventory and Source Apportionment Studies for Indian Cities*. Central Pollution Control Board.

Good discussion about site and probe placement criteria specifically for PM, also good description of emission inventory and data quality objectives for ambient monitoring. The emission inventory should include Point sources (industries, etc.), Area Sources (Municipal wood burnings, etc.), and Line sources (Traffic form Roads). Data should be gathered about these sources, such as type of fuel or vehicle frequency (line). Siting guidelines start page 33 of pdf.

8. Held K. & T. Kunkel. *Particulate Monitoring and Control in Lower Manhattan during Large Urban Redevelopment*. Air and Waste Management Association, Paper #70. June 26 2007.

   Describes application of fence-line monitoring of PM to a construction site in lower Manhattan. Briefly describes siting criteria, and averaging period of continuous monitors. While NAAQS require 30 min averaging periods, in this case they used 5 min averages, more real-time reporting, but without the variance of 1 min averaging. Four continuous monitors were used to surround the construction site, and mobile monitoring was accomplished with handheld detectors. Data from the monitors was uploaded to a secure website. When an alarm level was reached, and meteorological conditions indicate construction may be responsible for increase, construction was halted and the spike investigated.

9. Watson J.G., J. Chow, et al. *Guidance for Network Design and Optimum Site Exposure for PM2.5 and PM10*. Office of Air Quality Planning and Standards. December 15 1997.

   Describes Monitoring site criteria, but mostly in regards to satisfying NAAQS. It does deal with some geographical criteria however, section 5.

10. Gendron L., A. Sacco, I. Chadhuri. *Designing and Implementing Perimeter Air Monitoring Programs. Environmental Expert*. Jan 1 2004. http://www.environmental-expert.com/resultEachArticle.aspx?cid=4680&codi=3211&idCategory=0

    Article specifically discusses FLM. Goes over action levels and the risk assessment used to determine them. Also goes over what to consider when determining #, type, and sites of monitors. Good info but all slightly generic.

11. *Planning and Implementing a Real-Time Air Pollution Monitoring and Outreach Program for Your Community*. EPA/625/R-02/012. Nov 2002.

    Describes the process of instituting an ambient real-time monitoring system for neighborhood use. Slightly describes site selection, but with reference to ambient monitoring, and there was only one monitor used in the study. General discussion on data management, section 6.

12. *Monitoring Fugitive Dust Impacts From Surface Coal Mining-Phase I*. EPA-454/R94-024. July 1994.

    Gives a step by step description of a study determining the concentration of fugitive dust at a surface coal mine. This was accomplished with several ambient PM monitors in a pseudo fence-line fashion, including one continuous monitor. This study also includes a description of monitor siting criteria as well as a description of each site chosen and their

accordance with the criteria. It also describes the Data quality objectives (precision and accuracy) of the different monitors and from what regulation these objectives come from.

13. Bohn R., T. Cuscino, & C. Cowherd. *Fugitive Emissions from Integrated Iron and Steel Plants*. EPA-600/2-78-050. March 1978.

    Dealt with determining fugitive PM matter from Iron and Steel plants. Main focus of study was determining emission factors and discussing control techniques. However did go over measurement of the concentrations to quantify the emissions factors. Discussed the Upwind/Downwind method as well as the exposure profiling method slightly.

14. TRC Environmental Consultants. *Protocol for the Measurement of Inhalable Particulate Fugitive Emissions from Stationary Industrial Sources*. EPA contract 68-02-3115. March 1980.

    Provides a guide to using four different methodologies for measuring fugitive inhalable particulate matter. Only two of the methods really apply, the exposure profiling and upwind/downwind methods, mostly the upwind/downwind. The document provides guidelines to instrument a pre-test site survey and develop a test-plan. Also provides a good description of where to place sampling sites, based on equations and background concentration levels for Upwind/Downwind. Since these concentration levels are based on PM, which is a surrogate for metals, but not sure how they will translate, also these equations are based on a time integrated sampler, not a continuous one. These locations aren't exactly a fence-line setup they could be especially used for the primary downwind sampler location.

15. Operations Planning and Assessment Section, California EPA. *Monitoring Protocol for Naturally Occurring Asbestos at Oak Ridge High School*. June 2003.

    Describes testing plan for asbestos at a high school soccer field construction site. The monitors were used in a fence-line style surrounding the soccer fields. Continuous and time integrated samplers were both used. The location of the samplers around the field was based on CFR 40 part 58. Quality control checks were also discussed.

16. *Guidance on Systematic Planning Using the Data Quality Objective Process*. EPA QA/G-4. Feb 2006.

    Describes the process to develop data quality objectives. Good information discussing how to decide action levels as well as the possibilities of a false acceptance and false rejection. Also goes into detail about confidence intervals and different types of population estimators (section 6).

17. Hazardous Waste TSDF- *Fugitive Particulate Air Emissions Guidance Document*. EPA- 450/3-89-019. May 1989.

18. Bunton B. et al. *Monitoring and Modeling of Emissions from Concentrated Animal Feeding Operations: Overview of Methods*. Brogan and partners. Environmental Health Perspectives Vol. 115 No. 2. Feb 2007

19. Barton C., L. Butler, et. al. *Characterizing Perfluorooctanoate in Ambient Air near the Fence-line of a Manufacturing Facility: Comparing Modeled and Monitored Values*. Air & Waste Management Association. 2008

20. United States Army Corps of Engineers. *Design, Installation, and Utilization of Fixed-Fenceline Sample Collection and Monitoring Systems*. ECM-200-1-5. Oct 1997

21. Kolnsberg, H. *Technical Manual for Measurement of Fugitive Emissions: Upwind/Downwind Sampling Method for Industrial Emissions*. TRC. EPA-600/2-76-089a. April 1976.

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15.0 Glossary of Definition, Abbreviations, and Symbols

Ambient Limit: Average Ambient Concentration of a regulated species that cannot be exceed over a specified averaging time under applicable permits or regulation (Permitted concentration limit, PCL)

Averaging Time: A set interval of time that has multiple samples within the range of time, but is averaged to provide the best linear representation of the data.

ATSDR (Association for Toxic Substances and Disease Registry): A federal public health agency of the U.S. Department of Health and Human Services. ATSDR serves the public by using the best science, taking responsive public health actions, and providing trusted health information to prevent harmful exposures and diseases related to toxic substances.

Bias: A systematic favoritism that can lead to a misrepresentation in the data.

CAA (Clean Air Act): The law that defines EPA's responsibilities for protecting and improving the nation's air quality and the stratospheric ozone layer.

Calibration Drift: Difference in a FLM reported concentration of a stable reference measure at the beginning and end of a rest period during which no unscheduled maintenance or adjustment took place.

Calibration Drift Standard: A stable, thin film standard containing a known amount of metal used to establish drift in response of an X-Ray fluorescence module

California REL (California EPA Reference Exposure Level): The concentration level at or below which no adverse health effects are anticipated for specified exposure duration. RELs are

based on the most sensitive, relevant, adverse health effect reported in the medical and toxicological literature. RELs are designed to protect the most sensitive individuals in the population by the inclusion of margins of safety.

CEMS (Continuous Emissions Monitoring System): the total equipment necessary for the determination of a gas or particulate matter concentration or emission rate using pollutant analyzer measurements and a conversion equation, graph, or computer program to produce results in units of the applicable emission limitation or standard.

Ceiling: A ceiling REL or PEL (NIOSH/OSHA) is the ceiling concentration that should not be exceeded at any time.

Comparability: Comparability is a term, used in the lead National Ambient Air Quality Standard (NAAQS) rule to describe the accuracy or bias of a candidate method relative to a reference method.

Cycle Time: elapsed time between when a FLM begins to collect a sample (start) and when the measured concentration for that sample is reported

Data Recorder: Portion of a FLM that provides a record of analyzer output including, but not limited to metal concentrations, flags which indicate normal operation, flags indication abnormal operation, etc.

Detection Limit: the lowest quantity of a substance that can be distinguished from the absence of that substance within a stated confidence limit.

Emission Limit: The Emissions limit for a single metal is equal to the maximum amount allowed under the applicable regulation for its category assuming all the other metals in its category were not present.

Fugitive Emissions: non-ducted or otherwise controlled emissions

FRM (Federal Reference Method): A method recognized by the United States Environmental Protection Agency as appropriate for the measurement of a pollutant or pollutants in source emissions.

FLM (Fence-line Monitors): Ambient monitors that have the potential to measure multiple analytes.

HAPs (Hazardous Air Pollutants): Currently, 187 pollutants are required under Section 112 of the Clean Air Act to be limited. HAPs are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. 33 Pollutants, 8 of which are metals, are considered to present the greatest threat to public health in the largest number of urban areas.

HSDB (Hazardous Substances Data Base): Part of the United States National Library of Medicine's toxicology data network that includes comprehensive, peer-reviewed toxicology data for about 5,000 chemicals.

IDLH (Immediately Detrimental to Life and Health): Considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection should be permitted. In determining IDLH values, NIOSH considered the ability of a worker to escape without loss of life or irreversible health effects along with certain transient effects, such as severe eye or respiratory irritation, disorientation, and incoordination, which could prevent escape. As a safety margin, IDLH values are based on effects that might occur as a consequence of a 30-minute exposure. However, the 30-minute period was NOT meant to imply that workers should stay in the work environment any longer than necessary.

OEL (Occupational Exposure Limit): An upper limit on the acceptable concentration of a hazardous substance in workplace air for a particular class of materials. It is typically set by competent national authorities and enforced by legislation to protect occupational safety and health.

Open path, Path-integrated Optical Remote Sensing Technology: Uses multiple beam paths and optimizing algorithms to give a time-averaged, mass-equivalent concentration field across a plume of contaminant, from which the emission rate can be determined, without using estimated values from a dispersion model. Used to determine the strength of nonpoint sources, to identify hot spots, and to estimate mass flux of fugitive gases

MACT (Maximum Achievable Technology Standards): MACT standards are designed to reduce HAP emissions to a maximum achievable degree, taking into consideration the cost of reductions and other factors.

NAAQS (National Ambient Air Quality Standard): EPA standards for pollutants considered harmful to public health and the environment. ***Primary standards*** set limits to protect public health. ***Secondary standards*** set limits to protect public welfare.

NATA (National Air Toxics Assessments): Ongoing process of evaluating MACT standard promulgation and determining of residual risk that requires the standards to be strengthened in order to protect human health. Thus far, EPA has completed three assessments that characterize both cancer and non-cancer hazards from inhaling air toxics.

NESHAPS (National Emissions Standard for Hazardous Air Pollutants): Stationary source standards for hazardous air pollutants (HAPs), which are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. NESHAPs are found in 40 CFR Part 61 (resulting from the CAAA of 1970) and 40 CFR Part 63 (resulting from the CAAA of 1990).

NRT (Near-Real-Time): Ambient monitoring that provides hourly or shorter feedback to plant operators.

NIOSH (National Institute for Occupational Safety and Health): The United States federal agency responsible for conducting research and making recommendations for the prevention of work-related injury and illness. NIOSH is part of the Center for Disease Control and Prevention within the U.S. Department of Health and Human Services.

NTBE (Not-To-Be-Exceeded): Concentration of a toxic substance that is never to be exceeded (see IDLH)

OEL (Occupational Exposure Level): an upper limit on the acceptable concentration of a hazardous substance in workplace air for a particular material or class of materials. It is typically set by competent national authorities and enforced by legislation to protect occupational safety and health.

OSHA (Occupational Safety and Health Administration): An agency of the United States Department of Labor. it was created by the United States congress to prevent work-related injuries, illnesses, and occupational fatality by issuing and enforcing standards for workplace safety and health.

PM (Particulate Matter): A complex mixture of extremely small particles and liquid droplets. Particle pollution is made up of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals, and soil or dust particles.

Percent Relative Bias: One hundred percent times the ration of the difference between a reference value and the FLM Measured Value divided by the reference divided by the reference value times 100%.

PS-AA (Performance Specification AA): is to define the tests and performance requirements that must be met by fence-line monitors.

PEL (Permissible Exposure Limit): A legal limit in the United States for exposure of an employee to a chemical substance or physical agent. Permissible exposure limits are established by the Occupational Safety and Health Administration. These levels are a time-weighted average based on an 8-hour day and a 40-hour work week.

Precision: The degree of Mutual agreement between individual measurements of a parameter having the same value, namely repeatability and reproducibility.

QAG (Quantitative Aerosol Generator): An Aerosol generator system that uses analytes of known concentrations in aqueous solution to create aerosol emissions of known metal concentration.

Quantitative Spiking: The process of introducing a known amount of metal or metals into the sample stream

REL (Recommended Exposure Limit): A legal limit in the United States for exposure of an employee to a chemical substance or physical agent. RELs are established by the National

Institute for Occupational Safety and Health. The concentration is a time-weighted average for up to a 10-hour workday during a 40-hour workweek.

Reference material: A material of known values used to either calibration or check the calibration of your XRF multi-metal FLM such as thin film standards as discussed in IO 3.3 in EPA Compendium of Inorganic Methods

RSL (Regional Screening Level): Risk-based concentrations derived from standardized equations combining exposure information assumptions with EPA toxicity data. RSLs are considered by the EPA to be protective for humans (including sensitive groups) over a lifetime; however, RSLs are not always applicable to a particular site and do not address non-human health endpoints, such as ecological impacts.

Sample Interference: The portion of the FLM used for one or more of the following sample acquisition, sample transport, sample condition, or protection of the monitor from the effect of ambient air

Sampling module: the portion of the X-Ray fluorescence based multi-metal FLM that traps the metals and delivers them to an XRF analysis module

SIP (State Implementation Plan): state plan for complying with the federal Clean Air Act, administered by the Environmental Protection Agency. The SIP consists of narrative, rules, technical documentation, and agreements that an individual state will use to clean up polluted areas.

Spiking: The process of introducing a known concentration of metal or metals into a gas stream

Stability: Percent relative standard deviation of a value measured over an extended period of time

STEL (Short Term Exposure Limit): A 15-minute time-weighted average exposure that should not be exceeded at any time during a workday.

Traceability: A property of the result of a measurement of the value of a standard whereby it can be related to stated references, usually national or international standards, though an unbroken chain of comparisons all having stated uncertainties.

AMM (Xact 620 Ambient Metals Monitor): An automated multi-metals monitor based on reel-to-reel (RTR) filter tape sampling followed by nondestructive X-ray fluorescence analysis of metals in the resulting PM deposit. In the 620, ambient air is sampled through a PM size-selective inlet and drawn through a filter tape. The resulting PM deposit is then automatically advanced and analyzed by XRF for selected metals while the next sample is being collected. In the Xact 620, sampling and analysis is performed continuously and simultaneously except for the time required to advance the tape (~20 sec) and the time required for daily automated quality assurance checks.

XRF (X-Ray Fluorescence Module): The portion of an XRF based multi-metal FLM which identifies and quantitatively measure metal masses or concentration using X-Ray fluorescence

FLS (XRF Multi-Metals Continuous Fence-line System): All of the equipment required for determining metal concentrations in ambient air using x-ray fluorescence as an analytical technique. The system any consist of several major subsystems including but not limited to the following: Sample Interface, X-ray fluorescence module, data recorder, sample module and volume measurement module.

Zero Drift: One Hundred percent times the ration of the difference between a FLM zero reading of for the zero reference from their values after the most recent calibration, divided by the ambient limit for each element.

APPENDIX A

Performance Specification AA: Specifications and Test Procedures for X-ray Fluorescence Based Metals Continuous Fence-Line Monitors

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

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MACTEC Federal Programs
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Executive Summary

Performance Specification AA (PS-AA) details the initial performance requirements and procedures for multi-metals continuous fence-line monitors (CFLM) that utilize X-ray fluorescence as an analytical technique. Each CFLM must meet the criteria for accuracy, linearity, and stability found in PS-AA. Each CFLM must also meet the installation requirements found in PS-AA and the on-going quality control and assurance requirements set forth in *Procedure B*.

List of Symbols

A_i^T = The CFLM's reported value for the ith element on a NIST traceable standard

A_i^U = The measured value of the ith element

A_i^Z = The measured value of the ith element

b_o = The intercept of the least square fit of the ith element

b_1 = The slope of the least squares regression fit for the ith element

C_i^C = The corrected concentration for the ith element

CE_i = The XRF calibration error for the ith element of the CFLM expressed as a percent

C_i^{FLM} = The CFLM reported concentration for the ith element

$\overline{C_i^{FLM}}$ = The average daily CFLM reported concentration for the ith element

C_i^L = The concentration of the permitted limit for the ith element

C_i^{R1} = The reported concentration of the ith element from reference method sampler one.

C_i^{R2} = The reported concentration of the ith element from reference method sampler two.

D_i = The percent difference in reported concentration between the two reference method samplers for the ith element.

FD = The flow drift of the metals CFLM in percent

FE = Flow Error expressed as a percent

F_{FLM} = Flow as measured by the metals CFLM

F_P = The flow reading from the CFLM's primary flow meter used during normal operation

F_{QA} = The flow reading from the QA flow sensor

F_R = Flow as measured by the NIST traceable flow measurement device

M_i^U = The upscale reference value for the ith element

M_i^Z = The zero reference value for the ith element

n = The number of FLM sample periods in a day

R_i^T = The value the ith element on a NIST traceable standard

UD_i = The upscale drift for the ith element in percent

x = The reference aerosol or reference method concentration

$\bar{x}$ = The average reference aerosol or reference method concentration

x_i = An individual reference aerosol or reference method concentration

$\hat{y}$ = Concentration output of the CFLM as predicted by the linear least squares model

y_i = An individual reported CFLM concentration

$\bar{y}$ = The average reported CFLM concentration

ZD_i = The zero drift for the ith in percent

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1 Purpose and Application

1.1 Purpose

The purpose of Performance Specification AA (PS-AA) is to establish the initial performance requirements that must be met by X-ray fluorescence (XRF) based metals continuous fence line monitors (CFLM). These procedures assure the initial accuracy and precision for metals continuous fence line monitors. Instruments that have met the initial performance requirements of PS-AA may used by regulating agencies (local, state and federal) for the purposes of enforcing a permitted metals concentration either at the perimeter of a facility with fugitive metal emissions or in communities affected by metals emissions. Assurance of the continuing quality of metals CFLMs may be achieved by following the procedures defined in *Procedure B – XRF Based Metals Fence Line Monitor Quality Assurance Procedures.*[1]

1.2 Applicability

1.2.1 Analytes

Several analytes may be measured by XRF based metals continuous fence line monitors. These analytes include but are not limited to the following: Antimony (Sb), Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), and Selenium (Se).

1.2.2 Alternative methods

Metals monitoring approaches not entirely suitable to these specifications may be approvable under the alternative monitoring or alternative test method provisions of 40 CFR Part 60 and Part 63.[2,3]

2 Definitions

2.1 Metals Continuous Fence Line Monitor (CFLM)

A metals continuous fence line monitor is any monitor capable of measuring one or more metal concentrations on a continuous, real time basis. These monitors may be located at the fence line or perimeter of industrial facilities with fugitive metal emissions or in communities affected by metal emissions. These monitors generally consist of the following subsystems:

2.1.1 Sample Inlet

The sample inlet for a metals CFLM can include any standard federally recognized PM_{10}, $PM_{2.5}$, or high-volume TSP inlets.[4,5,6] Other types of sample inlets may be allowed or specified by applicable regulations or permits.

2.1.2 Analyzer Module

This is the portion of the metals continuous fence line monitor that measures the metal mass. For the XRF based monitors governed by this performance specification, this system consists of the filter media (if such filter material is necessary) designed to capture the particulate and/or vapor phase metals and the components of the X-ray analytical equipment (e.g. tube, detector, power supplies).

2.1.3 Sample Flow Module

The sample flow system includes those parts designed to generate and measure the flow into the CFLM.

2.1.4 Data Recorder

This is the portion of the metals CFLM that provides an electronic record of the instruments output in terms of ng/m^3 or $\mu g/m^3$.

2.2 Permitted Concentration Limit

This is the maximum concentration of a metal allowed by regulation, permit or other enforcement mechanism for a particular area or airshed. The metals continuous fence line monitor is used to determine a regulated facility's compliance with this limit.

2.2.1 Seven Day Calibration Drift Test

Calibration drift is the difference in the CFLM output readings from established reference values after a stated period of operation during which no unscheduled maintenance, repair or adjustments took place. Three calibration drift checks are required of x-ray fluorescence based metals CFLMs: a zero drift check, an upscale drift check, and a flow drift check.

2.2.2 Zero Drift

The Zero Drift is the difference in the reported value for the zero reference and its value at the last analyzer calibration divided by the permitted concentration limit and expressed as a percent.

2.2.3 Upscale Drift

The upscale drift is the difference in the reported value for the upscale reference from its value at the last analyzer calibration divided by the value at the last analyzer calibration and expressed as a percent.

2.2.4 Flow Drift

The flow drift is the difference between the flow measured by the CFLM and flow measured by the CFLM's flow check measurement device divided by the flow from the flow check measurement device and expressed as a percent

2.3 XRF Analyzer Audit

This is a test of the accuracy of the metals CFLM's XRF analyzer. Gravimetrically traceable to NIST thin film standards may be used to audit the accuracy of the metals analyzer (see Section 6.4). The results of this audit are used to calculate the calibration error (see Section 7.4)

2.4 Flow Audit

The flow audit measures the accuracy of the metals CFLM's flow sensor using a NIST traceable flow measurement device. The results of this audit are used to calculate the flow error (see Section 7.5)

2.5 Linear Accuracy Audit

This test assesses the linearity of the metals CFLM's response to a range of aerosol concentrations. The response of the CFLM is compared to the reference aerosol concentration.

2.6 Relative Accuracy Audit

The relative accuracy audit assesses the accuracy of a metals CFLM's response by comparing it to a reference method.

2.7 Measurement Range

This is the range of concentrations over which the metals continuous CFLM has demonstrated valid and accurate measurement. If a Linear Accuracy Audit is performed then this range extends from the lowest aerosol concentration level to the highest aerosol concentration level. If relative accuracy audit is performed the instrument range spans from the lowest recorded concentration for which there is accurate comparison data to the highest recorded concentration for which there is accurate comparison data.

2.8 Maximum Validated Concentration

The maximum validated concentration is the highest concentration that the metals CFLM has demonstrated it can accurately measure. If a Linear Accuracy Audit is performed against a reference aerosol the highest aerosol concentration level is the maximum validated concentration. If CFLM accuracy is validated using a relative accuracy audit, the maximum validated concentration is equal to the concentration of the highest recorded sample for which there is reference method data to compare.

3 Interferences

Please check with your metals CFLM's manufacturer for any potential interferences.

4 Safety

People using PS-AA may be exposed to hazardous materials, operational hazards and hazardous site conditions. PS-AA does not address all of the safety issues associated with its use. It is the responsibility of those using PS-AA to ensure their own safety. Some helpful references regarding safety may include the CFLM's manual and its manufacturer.

5 Equipment and Supplies

5.1 Metals Continuous Fence Line Monitor Equipment Specifications

5.1.1 Data Recorder

The metals continuous fence line monitor must be equipped with a means of electronically recording the metals concentration data generated by the monitor.

5.1.2 Flow Module

The metals continuous fence line monitor must be equipped with a means to generate and measure flow.

5.1.3 XRF Module

All XRF based CFLM's must have a module based on X-ray fluorescence (either energy or wavelength dispersive) to measure metals concentrations or masses.

5.1.4 Calibration Drift References

The metals CFLM must provide a means of performing the zero, upscale and flow calibration drift checks at the frequency required in both this document (Performance

Specification AA) and as required by *Procedure B – XRF Based Metals Fence Line Monitor Quality Assurance Procedures.*[1]

5.1.5 Sampler Inlet

The metals continuous fence line monitor must be equipped with a sample inlet. This sample inlet may include standard Federal Reference Method inlets such as PM_{10}, $PM_{2.5}$ or TSP inlets. If these standard inlets are used they must be used at the flows and in the conditions specified in appropriate guidance documentation provided in the Federal Register.[4,5,6] Other types of sampler inlets may be used if they are specified by regulation.

5.2 Reference Methods

If the accuracy of the metals continuous fence line monitor is determined using a relative accuracy audit then it is necessary to have all the equipment required to gather suitable reference method measurements. This equipment could include samplers, filters, additional sample inlets and laboratory analytical equipment. Sampling reference methods may include those found for sampling PM_{10}, $PM_{2.5}$ and TSP in Appendices J, L and B respectively, of 40 CFR 50.[4,5,6] Appropriate metals analysis procedures may be found in the Compendium of Methods for the Determination of Inorganic Compounds (I.O.) in Ambient Air.[7] Examples of appropriate analysis methods include, X-ray Fluorescence (I.O. 3.3), inductively coupled plasma (ICP) spectroscopy (I.O. 3.4), inductively coupled plasma/mass spectrometry (I.O. 3.5), and proton induced X-ray emission (PIXE) spectroscopy (I.O. 3.6).

5.3 Reference Aerosol Generator

If the accuracy of the metals continuous fence line monitor is determined using a reference aerosol generator then it necessary to have all the equipment required to generate a reference aerosol. The equipment and quality assurance procedures for such a generator may be found elsewhere.[8,9]

5.4 Other equipment and supplies

Other equipment as specified by the manufacturer of the CFLM, or for proper operation of the reference method, or the reference aerosol generator may be needed.

6 Reference Standards

6.1 Zero Drift Reference

All metals continuous fence line monitors must be equipped with a zero drift reference. The reported concentration for this reference value must be between 0 and 20 percent of the permitted concentration limit. For CFLM's utilizing filter tape to capture particulate and/or

vapor phase metals concentrations, a blank section of tape may be used as a zero reference. The concentrations of metals on the zero drift reference do not need to be NIST traceable.

6.2 Upscale Drift Reference

All metals continuous fence line monitors must be equipped with an upscale drift reference. This reference is used to test the stability of the XRF analyzer and must have a reported concentration equivalent to at least 80 percent of the permitted concentration limit. The concentrations of each metal on the upscale drift reference do not need to be NIST traceable.

6.3 Quality Assurance Flow Meter

All metals continuous fence line monitors must be equipped with a flow measurement device that can be used to automatically check the accuracy of the instrument's primary flow measurement device. This meter need not be NIST traceable and is used to perform the daily flow audits required for this performance specification.

6.4 NIST Traceable XRF Audit Standards

Most X-ray fluorescence analyzers used to determine metals concentrations on particulate matter (PM) filter samples are calibrated using thin film standards. An XRF based metals continuous fence line monitor may be calibrated in this same way. The accuracy of the XRF analyzer should be checked using these standards. Micromatter[10] produces gravimetrically traceable to NIST thin film standards that have been recognized as being useful for the purposes of calibrating XRF analyzers.[11] Other traceable to NIST thin film standards may be used if they are available. These standards are also required for quarterly XRF audits required by *Procedure B*.

6.5 NIST Traceable Flow Meter

During initial performance testing, a flow audit of the primary and QA flow meters is required. For this audit, a NIST traceable flow meter is required. Procedures for performing a flow audit with a NIST traceable flow meter can be found in Section 7.5. A NIST traceable flow meter is also required for quarterly flow audits as required by *Procedure B*.

7 Performance Specification Test Procedure

7.1 Installation and Measurement Location Specifications

7.1.1 Installation Location

The metals continuous fence line monitor should be located in accordance with the applicable regulation and the *Protocol for Developing and Implementing a Metals Fence Line Monitoring Plan Using X-ray Based Monitors.*[12]

7.1.2 Shelter

The instrument should be housed in a manner consistent with the manufacturer's specifications. This could include a climate controlled shelter for the sampling and analyzer modules and the data recorder.

7.1.3 Inlet location

The inlet locations for a metals continuous fence line monitor generally follow the same procedures as those for micro-scale particulate matter sampling. The inlet must be between 2 and 7 meters above the ground at least 2 meters horizontally away from any supporting structure walls and at least 1 meter above any supporting structure. Preferably, there should be no trees or shrubs located between the probe and the monitored facility. If this is not possible the probe should be located at least 10 meters away from the drip line of trees. For all other obstacles, the distance between the obstacle and the probe should be twice the height that the obstacle protrudes above the probe inlet.[13] Exceptions to these rules may be made at the discretion of the regulating agency.

7.2 Pretest Preparation

After properly locating, installing, and housing the metals continuous fence line monitor, it is recommended that it operate for a period of time to assure that the user is familiar with operation and to assure that the instrument is functioning properly. During this period of operation all daily quality assurance procedures should be performed as they would during normal operation (See *Procedure B*).

7.3 Seven Day Calibration Drift (CD) Test Procedures

The purpose of the seven day calibration drift test is to demonstrate the stability of the continuous fence line monitor's flow and XRF analyzer calibration. Prior to performing the calibration drift check, the CFLM's XRF analyzer should be calibrated according to the manufacturer's specifications. Following the calibration and appropriate calibration checks, the initial values for the Zero Drift Reference and the Upscale Drift Reference should be

determined according to the manufacturer's specifications. During the seven day calibration drift check no adjustments or calibrations may be made to the CFLM.

7.3.1 Analyzer Zero Drift

Determine the magnitude of the zero calibration drift at least once each day at 24 hour intervals for seven consecutive unit operating days. (The seven consecutive unit operating days need not be seven consecutive calendar days). The zero drift check may be performed automatically as a part of normal instrument function or it may be performed manually by the operator. Calculate the zero drift by determining the absolute value of the difference between the zero drift reference value (M_i^Z) and the CFLM's reported value (A_i^Z), divided by the permitted concentration limit (C_i^L) according to Equation AA-1. The zero drift reference value is determined according the manufacturers specifications immediately following the XRF calibration of the instrument.

$$ZD_i = \frac{\left|M_i^Z - A_i^Z\right|}{C_i^L} \times 100\% \qquad \text{Equation AA-1}$$

Where:

ZD_i = The zero drift for the ith in percent

M_i^Z = The zero reference value for the ith element

A_i^Z = The measured value of the ith element

C_i^L = The concentration of the permitted limit for the ith element

7.3.2 Analyzer Upscale Drift

Determine the magnitude of the upscale calibration drift at least once each day at 24 hour intervals for seven consecutive unit operating days. (The seven consecutive unit operating days need not be seven consecutive calendar days). The upscale drift check may be performed automatically as a part of normal instrument function or it may be performed manually by the operator. Calculate the upscale drift by determining the absolute value of the difference between the upscale reference value (M_i^U) and the metals CFLM's reported value (A_i^U) and dividing by the upscale reference value according to Equation AA-2. The upscale reference value is determined according to the manufacturers specifications immediately following the XRF calibration of the instrument.

$$UD_i = \frac{\left|M_i^U - A_i^U\right|}{M_i^U} \times 100\% \qquad \text{Equation AA-2}$$

Where:

UD_i = The upscale drift for the ith element in percent

M_i^U = The upscale reference value for the ith element

A_i^U = The measured value of the ith element

7.3.3 Flow Calibration Drift

Determine the magnitude of the flow calibration drift at least once each day at 24 hour intervals for seven consecutive unit operating days. (The seven consecutive unit operating days need not be seven consecutive calendar days). The flow drift check may be performed automatically as a part of normal instrument function or may be performed manually by the operator. The flow drift is determined by comparing the flow from the CFLM's primary flow sensor used during normal sampling, and a secondary flow sensor used only during quality assurance procedures. The flow rate during flow calibration drift check must be the same as that used during the normal operation of the instrument. The magnitude of the flow drift may be calculated by determining the absolute value of the difference between the quality assurance flow sensor reading and the primary flow sensor reading and dividing by the quality assurance flow sensor reading according to Equation AA-3.

$$FD = \frac{\left|F_{QA} - \quad {}_P\right|}{F_{QA}} \times 100\% \qquad \text{Equation AA-3}$$

Where:

FD = The flow drift of the metals CFLM in percent

F_{QA} = The flow reading from the QA flow sensor

F_P = The flow reading from the CFLM's primary flow meter used during normal operation

7.4 XRF Audit Test Procedures

An XRF Audit must be performed for each regulated or permitted metal measured by the metals continuous fence line monitor. The XRF audit reference must be a NIST traceable standard. An example of such audit standards are the gravimetrically traceable to NIST thin film standards commercially available from Micromatter[10]. The XRF audit checks the XRF analyzer portion of the CFLM for accuracy relative to these standards. The magnitude of the XRF calibration error (CE_i) is calculated by determining the absolute value of the difference between the value of the ith element on the NIST traceable reference standard (

R_i^T) and the value of reported by the CFLM for that standard (A_i^T), divided by the reference standard.

$$CE_i = \frac{\left|R_i^T - A_i^T\right|}{R_i^T} \times 100\% \qquad \text{Equation AA-4}$$

Where:

CE_i = The XRF calibration error for the ith element of the CFLM expressed as a percent

R_i^T = The value the ith element on a NIST traceable standard

A_i^T = The CFLM's reported value for the ith element on a NIST traceable standard

7.5 Flow Audit Test Procedures

A flow audit of both the CFLM's primary flow sensor and its quality assurance flow sensor must be performed. The flow audit checks the overall instrument's flow measurement accuracy by comparing the CFLM flow sensors' responses to a NIST traceable flow device. The flow audit shall incorporate as much of the CFLM's flow system tubing and components as practically possible. For metals CFLMs equipped with a PM_{10}, or $PM_{2.5}$ sampling inlet, remove remove the PM selective inlet(s), replace them with a flow cap adaptor, and perform the flow check in a manner similar to the procedures described in Appendix L of 40 CFR part 50.[5] Calculate the flow error according to Equation AA-5.

$$FE = \frac{\left|F_{FLM} - F_R\right|}{F_R} \times 100\% \qquad \text{Equation AA-5}$$

Where:

FE = Flow Error expressed as a percent

F_R = Flow as measured by the NIST traceable flow measurement device

F_{FLM} = Flow as measured by the metals CFLM

7.6 Overall Instrument Accuracy Test Procedures

The overall accuracy of a metals continuous fence line monitor may be determined using either one of two methods: 1) a linearity audit or 2) a relative accuracy audit. During a linearity audit, the metals CFLM is challenged with a reference aerosol or aerosols consisting of the regulated metals at several different concentration levels. A relative

accuracy audit consists of comparing the concentrations reported by the CFLM with that of a reference method.

There are advantages and disadvantageous to each approach. In general, spiking the instrument with a reference aerosol will give the user greater control over the time period required to complete the initial performance specifications and a larger and more robust verified concentration range. However, there may be metals for which reference aerosols are not available, or not available at the concentration levels likely to be observed during normal operation. In these cases, it is preferable to assess the instrument accuracy against a reference method.

7.6.1 Linearity Accuracy Test Procedures

If the accuracy of the metals continuous fence line monitor is determined using a linearity accuracy audit, the audit must be completed before the CFLM can be used for compliance purposes. The reference aerosol generator used for this test must be cable of delivering a traceable to NIST aerosol consisting of the regulated metal or metals at the concentration levels specified in this procedure. Quality control and assurance procedures for the reference aerosol generator can be found elsewhere.[8,9]

The aerosol must be delivered at a point such that as much of the metals CFLM as practically possible is challenged. For CFLM's outfitted with standard particulate matter sampling inlets (PM_{10}, $PM_{2.5}$ and TSP) the PM sampling inlet may be removed and the aerosol may be introduced into the downtube just below the size selective inlet. Aerosol introduction points for non-standard inlets may be determined at the discretion of the regulating agency.

The linearity test consists of at least three concentration levels and a zero level. The zero concentration may be determined by operating the instrument with a filter to remove any of the measured metals from the sampled air. This filter must be placed in the same location as the aerosol is introduced when spiking. The three concentration levels consist of the following for each regulated metal:

1. 10 to 30 percent of the permitted concentration limit
2. 30 to 60 percent of the permitted concentration limit
3. 80 to 120 percent of the permitted concentration limit.

Although a Linear Accuracy Audit is only required up to the concentration level of the permitted limit, it is recommended that the CFLM is challenged with even higher concentration levels. Concentrations on the fence lines of metals producing facilities have demonstrated a wide range of variability, with very high concentrations occurring for very short time intervals. It is reasonable to expect, for example, an hourly average concentration to be 10 or 20 times the daily average concentration. The linearity accuracy audit should be expanded to include these higher concentration levels. The

highest spiked concentration is considered to be the maximum validated concentration for the CFLM.

Five valid data points are required at each concentration level. These data points may be acquired at the normal instrument sampling interval or they may be acquired at shorter intervals to decrease total testing time. However, if shorter intervals are used, at least one measurement must be made at the desired sampling time period. For example, if the metals CFLM will normally acquire one hour samples the linearity testing can be done with a shorter sampling period, such as 15 minutes, provided at least one sample from each concentration level is determined at the normal sampling interval. The concentration reported during the normal sampling interval (e.g. 1 hour) must not differ from the average concentration of the shorter sampling intervals (e.g. 15 minutes) by more than three standard deviations.

After completing the aerosol spiking procedure, plot the concentrations reported by metals continuous fence line monitor versus the reference aerosol concentrations. Perform a linear least squares regression fit for each metal tested. All collected data must be used in the regression fit unless the operator can demonstrate a failure in the aerosol generator or in the instrument (outlier data may not be removed on a statistical basis only). If the slope of the least squares regression fit is between 0.85 and 1.15, the intercept is less than 20% of the permitted concentration level, and the correlation coefficient is greater than 0.90, the CFLM may be used for compliance without correction. If the slope or the intercept falls outside of their acceptable ranges, a correction factor may be applied to the metals CFLM data provided the following is true:

1. The slope of the best fit line is not greater than 1.3 or less than 0.70
2. The intercept is not greater than 40% of the permitted concentration limit
3. The correlation coefficient is greater than 0.90.

If these three criteria are not met the CFLM has failed the linearity accuracy audit. The slope and intercept correction factors can be calculated using Equations AA-6 and AA-7 respectively. Correcting both the slope and intercept simultaneously can be done using Equation AA-8. The symbols for slope and intercept refer to Equation AA-11 in Section 11.

$$C_i^C = \frac{C_i^{FLM}}{b_1} \qquad \text{Equation AA-6}$$

Where:

C_i^C = The corrected concentration for the ith metal

C_i^{FLM} = The CFLM reported concentration for the ith metal

b_1 = The slope of the least squares regression fit for the ith metal (see Equation AA-11 in Section 11)

$$C_i^C = C_i^{FLM} - b_o \qquad \text{Equation AA-7}$$

Where:

b_o = The intercept of the least square fit of the ith metal (see Equation AA-11 in Section 11)

$$C_i^C = \frac{C_i^{FLM} - b_0}{b_1} \qquad \text{Equation AA-8}$$

7.6.2 Relative Accuracy Audit Procedures

The accuracy of a metals continuous fence line monitor may also be determined by comparing the concentrations reported by the CFLM with those reported by a reference method. Suitable reference methods may include sampling using a Federal Reference Method (FRM) samplers or Federal Equivalent Method (FEM) samplers for PM_{10}, $PM_{2.5}$ or TSP. A list of acceptable samplers may be found in the Federal Register. All applicable quality assurance procedures and criteria must be followed for each sampler. Quality assurance criteria for PM_{10}, $PM_{2.5}$ and TSP may be found in Appendices J, L, and B respectively of 40 CFR 50.[4,5,6] Metals concentrations should be determined using those procedures commonly used and listed in the US EPA Compendium of Methods for the determination of Inorganic Compounds in Ambient Air.[7] These analytical methods include, X-ray fluorescence (IO 3.3), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (IO 3.5) Inductively Coupled Plasma Spectroscopy (IO 3.4) and Proton Induced X-ray Emission (PIXE) spectroscopy (IO 3.6). During the relative accuracy audit, the metals CFLM must be operating in accordance with the procedures found in *Procedure B – XRF Based Metals Fence Line Monitor Quality Assurance Procedures,*[1] including all applicable calibration checks.

For the relative accuracy audit at least two reference method samplers must be co-located with the CFLM. For high volume samplers, sample inlets for the reference method and the CFLM must be between 2 and 4 meters from any other sampler inlet. For low volume samplers, sample inlets for the reference method and the CFLM must be located between 1 and 4 meters from any other inlet.[14]

Most available reference methods are only capable of producing one analyzable sample per day. The comparison between the reference method and the fence line monitor, must then be between the daily reference method sample concentration and the daily average concentration reported by the CFLM. The reference method sampler should be programmed so that its sampling time coincides with the sampling time of the CFLM. If the CFLM is not sampling for any significant period of time due to quality assurance

procedures the reference method sampler should also not be sampling for that same period of time. The daily average for the CFLM should be calculated by adding all of the individual concentrations reported by the CFLM for each day and dividing by the total number of sampling periods as shown in Equation AA-9.

$$\overline{C_i^{FLM}} = \frac{\sum C_i^{FLM}}{n} \qquad \text{Equation AA-9}$$

Where:

$\overline{C_i^{FLM}}$ = The average daily CFLM reported concentration for the ith metal

C_i^{FLM} = An CFLM reported concentration for the ith metal for one sample period

n = The number of FLM sample periods in a day

Reference method data may be eliminated from comparison for days on which concentrations reported from each reference method sample differ by greater than 15%. The percent difference between each reference method may be calculated using Equation AA-10.

$$D_i = \frac{2(C_i^{R1} - C_i^{R2})}{\left(C_i^{R1} + C_i^{R2}\right)} \times 100\% \qquad \text{Equation AA-10}$$

Where:

D_i = The percent difference in reported concentration between the two reference method samplers for the ith metal.

C_i^{R1} = The reported concentration of the ith metal from reference method sampler one.

C_i^{R2} = The reported concentration of the ith metal from reference method sampler two.

Nine valid points of comparison must be generated for each regulated metal. Valid data points are generated on days in which the reference method comparability criteria are met, and where the average concentration reported by the reference method is at least 5% of the permitted concentration limit. After obtaining at least nine valid points of comparison, plot the daily average reported by the CFLM versus the average reference method concentration (the average of the two reference method samplers). Perform a least squares regression fit for each regulated metal and determine the slope, intercept and correlation coefficient for the best fit line. If the slope is between 0.85 and 1.15, the intercept is less than 20 percent of the permitted concentration limit, and the correlation coefficient is greater than 0.90 the metals continuous fence line monitor may be used

without correction. If the slope and/or intercept fall outside of their acceptable ranges a correction factor may be applied provided the following three criteria are met:

1. The slope of the best fit line is not greater than 1.3 or less than 0.70
2. The intercept is not greater than 40% of the permitted concentration limit
3. The correlation coefficient is greater than 0.90

If these criteria are not met the metals CFLM has failed the relative accuracy audit. Correction factors can be calculating using Equations AA-6 to AA-8 as appropriate.

7.7 Measurement Range

The CFLM's measurement range is determined during either the Linear Accuracy Audit or during the Relative Accuracy Audit, depending on which is performed. For the Linear Accuracy Audit the CFLM's validated measurement range extends from the lowest to the highest spiked concentration level. For the Relative Accuracy Audit, the measurement range extends from the lowest to the highest recorded concentrations for which there is reference method data to compare.

7.8 Reporting

At a minimum summarize all the results of the calibration drift checks, the XRF and flow audits and the results of the either the linearity audit or the relative accuracy audit. Include all data sheets, calculations, charts and any other information necessary to confirm that the metals CFLM meets the performance criteria.

8 Quality Control (Reserved)

9 Calibration and Standards (Reserved)

10 Analytical Procedures (Reserved)

11 Calculations and Data Analysis

11.1 Consistent Basis

All CFLM, reference method and aerosol generator data must be compared in units of micrograms or nanograms per standard cubic meter at 25 °C and 760 mm Hg.

11.2 Linear Regression

Both the linearity audit and the relative accuracy audit utilize linear least squares fitting. For this fitting, the CFLM's response is modeled as a linear function of either the reference aerosol concentration or the reported reference method concentration. The form of this simple linear least squares relationship can be found in Equation AA-11

$$\hat{y} = b_o + b_1 x \qquad \text{Equation AA-11}$$

Where:

$\hat{y}$	=	Concentration output of the CFLM as predicted by the linear least squares model
b_1	=	The slope of the best fit line
b_o	=	The intercept of the best fit line
x	=	The reference aerosol or reference method concentration

The slope of the simple least squares line is given by Equation AA-12

$$b_1 = \frac{\sum_{i=1}^{n}(x_i - \bar{\ })(y_i - \bar{y})}{\sum_{i=1}^{n}(x_i - \bar{\ })^2} \qquad \text{Equation AA-13}$$

Where:

b_1	=	The slope of the best fit line
x_i	=	An individual reference aerosol or reference method concentration
$\bar{x}$	=	The average reference aerosol or reference method concentration
y_i	=	An individual reported CFLM concentration
$\bar{y}$	=	The average reported CFLM concentration

Using the slope calculated in Equation AA-13 the intercept can be calculated using Equation AA-14.

$$b_o = \bar{y} - b_1 \bar{x} \qquad \text{Equation AA-14}$$

Finally the correlation coefficient (r) can be calculated using Equation AA-15.

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{\ })(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{\ })^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}}$$

12 Method Performance

12.1 Zero Drift

The magnitude for the zero drift must not exceed 15% of the permitted concentration limit each day for seven consecutive instrument operating days.

12.2 Upscale Drift

The magnitude of the upscale drift must not exceed 15% of the reference value each day for the upscale standard for seven consecutive instrument operating days.

12.3 Flow Drift

The magnitude of the flow drift must not exceed 20% of the reading of the CFLM's quality assurance flow meter each day for seven consecutive instrument operating days.

12.4 XRF Calibration Error

For each regulated metal the XRF calibration error must not exceed 10% of the value of the traceable to NIST reference standard.

12.5 Flow Error

The flow error must not exceed 10% of the NIST traceable reference flow meter.

12.6 Linearity Audit Criteria

Plot the CFLM reported concentration versus the reference aerosol concentration. If the slope of the best fit line is between 0.85 and 1.15, the intercept is less than 20% of the permitted concentration limit, and the correlation coefficient is greater than 0.90 the metals CFLM may be used without a correction factor. If the slope or the intercept fall outside of this range a correction factor may be applied to the CFLM data if the following three criteria are met:

1. The slope of the best fit line is not greater than 1.3 or less than 0.70
2. The intercept is not greater than 40% of the permitted concentration limit
3. The correlation coefficient is greater than 0.90.

If these three criteria are not met the CFLM has failed the Linear Accuracy Audit.

12.7 Relative Accuracy Audit

Plot the daily CFLM average versus the daily average reference method concentration for each day. If the slope of the best fit line is between 0.85 and 1.15, the intercept is less than 20% of the permitted concentration limit, and the correlation coefficient is greater than 0.90 the metals CFLM may be used without a correction factor. If the slope or the intercept fall outside of this range a correction factor may be applied if the following three criteria are met:

1. The slope of the best fit line is not greater than 1.3 or less than 0.70
2. The intercept is not greater than 40% of the permitted concentration limit
3. The correlation coefficient is greater than 0.90.

If these three criteria are not met the CFLM has failed the Linear Accuracy Audit.

13 Pollution Prevention (Reserved)

14 Waste Management (Reserved)

15 Alternative Procedures (Reserved)

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17 Tables and Figures

Table 1. Summary of Performance Specification AA Requirements

Test Category	Test	Test Requirements	Test Criteria
7 Day Stability	Upscale	Monitor Upscale Standard once per day for 7 consecutive days. Each check must run for the monitor's intended sampling time.	Must be less than 15% of the calibrated upscale standard value
	Zero	Monitor the zero standard once per day for 7 consecutive days. Each check must run for the monitor's intended sampling time.	Zero value must be less than 15% of the permitted concentration limit for all days
	Flow	Monitor the Flow drift once per day for seven consecutive days	Must be less than 20% difference between the reference flow meter and measuring flow sensor everyday for 7 days
Calibration Check	XRF Audit	Test the analyzer response to each permitted element using a NIST traceable standard.	Less than 10% difference between the standard and the instruments reported value
	Flow Audit	Test the measurements made by the analyzer's flow system using an independent flow measurement device. Average at least 9 individual measurements of flow	Average percent difference between the instrument flow and the Reference flow meter must be less than 10%
Accuracy	**Option A** Linearity Audit	• Generate a NIST Traceable Aerosol Concentration for each metal being permitted by the instrument • Measure a zero concentration and at least 3 concentration levels including i) Between 10 and 30 % of PCL[a] ii)Between 30 and 60% of the PCL[a] iii) 80 and 120% of the PCL[a] Spike must be as close as practically possible to the sampling inlet. Standard size selection inlets such as PM_{10}, $PM_{2.5}$ and TSP may be bypassed a. PCL = Permitted Concentration Limit	• Slope = 0.85 to 1.15 • Intercept = must be less than 20% of the permitted limit for each element • Correlation Coefficient (r) greater than 0.90 • A correction factor may be applied if the slope and/or intercept criteria are not met but the correlation coefficient criteria is achieved
	Option B Comparability with Reference Method	• Compare Metals FLM with two collocated Reference Methods. • Obtain 9 samples for each permitted metal where the reported concentration is greater than 5% of the permitted concentration limit and where the precision requirement for the reference method is met • Perform Linear Regression fit for each element	• Reference Method Precision – 15% • Linear Regression fit i) Slope = 0.85 to 1.15 ii) Intercept = less than 20% of permitted limit iii) Correlation (r) coefficient greater than 0.90. • Correction factors may be applied if correlation coefficient criteria are met

APPENDIX B

Procedure BB: On-Going Quality Assurance Requirements and Procedures for X-ray Fluorescence Based Metals Continuous Fence-Line Monitors

DRAFT

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Executive Summary

Procedure B specifies the on-going quality control and assurance requirements for X-ray based metals continuous fence-line monitors (CFLM) used for regulatory purposes. Procedure B requires X-ray based metals CFLMs to undergo daily upscale and flow calibration drift checks, weekly zero drift checks, quarterly XRF and flow calibration audits and annual Linear Accuracy or Relative Accuracy audits.

List of Symbols

A_i^T	=	The CFLM's reported value for the ith metal on a traceable to NIST standard
A_i^U	=	The measured value of the ith metal on the upscale standard
A_i^Z	=	The measured value of the ith metal on the zero drift standard
b_o	=	The intercept of the best fit line
b_1	=	The slope of the best fit line
C_i^C	=	The corrected concentration for the ith metal
C_i^{FLM}	=	An CFLM reported concentration for the ith metal for one sample period
$\overline{C_i^{FLM}}$	=	The average daily CFLM reported concentration for the ith metal
C_i^L	=	The concentration of the permitted limit for the ith metal
C_i^{R1}	=	The reported concentration of the ith metal from reference method sampler one.
C_i^{R2}	=	The reported concentration of the ith metal from reference method sampler two.
CE_i	=	The XRF calibration error for the ith metal of the CFLM expressed as a percent
D_i	=	The percent difference in reported concentration between the two reference method samplers for the ith metal.
F_{FLM}	=	Flow as measured by the metals CFLM
F_P	=	The flow reading from the CFLM's primary flow meter used during normal Operation
F_{QA}	=	The flow reading from the QA flow sensor
F_R	=	Flow as measured by the NIST traceable flow measurement device
FD	=	The flow drift of the metals CFLM in percent
FE	=	Flow Error expressed as a percent
M_i^U	=	The upscale reference value for the ith metal
M_i^Z	=	The zero reference value for the ith metal
n	=	The number of FLM sample periods in a day
R_i^T	=	The value the ith metal on a traceable to NIST standard

UD_i = The upscale drift for the ith metal in percent
x = The reference aerosol or reference method concentration
x_i = An individual reference aerosol or reference method concentration
$\bar{x}$ = The average reference aerosol or reference method concentration
$\hat{y}$ = Concentration output of the CFLM as predicted by the linear least squares model
y_i = An individual reported CFLM concentration
$\bar{y}$ = The average reported CFLM concentration
ZD_i = The zero drift for the ith metal in percent

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1.0 Purpose and Application

1.1. Purpose

The purpose of Procedure B is to define on-going quality control and assurance requirements for X-ray fluorescence (XRF) based metals continuous fence-line monitors (CFLM). Following the procedures in this document will assure the data integrity and accuracy of metals CFLMs. Additionally Procedure B contains reporting requirements and procedures for demonstrating that out of control CFLMs have been repaired and are producing accurate data. Initial performance requirements for CFLMs can be found in *Performance Specification AA – Specifications and Test Procedures for X-ray Fluorescence Based Metals Continuous Fence-Line Monitors (PS-AA).*[1] Metals monitors meeting the performance criteria in procedure B and PS-AA may be used by regulating agencies (local, state, and federal) for the purposes of enforcing a permitted metals concentration either at the perimeter of a facility with fugitive metal emissions or in communities affected by metal emissions.

1.2. Applicability

Metals CFLM's used to determine a facility's compliance with a permitted concentration level must follow the procedures found in Procedure B immediately following the successful completion of the initial performance specifications found in PS-AA.

1.2.1. Analytes

Procedure B covers the measurement of several metal analytes including, but not limited to: Antimony (Sb), Arsenic (As), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), and Selenium (Se).

1.2.2. Additional Quality Control and Assurance Procedures

Procedure B specifies the minimum requirements for controlling and assessing the quality of a metals continuous fence-line monitor's data. You are encouraged to develop and implement a more extensive QA program or to continue such programs where they already exist.

2.0 Definitions

2.1. Metals Continuous Fence-Line Monitor (CFLM)

A metals CFLM is any monitor capable of measuring one or more metal concentrations on a continuous, real time basis. These monitors may be located at the fence-line or perimeter of industrial facilities with fugitive metal emissions or in communities affected by metal emissions. These monitors generally consist of the following subsystems:

2.1.1. Sample inlet

The sample inlet for a metals CLFM can include any standard, federally recognized PM_{10}, $PM_{2.5}$ or high-vol TSP inlets.[2,3,4] Other types of sample inlets may be allowed or specified by applicable regulations or permits.

2.1.2. Sampling and Analysis Module

This is the portion of the metals CFLM that samples the air and measures the metal mass. For the XRF based monitors governed by this performance specification, this system consists of the filter media (if such filter material is necessary) designed to capture the particulate and/or vapor phase metals and the components of the X-ray analytical equipment (e.g. tube, detector, power supplies).

2.1.3. Sample Flow Module

The sample flow system includes those parts designed to generate and measure the flow into the CFLM.

2.1.4. Data Recorder

This is the portion of the metals CFLM that provides an electronic record of the instrument's output in terms of ng/m^3 or $\mu g/m^3$.

2.2. Permitted Concentration Limit

This is the maximum concentration of a metal allowed by regulation, permit or other enforcement mechanism for a particular area or airshed. The metals continuous fence-line monitor is used to determine a regulated facility's compliance with this limit.

2.3. Calibration Drift Tests

Calibration drift is the difference in the CFLM output readings from established reference values after a stated period of operation during which no unscheduled maintenance, repair or adjustments took place. Three calibration drift checks are required of x-ray fluorescence based metals CFLMs: a zero drift check, an upscale drift check, and a flow drift check. The upscale and flow drift checks are required on a daily basis, while the zero drift check is required on a weekly basis.

2.3.1. Zero Drift

Zero drift is the difference in a reported value for a zero reference sample and its value at the last analyzer calibration, divided by the permitted concentration limit, expressed as a percent.

2.3.2. Upscale Drift

Upscale drift is the difference in a reported value for an upscale reference sample from its value at the last analyzer calibration, divided by the value at the last analyzer calibration, expressed as a percent.

2.3.3. Flow Drift

Flow drift is the difference between a flow measured by the CFLMs primary flow sensor and flow measured by the CFLM's flow check measurement device divided by the flow from the flow check measurement device, expressed as a percent

2.4. XRF Analyzer Audit

This is a test of the accuracy of the metals CFLM's XRF analyzer. Gravimetrically traceable to NIST thin film standards may be used to audit the accuracy of the metals analyzer (see Section 5.4). The results of this audit are used to calculate the calibration error (see Section 7.4)

2.5. Flow Audit

The flow audit measures the accuracy of the metals CFLM's flow sensor using a NIST traceable flow measurement device. The results of this audit are used to calculate the flow error (see Section 7.5).

2.6. Linear Accuracy Audit

This test assesses the linearity of the metals CFLM's response to a range of aerosol concentrations. The response of the CFLM is compared to the reference aerosol concentration.

2.7. Relative Accuracy Audit

The relative accuracy audit assesses the accuracy of a metals CFLM's response by comparing it to a reference method.

2.8. Measurement Range

This is the range of concentrations over which the metals continuous CFLM has demonstrated valid and accurate measurement. If a Linear Accuracy Audit is performed then this range extends from the lowest aerosol concentration level to the highest aerosol concentration level. If relative accuracy audit is performed the instrument range spans from the lowest recorded concentration for which there is accurate comparison data to the highest recorded concentration for which there is accurate comparison data.

2.9. Maximum Validated Concentration

The maximum validated concentration is the highest concentration that the metals CFLM has demonstrated it can accurately measure. If a Linear Accuracy Audit is performed against a

reference aerosol the highest aerosol concentration level is the maximum validated concentration. If CFLM accuracy is validated using a relative accuracy audit, the maximum validated concentration is equal to the concentration of the highest recorded sample for which there is reference method data to compare.

2.10. Out of Control Period

If the metals CFLM fails any of the required calibration drift checks or audits, the CFLM is out of control and cannot be used for compliance purposes until it demonstrates that it can successfully pass the drift check or audit that initiated the failure.

3.0 Interferences

Please check with your metals CFLM's manufacturer for any potential interferences.

4.0 Safety

Persons using procedure B may be exposed to hazardous materials, equipment and operations. Procedure B does not purport to address all of the safety issues associated with its use. It is your responsibility to establish appropriate safety and health practices before using this procedure. You may contact your metals CFLM manufacturer regarding hazards and precautions specific to the monitor. If standard reference methods are used you may also consult the appropriate reference methods to address safety concerns.

5.0 Reference Standards and Equipment

5.1. Zero Drift Reference

All metals continuous fence-line monitors must be equipped with a zero drift reference. The reported concentration for this reference value must be between 0 and 20 percent of the permitted concentration limit. For CFLM's utilizing filter tape to capture particulate and/or vapor phase metals concentrations, a blank section of tape may be used as a zero reference.

5.2. Upscale Drift Reference

All metals continuous fence-line monitors must be equipped with an upscale drift reference for each regulated metal being monitored. This reference is used to test the stability of the XRF analyzer and must have a reported concentration equivalent to at least 80 percent of the permitted concentration limit.

5.3. Quality Assurance Flow Meter

All metals CFLMs must be equipped with a flow measurement device that can be used to automatically check the accuracy of the instrument's primary flow measurement device.

5.4. XRF Audit Standards

Most XRF analyzers used to determine metals concentrations on particulate matter (PM) filter samples are calibrated using thin film standards. An XRF based metals CFLM may be calibrated in this same way. The accuracy of the XRF analyzer should be checked using these standards. Micromatter[5] produces gravimetrically traceable to NIST thin film standards that have been recognized as being useful for the purposes of calibrating XRF analyzers.[6] Other traceable to NIST thin film standards may be used if available.

5.5. NIST Traceable Flow Meter

Both the fence-line monitor's primary and quality assurance flow meters should be checked using a NIST traceable flow meter. NIST traceable flow meters are available from a variety of manufacturers. Procedures for performing a flow audit with a NIST traceable flow meter can be found in Section 7.5.

5.6. Reference Aerosol Generator

If the accuracy of the metals continuous fence-line monitor is determined using a reference aerosol, then it is necessary to have all the equipment required to generate a reference aerosol. The quality assurance procedures for such a generator may be found elsewhere.[7,8]

5.7. Reference Method

If the accuracy of the metals CFLM is determined using a relative accuracy audit, then it is necessary to have all the equipment required to gather suitable reference method measurements. This equipment could include samplers, filters, additional sample inlets and laboratory analytical equipment. Sampling reference methods may include those found for sampling PM_{10}, $PM_{2.5}$ and TSP in Appendices J, L and B respectively of 40 CFR 50.[2,3,4] Appropriate metals analysis procedures may be found in the Compendium of Methods for the Determination of Inorganic Compounds (I.O.) in Ambient Air.[9] Examples of appropriate analysis methods include X-ray Fluorescence (I.O. 3.3), inductively coupled plasma (ICP) spectroscopy (I.O. 3.4), inductively coupled plasma/mass spectrometry (I.O. 3.5), and proton induced X-ray emission (PIXE) spectroscopy (I.O. 3.6).

6.0 Quality Control Requirements

Each owner and operator of a continuous metals fence-line monitor must develop and implement a quality control (QC) program. At a minimum each QC program must include written documents which should provide in detail, complete step-by-step procedures and operations for each of the following activities as applicable:

1. Procedures for performing zero, upscale and flow drift checks.
2. Procedures for determining the zero drift, upscale drift and flow drift and methods of adjusting your metals CFLM in response to the results of the drift checks.
3. Routine and preventative maintenance procedures for the metals CFLM.
4. Data recording, calculations and reporting procedures

5. Procedures for performing all required audits including the XRF Analyzer Audit, the Flow Audit, and the Linearity or Relative Accuracy Audits (as applicable).
6. Procedures for adjusting your metals CFLM based on audit results.
7. A program of corrective action in case of a CFLM malfunction and an out of control period.

These written procedures must be kept on record and available for inspection by the responsible enforcement agency for the lifetime of the CFLM or until you are no longer subject to the requirements of this procedure. If you fail two consecutive audits you must revise your quality control and assurance procedures.

7.0 Calibration Drift Check and Audit Procedures

7.1. Zero Drift Check

The zero drift check must be performed at least once every seven unit operating days. The length of the analysis time of the zero reference shall be equivalent to the analysis time used during the metals CFLM's normal sampling. Calculate the zero drift by determining the absolute value of the difference between the zero drift reference value (M_i^Z) and the CFLM's reported value (A_i^Z), divided by the permitted concentration limit (C_i^L) according to Equation B-1. The zero drift reference value is determined according the manufacturers specifications immediately following the XRF calibration of the instrument.

$$ZD_i = \frac{\left|M_i^Z - A_i^Z\right|}{C_i^L} \times 100\% \qquad \text{Equation B-1}$$

Where:

ZD_i = The zero drift for the ith metal in percent

M_i^Z = The zero reference value for the ith metal

A_i^Z = The measured value of the ith metal

C_i^L = The concentration of the permitted limit for the ith metal

7.2. Upscale Drift Check

Your metals continuous fence-line monitor must perform an upscale drift check at least once daily at approximately 24 hour intervals every unit operating day. The analysis time for the upscale drift check need not be equivalent to the normal sample analysis period, provided it is long enough to give an adequate measure of the instrument's upscale drift. Calculate the upscale drift by determining the absolute value of the difference between the upscale reference value (M_i^U) and the metals CFLM's reported value (A_i^U) and dividing by the upscale reference

value according to Equation B-2. The upscale reference value is determined according to the manufacturers specifications immediately following the XRF calibration of the instrument.

$$UD_i = \frac{\left|M_i^U - A_i^U\right|}{M_i^U} \times 100\% \qquad \text{Equation B-2}$$

Where:

UD_i = The upscale drift for the ith metal in percent

M_i^U = The upscale reference value for the ith metal

A_i^U = The measured value of the ith metal

7.3. Flow Drift Check

Your metals CFLM must be able to perform a flow drift check at least once daily at approximately 24 hour intervals. The time interval for the flow drift check should be long enough to adequately check the accuracy of the metals CFLM's primary flow sensor, but need not be the length of a normal sampling period. The flow drift is determined by comparing the flow from the CFLM's primary flow sensor used during normal sampling, and a secondary flow sensor used only during quality assurance procedures. The flow rate during the flow calibration drift check must be the same as that used during the normal operation of the instrument. The magnitude of the flow drift may be calculated by determining the absolute value of the difference between the quality assurance flow sensor reading and the primary flow sensor reading and dividing by the quality assurance flow sensor reading according to Equation B-3.

$$FD = \frac{\left|F_{QA} - \quad {}_P\right|}{F_{QA}} \times 100\% \qquad \text{Equation B-3}$$

Where:

FD = The flow drift of the metals CFLM in percent

F_{QA} = The flow reading from the QA flow sensor

F_P = The flow reading from the CFLM's primary flow meter used during normal operation

7.4. XRF Analyzer Audit

An XRF analyzer audit must be performed at least once every calendar quarter. The minimum allowed time between regularly scheduled quarterly audits shall be two months and the maximum allowed time between regularly scheduled quarterly audits shall be four months. XRF analyzer audits may be performed more often if the audit is required to demonstrate the instrument is producing accurate data following a repair or calibration change made to the

metals CFLM. The XRF analyzer portion of the metals continuous fence-line monitor must be audited for each regulated metal using traceable to NIST reference standard. An example of such audit standards are available commercially from Micromatter.[5] The XRF audit, checks the XRF analyzer portion of the CFLM for accuracy relative to these standards and the audit results are used to calculate the XRF calibration error. The magnitude of the XRF calibration error (CE_i) is calculated by determining the absolute value of the difference between the value of the ith metal on the NIST traceable reference standard (R_i^T) and the value of reported by the CFLM for that standard (A_i^T), divided by the reference standard (see Equation B-4).

$$CE_i = \frac{\left|R_i^T - A_i^T\right|}{R_i^T} \times 100\% \qquad \text{Equation B-4}$$

Where:

CE_i = The XRF calibration error for the ith metal of the CFLM expressed as a percent

R_i^T = The value the ith metal on a traceable to NIST standard

A_i^T = The CFLM's reported value for the ith metal on a traceable to NIST standard

7.5. Flow Audit

A flow audit of your metals continuous fence-line monitor is required at least once every calendar quarter. The minimum time between regularly scheduled quarterly audits shall be two months, while the maximum allowed time between regularly scheduled quarterly audits shall be four months. Flow audits may be performed more frequently if the audit is required to demonstrate the accuracy of the metals CFLM's flow module following a repair or calibration adjustment. As in PS-AA, the accuracy of both the CFLM's primary and quality assurance flow meters must be audited by comparing their flow measurement to the measurement of the same flow using a NIST traceable reference flow meter. The flow audit shall incorporate as much of the CFLM's flow system tubing and components as practically possible. For metals CFLMs equipped with a PM_{10}, or $PM_{2.5}$ sampling inlet, remove the PM selective inlet(s), replace it with a flow cap adaptor, and perform the flow check in a manner similar to the procedures described in Appendix L of 40 CFR part 50.[3] Calculate the flow error according to Equation B-5.

$$FE = \frac{\left|F_{FLM} - F_R\right|}{F_R} \times 100\% \qquad \text{Equation B-5}$$

Where:

FE = Flow Error expressed as a percent

F_R = Flow as measured by the NIST traceable flow measurement device

F_{FLM} = Flow as measured by the metals CFLM

7.6. Overall CFLM Accuracy Test Procedures

As in Performance Specification AA, the accuracy of the entire metals CFLM system must be checked using either a linearity audit or a relative accuracy audit. These audits must be performed on an annual basis with a minimum required time between of audits of 9 months and a maximum time between audits of 15 months. Either method may be used to assess the accuracy of the metals CFLM on an on-going basis regardless of how the CFLM's accuracy has been assessed previously. For example, you may perform a linearity audit during the first required annual audit even if the accuracy during the initial performance specification was determined using a relative accuracy audit. The advantages and drawbacks of each approach are addressed in Performance Specification AA.[1]

7.6.1. *Linearity Audit*

The reference aerosol generator used for this test must be cable of delivering a traceable to NIST aerosol consisting of the regulated metal or metals at the concentration levels specified in this procedure. Quality control and assurance procedures for the reference aerosol generator can be found elsewhere.[7,8]

The aerosol must be delivered at a point such that as much of the metals CFLM as practically possible is challenged. For CFLM's equipped with standard particulate matter sampling inlets (PM_{10}, $PM_{2.5}$ and TSP) the PM sampling inlet may be removed and the aerosol may be introduced into the downtube just below the size selective inlet. Aerosol introduction points for non-standard inlets may be determined at the discretion of the regulating agency.

The linearity test consists of at least three concentration levels and a zero level. The zero concentration may be generated by operating the instrument with a filter to remove any of the measured metals from the sampled air. This filter must be placed in the same location as the aerosol is introduced when spiking. The three concentration levels consist of the following for each regulated metal:

1. 10 to 30 percent of the permitted concentration limit for each metal
2. 30 to 60 percent of the permitted concentration limit for each metal
3. 80 to 120 percent of the permitted concentration limit for each metal

Performance Specification AA recommends challenging the metals CFLM with higher concentrations of the reference aerosol to obtain a wider validated measurement range for the instrument. If the metals CFLM was challenged at higher concentrations during the initial performance specification, it does not need to be revalidated at those higher concentration levels during each annual Linear Accuracy Audit. If the instrument is challenged using a Linear Accuracy Audit the maximum validated concentration for the CFLM will be the concentration of

the highest reference aerosol concentration it has demonstrated accurate measurement, whether that concentration was measured during the initial performance test or subsequent annual audits.

Five valid data points are required at each concentration level. These data points may be acquired at the normal instrument sampling interval or they may be acquired at shorter intervals to decrease total testing time. However, if shorter intervals are used, at least one measurement must be made at the desired sampling time period. For example, if the metals CFLM will normally acquire one hour samples the linearity testing can be done with a shorter sampling period, such as 15 minutes, provided at least one sample from each concentration level is determined at the normal one hour sampling interval and that the concentration reported by the instrument for this sample is not significantly different from those reported at shorter time intervals

After completing the aerosol spiking procedure, plot the concentrations reported by metals continuous fence-line monitor versus the reference aerosol concentrations. Perform a linear least squares regression fit for each metal tested and from this fit determine the slope, intercept and correlation coefficient. Equations for these parameters may be found in Section 9.0. All collected data must be used in the regression fit unless the operator can demonstrate a failure in the aerosol generator or in the instrument (outlier data may not be removed on a statistical basis only). Linear Accuracy Test Criteria may be found in Section 8.0.

7.6.2. Relative Accuracy Audit Procedures

The accuracy of a metals continuous fence-line monitor may also be determined by comparing the concentrations reported by the CFLM with those reported by a reference method. Suitable reference methods may include sampling using Federal Reference Method (FRM) samplers or Federal Equivalent Method (FEM) samplers for PM_{10}, $PM_{2.5}$ or TSP. A list of acceptable samplers may be found in the Federal Register. All applicable quality assurance procedures and criteria must be followed for each sampler. Quality assurance criteria for PM_{10}, $PM_{2.5}$ and TSP may be found in Appendices J, L, and B respectively of 40 CFR 50.[2,3,4] Metals concentrations should be determined using those procedures commonly used and listed in the US EPA Compendium of Methods for the determination of Inorganic Compounds in Ambient Air.[9] These analytical methods include, X-ray fluorescence (IO 3.3), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (IO 3.5) Inductively Coupled Plasma Spectroscopy (IO 3.4) and Proton Induced X-ray Emission (PIXE) spectroscopy (IO 3.6). During the relative accuracy audit, the metals CFLM must be operating and performing all applicable calibration checks.

For the relative accuracy audit, at least two reference method samplers must be co-located with the CFLM. For high volume samplers, sample inlets for the reference method and the CFLM must be between 2 and 4 meters from any other sampler inlet. For low volume sampler inlets, they must be located between 1 and 4 meters from any other inlet.[10]

Most available reference methods are only capable of producing one analyzable sample per day. The comparison between the reference method and the fence-line monitor, must then be between the daily reference method sample concentration and the daily average concentration reported by the CFLM. The reference method sampler should be programmed so that its sampling time coincides with the sampling time of the CFLM. If the CFLM is not sampling for any significant period of time due to quality assurance procedures the reference method sampler should also not be sampling for that same period of time. The daily average for the CFLM should be calculated by adding all of the individual concentrations reported by the CFLM for each day and dividing by the total number of sampling periods as shown in Equation B-6.

$$\overline{C_i^{FLM}} = \frac{\sum C_i^{FLM}}{n} \qquad \text{Equation B-6}$$

Where:

$\overline{C_i^{FLM}}$ = The average daily CFLM reported concentration for the ith metal

C_i^{FLM} = An CFLM reported concentration for the ith metal for one sample period

n = The number of FLM sample periods in a day

Reference method data may be eliminated from comparison for days on which concentrations reported from each reference method sample differ by greater than 15%. The percent difference between each reference method must be calculated using Equation B-7.

$$D_i = \frac{2(C_i^{R1} - C_i^{R2})}{\left(C_i^{R1} + C_i^{R2}\right)} \times 100\% \qquad \text{Equation B-7}$$

Where:

D_i = The percent difference in reported concentration between the two reference method samplers for the ith metal.

C_i^{R1} = The reported concentration of the ith metal from reference method sampler one.

C_i^{R2} = The reported concentration of the ith metal from reference method sampler two.

Nine valid points of comparison must be generated for each regulated metal. Valid data points are generated on days in which the reference method comparability criteria are met, and where the average concentration reported by the reference method is at least 5% of the permitted concentration limit. After obtaining at least nine valid points of comparison, plot the daily average reported by the CFLM versus the average reference method concentration (the

average of the two reference method samplers). Perform a least squares regression fit for each regulated metal and determine the slope, intercept and correlation coefficient for the best fit line.

8.0 Performance Criteria and Out of Control Procedures

8.1. Zero Drift Check

The zero drift, calculated using Equation B-1, must be less than 20 percent of the permitted concentration limit each unit operating day. If the 20 percent criterion is not met then you are required to immediately reanalyze the zero drift standard and recalculated the zero drift. If the metals CFLM meets the zero drift criterion during the second test the unit may continue to operate. If the CFLM fails to meet the zero drift criterion during the second zero drift check the CLFM is out of control. It is recommended that the CFLM be examined for defects. After appropriate repairs have been completed you are required to run at least three consecutive zero drift checks for which the zero drift criterion is met. After the three checks have been completed the CFLM is in control. If repairs were made to the XRF analyzer equipment you are also required to perform and X-ray analyzer audit to verify the accuracy of your X-ray fluorescence calibration.

8.2. Upscale Drift Check

The upscale drift, calculated using Equation B-2, must be less than 15 percent of the upscale reference value each unit operating day. If the one day upscale drift exceeds 15% you are required to immediately reanalyze the upscale drift reference. If the CFLM meets the upscale drift criterion during the second test, the instrument may continue to operate, however, if it fails to meet the upscale drift criterion during the second test, the instrument is out of control. If this occurs, it is recommended that the CFLM be examined for defects. After repairs to the CFLM have been completed you are required to pass at least three consecutive upscale drift checks to demonstrate that the instrument is back in control. If repairs were made to the XRF analyzer equipment you are also required to perform an X-ray analyzer audit to verify the accuracy of you XRF calibration.

8.3. Flow Drift Check

The flow drift, calculated using Equation B-3, must be less than 20 percent of the flow as measured by metals CFLM's quality assurance flow meter each unit operating day. If the one day flow drift exceeds 20 percent you are required to immediately perform another flow drift check. If the CFLM meets the flow drift criterion during the second drift check the instrument may continue to operate, however if it fails the second flow drift check the CFLM is out of control. If this occurs, it is recommended that the CFLM be examined for defects. After repairs to the CFLM have been completed the CFLM is required to pass at least three consecutive flow drift checks to demonstrate that the instrument is back in control. Additionally, the CFLM must pass a flow audit.

8.4. XRF Analyzer Audit

The magnitude of the XRF calibration error (as calculated in Equation B-4) must not exceed 10 percent of the value of the traceable to NIST reference standard for any metal regulated by the instrument. If the calibration error exceeds 10 percent for any regulated metal the NIST traceable standard for that metal may be analyzed two additional times and the average of the three measurements must be calculated. If the average of the three measurements meets the 10% criteria the CFLM has passed the XRF Analyzer Audit. However, if the average of these three measurements still exceeds 10 percent of the reference value, the CFLM is out of control. It is recommended that the metals CFLM be examined for defects. After the CFLM has been repaired an XRF audit must be successfully completed.

8.5. Flow Audit

The magnitude of the flow error (calculated using Equation B-5) must not exceed 10 percent of the flow as measured by the reference flow meter. If the flow error exceeds 10 percent the CFLM is out of control. It is recommended that the CFLM may be checked for defects and repaired. Following repairs a flow audit must be performed. If the CFLM successfully passes the flow audit it is back in control.

8.6. Linearity Audit

A metals CFLM may be used for compliance without correction if the slope of the best fit line is between 0.85 and 1.15, the intercept is less than 20% of the permitted concentration limit and the correlation coefficient is greater than or equal to 0.90. If these criteria are not met a correction factor may be applied concentrations reported by the metals CFLM provided the following criteria are met:

1. The slope of the best fit line is not greater than 1.30 or less than 0.70
2. The intercept is not greater than 40% of the permitted concentration limit
3. The correlation coefficient is greater than 0.90

If these criteria are not met the CFLM has failed the Linear Accuracy Audit and is out of control. It is recommended that the CFLM be examined for defects and repaired. Following these repairs, the CFLM must pass a linearity audit or a relative accuracy audit before it is back in control.

The slope and intercept correction factors can be calculated using Equations B-8 and B-9 respectively. Use Equation B-10 to apply a correction to the slope and to the intercept simultaneously.

$$C_i^C = \frac{C_i^{FLM}}{b_1} \qquad \text{Equation B-8}$$

Where:

C_i^C = The corrected concentration for the ith metal

C_i^{FLM} = The CFLM reported concentration for the ith metal

b_1 = The slope of the least squares regression fit for the ith metal

$$C_i^C = C_i^{FLM} - b_o \qquad \text{Equation B-9}$$

Where:

b_o = The intercept of the least square fit of the ith metal

$$C_i^C = \frac{C_i^{FLM} - b_0}{b_1} \qquad \text{Equation B-10}$$

8.7. Relative Accuracy Audit

A metals CFLM may be used for compliance without correction if the slope of the best fit line is between 0.85 and 1.15, the intercept is less than 20% of the permitted concentration limit, and the correlation coefficient is greater than or equal to 0.90. If these criteria are not met a correction factor may be applied concentrations reported by the metals CFLM provided the following criteria are met:

1. The slope of the best fit line is not greater than 1.30 or less than 0.70
2. The intercept is not greater than 40% of the permitted concentration limit
3. The correlation coefficient is greater than 0.90

If these criteria are not met the CFLM has failed the Relative Accuracy Audit and is out of control. It is recommended that the CFLM be examined for defects and repaired. Following these repairs, the CFLM must pass a linearity audit or a relative accuracy audit before it is back in control. Following these repairs, the CFLM must pass a relative accuracy audit or a linearity audit before it is back in control.

8.8. Data During Out-of-Control Periods

During a period when the metals CFLM is out of control, the CFLM data may not be used to determine compliance with a permitted concentration limit or to meet a minimum data availability requirement specified in an applicable regulation or permit.

9.0 Calculations

9.1. Consistent Basis

All CFLM, reference method and aerosol generator data must be compared in units of micrograms or nanograms per standard cubic meter at 25 °C and 760 mm Hg.

9.2. Linear Regression

Both the linearity audit and the relative accuracy audit utilize linear least squares fitting. For this procedure, the CFLM's response is modeled as a linear function of either the reference aerosol concentration or the reported reference method concentration. The form of this simple linear least squares relationship can be found in Equation B-11

$$\hat{y} = b_o + b_1 x \qquad \text{Equation B-11}$$

Where:

$\hat{y}$ = Concentration output of the CFLM as predicted by the linear least squares model

b_1 = The slope of the best fit line

b_o = The intercept of the best fit line

x = The reference aerosol or reference method concentration

The slope of the simple least squares line is given by Equation B-12

$$b_1 = \frac{\sum_{i=1}^{n}(x_i - \bar{\ })(y_i - \bar{y})}{\sum_{i=1}^{n}(x_i - \bar{\ })^2} \qquad \text{Equation B-12}$$

Where:

b_1 = The slope of the best fit line

x_i = An individual reference aerosol or reference method concentration

$\bar{x}$ = The average reference aerosol or reference method concentration

y_i = An individual reported CFLM concentration

$\bar{y}$ = The average reported CFLM concentration

Using the slope calculated in Equation B-13 the intercept can be calculated using Equation B-13.

$$b_o = \bar{y} - b_1 \bar{x} \qquad \text{Equation B-13}$$

Finally the correlation coefficient (r) can be calculated using Equation B-14.

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}}$$ Equation B-14

10.0 Reporting Requirements

At the reporting interval specified in the applicable regulation or permit, report the results of all drift checks and audits performed during the reporting interval for each metals CFLM. For each out of control period, report the results of the drift check or audit that caused the out of control period and those results that demonstrate the CFLM is back in control. Also document all repairs and corrective actions undertaken during out of control periods.

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12.0 QA Table

Table 1. Metals Continuous Fence-line Monitor On-going Quality Assurance Requirements

Test Frequency	Test	Test Requirements	Test Criteria
Daily	**Upscale**	Monitor Upscale Standard once per day.. Check may be shorter than normal sampling time.	Less than 15% of the calibrated upscale standard value
	Flow	Monitor the Flow drift once per day.. Check maybe shorter than normal sampling time	Less than 20% difference between the reference flow meter and measuring flow.
Weekly	**Zero**	Monitor the zero standard once every 7 unit operating days. Each check must run for the monitor's intended sampling time.	Zero value must be less than 20% of the permitted concentration limit for all days
Quarterly	**XRF Analyzer Audit**	Test the analyzer response to each permitted element using a NIST traceable standard.	Less than 10% difference between the standard and the CFLM reported value
	Flow Audit	Test the measurements made by the analyzer's flow system using an independent flow measurement device.	Less than 10% difference between the instrument flow and the Reference flow meter
Annually	**<u>Option A</u>** **Linearity Audit with Reference Aerosol**	• Generate a NIST Traceable Aerosol Concentration for each metal being permitted by the instrument (metals may co-exist) in the same aerosol. • Measure a zero concentration and at least 3 concentrations levels including i) Between 10 and 30% of the span ii)Between 30 and 80% of the span iii) 80 and 120 percent of the span • Spike must be as close as practically possible to the sampling inlet. Standard size selection inlets such as PM_{10}, $PM_{2.5}$ and TSP may be bypassed	• Slope = 0.85 to 1.15 • Intercept = less than 20% of the permitted limit for each element • Correlation Coefficient (r) greater than 0.90 Corrections allowed as long as correlation coefficient is greater than 0.90
	<u>Option B</u> **Comparability with Reference Method**	• Compare Metals CFLM with 2 collocated Reference Methods. • Obtain 9 samples for each permitted metal where the reported concentration is greater than 20 percent of the permitted concentration • Perform Linear Regression fit for each element	• Reference Method Precision – 15% • Linear Regression fit i) Slope = 0.85 to 1.15 ii) Intercept = less than 20% of permitted limit iii) Correlation (r) coefficient greater than 0.90. Corrections allowed as long as correlation coefficient is greater than 0.90

APPENDIX B-1

Traceability Protocol for Certification of Reference Aerosol Generators

DRAFT

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

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Executive Summary

A reference aerosol generator produces an aerosol of known analyte concentration by nebulizing or atomizing a solution of known concentration, at a measured rate into a measured carrier gas flow. This reference aerosol can then be used to challenge the accuracy of monitors designed to measure species contained in aerosols. These monitors include metals and particulate matter continuous emissions monitors (CEM), ambient PM_{10} and $PM_{2.5}$ beta gauges, and metals continuous fence line monitors (CFLM). Typically gas monitors are challenged using NIST traceable gases, whose concentrations have been established using an unbroken chain of comparisons of a candidate gas standard to a primary NIST gas standard. No such primary NIST standards exist for analytes in aerosols. This document outlines the general requirements to certify and evaluate whether an aerosol concentration produced by a reference aerosol generator is traceable to NIST. This traceability protocol requires that all measurements required to produce the aerosol be NIST traceable. This includes using solutions with NIST traceable concentrations, using NIST traceable gas flow meters, and using NIST traceable balances or NIST traceable liquid flow meters. In addition, the output of the aerosol generator must be evaluated using an appropriate reference method.

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1. Introduction

A reference aerosol generator is a device which produces an aerosol containing a known concentration of an analyte or analytes of interest. Traditionally, calibration gases have been used to establish the accuracy of continuous gas monitors. Similarly, a reference aerosol generator can be used to establish the accuracy of monitors measuring analytes in an aerosol. A reference aerosol generator could be a useful calibration and auditing tool for several types of monitors including particulate matter continuous emissions monitors (CEMS), multi-metal CEMS, metals continuous fence line monitors (CFLM), and ambient PM_{10} and $PM_{2.5}$ monitors.

Typically the traceability of gas standards has been established using an unbroken chain of comparisons of a candidate gas standard to a primary National Institute of Standards and Technology (NIST) gas standard. Currently, there is not an established NIST primary standard for aerosols or for many of the analytes found in aerosols. Instead, of relying on comparisons to NIST standards, this protocol relies on an approach of establishing NIST traceability for the individual components and measurements of a reference aerosol generator that are critical to establishing the analyte concentration. **This approach is very similar to the approach EPA has taken recently proposed to establish NIST traceability for mercuric chloride ($HgCl_2$) gas generators.**[1] Additionally, this procedures recommends that aerosol concentrations be checked using reference methods as a part of the monitor calibration and/or auditing process.

2. Definitions

2.1. Reference Aerosol Generator

A device which creates an aerosol with an analyte concentration that is traceable to NIST standards. This aerosol can then be used to audit or calibrate monitors for that analyte.

2.2. Total Capture Test

This is a test of the accuracy of the output concentration of a reference aerosol generator. For this test, the entire mass of aerosol emitted by a reference aerosol generator over a period of time is collected on a filter. The total mass of the analyte of interest on the filter is compared with the total predicted emitted mass of the analyte from the aerosol generator.

2.3. Aerosol

A suspension of solids and/or liquids in a gas.

2.4. Nebulization

To convert a liquid to a fine spray

2.5. Traceability to NIST

A documented procedure by which a measured response is related to a standard with accuracy defined and certified by the National Institute of Standards and Technology (NIST).

2.6. Transport Efficiency

To challenge a pollutant monitor, the generated aerosol will have to be transported from the aerosol generation point to a point where it can be used. The transport efficiency is a measure of the percentage of the generated aerosol that reaches the monitor. The transport efficiency can be calculated by dividing the mass or concentration of each analyte as measured by the reference method or by the total capture test by the predicted aerosol concentration or mass. The transport efficiency can be calculated using Equation 4 in Section 5.3.

3. Aerosol Generator Equipment

A reference aerosol generator produces an aerosol by nebulizing a solution containing a known analyte concentration, at a measured rate, into a measured flow and transports it to a point with a defined efficiency. The concentration of each analyte in the aerosol can be calculated using Equation 1.

$$C_i^A = \frac{R_i^S \times C_i^S}{F_t} \times TE_i \qquad \text{Equation 1}$$

Where:

C_i^A = The concentration of the ith analyte in the reference aerosol

R_i^S = The solution loss rate for the ith analyte

C_i^S = The concentration of the ith analyte in the nebulized solution

F_t = The carrier flow for the aerosol

TE_i = The transport efficiency ith element

An aerosol generator consists of the following systems and modules

1) Solution Delivery Module – This module includes any equipment necessary to contain and deliver the solution to the aerosol generation point. This module will often include a solution reservoir, solution delivery lines, a pump to generate flow, and a means of measuring the liquid nebulization rate (e.g. a liquid flow meter or a balance).

2) Aerosol Generation System – This system includes all of the equipment required to aerosolize the solution. This could include nebulizers, compressed air, and electronic equipment.

3) An Evaporation Zone – This is the zone where the nebulized solution droplets are evaporated to remove liquid water.

4) Gas Flow System – This system consists of any of the components required to generate, measure and treat the aerosol carrier gas flow. Key components could often include a pump or a blower, compressed air, flow meters, and valves.

5) Aerosol Transport Line – The aerosol transport line delivers the aerosol from the generation point to a point where it can be used to calibrate or audit a monitor.

4. Quality Assurance Procedures

4.1. Traceability to NIST

The aerosol concentrations produced by a reference aerosol generator are traced to NIST standards through the traceability of the solution concentration, and the traceability of the devices used to measure the liquid flow rate, and aerosol carrier gas flow rate. Additionally, in this procedure, the accuracy of the analyte concentrations are confirmed by checking them with reference methods.

4.1.1. Solution Concentration

NIST traceable solutions are available commercially for many different types of analytes. Often these solutions are traceable to NIST standard reference materials (SRM), their concentrations are known to within a percent, and they are known to be stable for long periods of time. Because they are independently produced, well characterized and widely available, it is best to use these types of solutions whenever possible. However, solutions may not be available for all analytes of interest or at the desired concentrations. It is also possible that other components of these solutions (such as acids) could be incompatible with the monitors being challenged with the reference aerosol. For these reasons other potential methods for demonstrating NIST traceability of the solution are necessary. Two approaches for demonstrating the NIST traceability of the solution include:

1) Dilution or serial dilution of a commercially available NIST traceable solution

2) Determination of a solution concentration utilizing an appropriate analytical method

Any dilution of a commercially available NIST traceable solution should be done in a manner so that each measurement in the dilution process is traceable to NIST. This includes assuring that any gravimetric or volumetric measurements are done using balances and/or glassware that are NIST traceable. Also, all dilutions should be done using ultra pure deionized water, with high resistivity (16 megaohms or higher). If solutions are diluted with acid they should be high purity and free from contaminates. Generally, acids that are listed as being for use in trace metal analysis are of sufficient purity.

The NIST traceability of a solution can also be established by determining the concentrations of the analyte of interest in a solution using an appropriate analytical method. Examples of such analytical methods include, but are not limited to ICP, ICP-MS, and AA. Often these analytical

methods operate by comparing the instrument response to a known NIST traceable solution concentration with the instrument response to the unknown concentration. To demonstrate NIST traceability using this approach, it is important to document the NIST traceability of the calibrating solution(s).

4.1.2. Liquid Flow Measurement

The aerosolization rate of the analyte containing solution can be determined using either a liquid flow meter or a balance. Commercially available NIST traceable liquid flow meters and balances are readily available. The accuracy of the balance in a reference aerosol generator should be checked before and after use with NIST traceable masses (which are also readily available commercially). The accuracy of a liquid flow meter should be checked by comparing the mass of solution metered out over a specified period of time with a NIST traceable balance.

4.1.3. Carrier Gas Flow Measurement

All carrier gas flows used to calculate the aerosol concentrations should be measured using NIST traceable flow meters. These flow meters are readily available, usually with specified calibration periods. Before and after using a reference aerosol generator to calibrate or audit a monitor, all generator flow meters should be checked using an independent NIST traceable flow meter to verify their accuracy.

4.2. Comparison with a Reference Method

The output concentration of a reference aerosol generator should be confirmed using a reference method. The type of reference method may depend on the type of analyte as well as the overall aerosol flow rate. Some examples of the procedures and approaches to use are contained in the following sections. When making the comparison it is important to consider the overall uncertainty in both the reference aerosol concentration and in the reference method measurement.

4.2.1. Metal Analytes

The mass of particulate metal analytes is probably best determined using a total capture test. During a total capture test, a filter, free of metal contaminates (e.g. stretch Teflon), is placed at the end of the aerosol transport line (at a point as close as possible to the point where the aerosol is introduced into the audited monitor) in such a way that all the particulate matter in the aerosol is captured on the filter. The mass of each metal analyte on the filter can then be determined using appropriate analytical techniques. Appropriate metals analysis procedures may be found in the Compendium of Methods for the Determination of Inorganic Compounds (I.O.) in Ambient Air.[2] Examples include X-ray Fluorescence (I.O. 3.3), inductively coupled plasma (ICP) spectroscopy (I.O. 3.4), inductively coupled plasma/mass spectrometry (I.O. 3.5), and proton induced X-ray emission (PIXE) spectroscopy (I.O. 3.6). Alternatively, the metals concentration in the reference aerosol can be determined using a reference method that acquires a subsample of the total aerosol stream. Reference Method 29[3] and Other Test Method (OTM) 17[4] are two examples of such methods.

4.2.2. Total Particulate Matter

If the analyte of interest in the aerosol is particulate matter (as would be the case when calibrating a PM CEMS or an ambient PM_{10} or $PM_{2.5}$ monitor) then a total capture procedure may also be appropriate. Because the desired aerosol concentrations may be higher than for metals, care must be taken in choosing an appropriate filter. Filters used for ambient high volume sampling are likely to meet the need for high loading capacity. The total emitted PM is determined by subtracting the tare weight of the filter from the mass the filter following sampling. Additionally the total particulate matter concentration in the reference aerosol can be determined using Method 5,[5] 5i,[6] or other EPA recognized procedure for measuring PM mass.

4.2.3. Reference Method Accuracy Checking Procedures

The accuracy of the aerosol generator must be checked once at each of the concentration levels used during the monitor audit or calibration and at a zero concentration, if one is not already required as part of the monitor calibration or auditing procedure. The total carrier gas flow, liquid nebulization rate and solution concentrations used during the reference method check of the reference aerosol generator should all be within 20 percent of those used during the monitor audit or calibration for each concentration level. The zero output of the aerosol generator should be determined when nebulizing the solution matrix used during the calibration or audit (i.e. if the analyte is dissolved in an acid solution nebulizer an acid at the same solution concentration).

4.3. Solution Evaporation Rate

Some types of nebulization processes cause solution evaporation without aerosolization of the salts dissolved in the solutions. For these nebulization processes, it is necessary to make corrections to account for solution evaporation. The measurements required to account for evaporation should also be traceable to NIST and well documented in the standard operating procedures for the reference aerosol generator.

5. Reference Method Comparability Criteria

5.1. Total Capture Tests

If the output of the reference aerosol generator is evaluated using a total capture test, then the difference between the measured mass of the analyte on the filter and the predicted mass from the aerosol generator should be 15% or less for each concentration level. Alternatively, if the uncertainty of the measured analyte on the filter is greater than 15% then the percent difference should be equal to the measurement uncertainty plus the uncertainty in the generated aerosol mass. The percent difference between the mass of the analyte on the total capture filter is calculated according to Equation 2. Uncertainty calculations for the aerosol output can be found in Section 6.

$$D_i^{TC} = \frac{\left|M_i^A - M_i^{TC}\right|}{M_i^{TC}} \times 100\% \qquad \text{Equation 2}$$

Where:

D_i^{TC} = The percent difference between the mass of the ith analyte as measured on the total capture filter and the predicted emitted mass of the ith analyte from the aerosol generator

M_i^A = The predicted mass of the ith analyte emitted from the reference aerosol generator

M_i^{TC} = The measured mass of the ith analyte on the total capture filter

Total capture testing only evaluates the mass emission. Because of this all carrier gas flows must also be evaluated by comparing the total carrier gas flow rate with a NIST traceable reference flow meter. The total reference aerosol flow may also be determined using other procedures such as gas dilution. The percent difference between the reference aerosol measured flow and the NIST traceable flow meter must be less than 5%.

5.2. Other Reference Methods

If output of the reference aerosol generator is evaluated using other types of reference method testing (such as method 29 or method 5), then the percent difference between the concentration measured by the reference method and the predicted aerosol concentration must be calculated using Equation 3. This percent difference must be 15% for analyte and each concentration level used during the monitor audit. Alternatively if the reference method uncertainty exceeds 15% than the percent error must be less than the sum of the uncertainties in the reference method and the reference aerosol concentration. Uncertainties in the reference aerosol concentration may be calculated using the equations in Section 6.0.

$$D_i^{RM} = \frac{\left|C_i^A - C_i^{RM}\right|}{C_i^{RM}} \times 100\% \qquad \text{Equation 3}$$

Where:

D_i^{RM} = The percent difference between the reference method measured concentration and the predicted aerosol concentration for the ith analyte

C_i^A = The predicted aerosol concentration of the ith analyte

C_i^{RM} = The reference method measured concentration for the ith analyte

5.3. Aerosol Transport Efficiency Corrections

A transport efficiency correction can be made to the reference aerosol concentration based on the total capture or reference method measurements. The transport efficiency correction can be calculated according to Equation 4. For a reference aerosol generator the transport efficiency correction cannot exceed 0.85.

$$TE_i = \frac{C_i^{RM}}{C_i^A} \qquad \text{Equation 4}$$

TE_i = The transport efficiency for the ith analyte

C_i^{RM} = The concentration of the ith analyte as measured by the reference method

C_i^A = The predicted aerosol concentration for the ith element

6. Uncertainty Calculations

6.1. Uncertainty of Reference Aerosol Generator

The uncertainty of the reference aerosol generate can be calculated using standard propagation of error analysis and a coverage factor of 2 using Equation 5.

$$\delta_i^A = 2C_i^A \left[\frac{\delta^R}{R_s} + \frac{\delta_i^S}{C_i^s} + \frac{\delta^F}{F_t} \right] \qquad \text{Equation 5}$$

Where:

δ_i^A = The uncertainty in the concentration of the ith analyte in the aerosol

C_i^A = The concentration of the ith analyte in the aerosol

δ^R = The uncertainty of the solution loss rate

R_s = The solution loss rate

δ_i^S = The uncertainty in the solution concentration

C_i^s = The concentration of the ith analyte in solution

δ^F = The uncertainty in the carrier gas flow rate

F_t = The flow rate of the carrier gas

6.2. Calculation of Diluted Solution Concentrations and Uncertainties

If a commercially available solution has to be diluted to create a working solution for aerosolizing then the concentration of that solution may be calculated using the following equation.

$$C_i^w = \frac{C_i^S \times M^s}{M^t} \qquad \text{Equation 6}$$

Where:

C_i^w = The concentration of the ith analyte in the working solution to be aerosolized

C_i^S = The concentration of the ith analyte in the stock solution

M^s = The mass of the stock solution

M^t = The mass of the solution after dilution

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APPENDIX C

Overview of Airborne Metals Regulations, Exposure Limits, Health Effects, and Contemporary Research

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Health Effects Summary

One of the consequences of the current state of industrialization and an increasing demand for modern conveniences and improved quality of life has been an increased exposure to air pollutants from industrial activities, traffic, and energy production. Regulatory bodies, such as federal, state, and local environmental protection agencies, are responsible for assuring the public that the air is safe to breathe. These agencies are required to set standards, levels, and/or goals that will protect public health with an adequate margin of safety. These standards are established not only to protect healthy individuals, but also to protect sensitive population subgroups, such as children, asthmatics, the elderly, and individuals with emphysema, chronic obstructive pulmonary disease, or other conditions that render the group particularly vulnerable to air pollution. Although there is only one metal National Ambient Air Quality Standard (NAAQS) for lead, there are numerous other workplace and community-based screening levels, exposure limits, and reference concentrations for airborne metals that can be used as guidelines to set acceptable and appropriate levels of exposure and concern.

Assessing risk for metals in ambient air is difficult for a variety of reasons. Because organisms have always been exposed to metals, unlike synthetic organic substances, organisms have developed various means of responding to metals. There are major differences between the persistence of metals or inorganic metal compounds in the body and the persistence of organic compounds. Metals are neither created nor destroyed by biological and chemical processes, but may be biotransformed from one chemical species to another. That is, the metal ion thought to be responsible for the toxicity of a metal may persist in the body regardless of how the metal is metabolized. Some metals are considered essential for normal metabolic function, which is one of the primary factors that differentiate risk assessment for metals and metal compounds from that of synthetic organic chemicals.

Exposure to metals in the air is capable of causing a myriad of human health effects, ranging from cardiovascular and pulmonary inflammation to cancer and damage of vital organs. Contemporary research into air pollution is revealing that the metals components of particulate matter (PM) are contributing significantly to adverse health effects, even at the low concentrations found in ambient air. The EPA set health-based standards for fine particulates in 1997, but the standards do not take into account new research on the composition of the particulate matter or the toxicity of its components. The toxicity of particulate matter, in particular the fine (1 to 2.5 microns [µm]) and ultrafine particles (0.1 to 1 µm), has been proven to cause severe mortality and morbidity in humans over the past 25 years; however, in the past decade, emerging research is providing evidence that the metallic particles may be more dangerous than other PM components. In fact, current evidence is showing that mass concentration of PM alone may not be the best indices for associating health effects with exposure to PM.

The aerodynamic size and associated composition of particles determine their behavior in the mammalian respiratory system. Furthermore, particle size is one of the most important parameters in determining the atmospheric lifetime of particles, which may be a key consideration in assessing inhalation exposures, as well as exposures related to exposure pathways involving deposition onto soil or water. Metals emitted by combustion processes (e.g., the burning of fossil fuels or wastes) generally occur in small particles or the fine fraction, which is often characterized by particles less than 2.5 µm in diameter ($PM_{2.5}$). In contrast, the larger sized, course mode particles result from mechanical disruption, such as crushing, grinding, evaporation of sprays, or suspensions of dust from construction and agricultural operations. Accordingly, metals in course mode particles (i.e., those larger than approximately 1–3 µm) are primarily those of crustal origin, such as aluminum, zinc, and iron.

Generally, the evaluation of most studies shows that the smaller the size and greater the solubility of the PM, the higher the toxicity through mechanisms of oxidative stress and inflammation. A study of $PM_{2.5}$ in 2010 showed that metals were the important source for cellular oxidant generation and subsequent health effects. Health effects are stronger for fine and ultrafine particles for a variety of reasons:

- The studies of the size distribution of metals show that most of the toxic metals accumulate in the smallest particles ($PM_{2.5}$ or less).
- This size fraction can penetrate deeper into the airways of the respiratory tract and predominantly deposits in the alveolar region of the lungs, where the adsorption efficiency for trace elements varies from 60–80%.
- A fine metallic particle in contact with lung tissue/cells involves the release of metal ions into the biological system.
- Ultrafine particles are known to have increased solubility, as compared to larger size particles of the same composition because of the increased surface-to-volume ratio for smaller particle sizes.
- Fine and ultrafine particulate matter have the longest residence time in the atmosphere (~100 days), which allows for a large geographic distribution.
- Recent studies have shown that the metals component in fine and ultrafine PM is particularly toxic and are the primary contributors to negative human health.
- Furthermore, these particles also play a significant role in global climate change and can be transported over long distances by prevailing winds.

These consequences require us to give priority to the chemical characterization of the fine and ultrafine fraction of airborne particles to understand their possible implication to health effects.

In conclusion, for the effective management of air quality, great importance must be attached to the identification of both the sources and characterization of suspended PM. Source apportionment provides an estimate on the PM contribution of various sources to the levels at the receptor; it is also a key component necessary for developing and achieving desired air-quality objectives. The results of source apportionment can be used to evaluate emissions reduction on the PM levels and to devise more efficient emission reduction strategies. Therefore, estimating the airborne PM mass concentration, as well as individual chemical/metal speciation, is critical not only for comparing with recommended values, but also to identify the major sources that affect a particular area. This knowledge will also help regulators both foresee and prevent threats and risks before they become problems.

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1.0 Air Pollution Overview and Summary of Airborne Metals Regulations

1.1 Air Pollution History

Air pollution is not a modern concept; history clearly demonstrates that air pollution has been present for many centuries. Soot found on ceilings of prehistoric caves provides evidence of the high levels of pollution associated with inadequate ventilation of open fires. The forging of metals appears to be a key turning point in the creation of significant air pollution levels outside the home. Core samples of glaciers in Greenland indicate increases in pollution associated with Greek, Roman, and Chinese metal production. The United States (U.S.) Environmental Protection Agency (EPA) states that "an air pollutant is any substance in the air that can cause harm to humans or the environment. Pollutants may be natural or man-made and may take the form of solid particles, liquid droplets or gases." Currently, about four percent of deaths in the United States can be attributed to air pollution, according to the Environmental Science Engineering Program at the Harvard School of Public Health (Schwartz 2000).

In the past century, characterized by the industrial revolution, there are several key events that triggered the increase in air pollution monitoring and regulation. Several key air pollution event s occurred between the 1930's and early 1950's that prompted the development of clean air legislation both nationally and internationally. One initial event occurred in the Neuse Valley of Belgium in December 1930. A thermal inversion trapped fog over a 15-mile-long stretch of high-walled Meuse Valley that contained many farms, villages, steel mills, and chemical plants. At the end of the first day, many residents complained of nausea, shortness of breath, stinging eyes, and burning throats. After 3 days, 60 people had died and a thousand more were ill. The illness and deaths were caused by over thirty different chemical pollutants trapped beneath the dense fog clouds. Death rates were subsequently made ten times above normal (Anderson 2000).

The next event occurred in 1948 in Donora, Pennsylvania, an event also known as the "Donora Smog of 1948." Between October 26, and October 31, 1948 an air inversion trapped industrial effluent (air pollution) from the American Steel and Wire plant and Donora Zinc Works. Within three days, 20 people died; after the inversion lifted, another 50 died. Another 6,000 residents became sick from the fog and smoke combination; hundreds more finished the rest of their lives with damaged lungs and hearts (Pennsylvania DEP 2010).

Another key event was "The Great Smog of '52," a severe air pollution event that affected London, England in December 1952. A period of cold weather, combined with an anticyclone and windless conditions, collected airborne pollutants mostly from the use of coal to form a thick layer of smog over the city. It lasted from Friday to Tuesday, 9 December, 1952, and then quickly dispersed after a change in the weather. Although it caused major disruption due to the effect on visibility, and even penetrated indoor areas, it was not thought to be a significant event at the time, with London having experienced many smog events in the past. In the following weeks however, medical reports estimated that 4,000 had died prematurely and 100,000 more were made ill because of the smog's effects on the human respiratory tract. More recent research suggests that the number of fatalities was considerably higher at around 12,000 (Davis et al. and Bates 2002). It is considered the worst air pollution event in the history of the United Kingdom, and the most significant in terms of its impact on environmental research, government regulation, and public awareness of the relationship between air quality and health. It led to several changes in practices and regulations, including the U.K.'s Clean Air Act 1956.

An overview of U.S. regulations regarding metals and their presence in industrial emissions and ambient air is presented below. Information presented here was procured primarily from the Clean Air Act as written in the United States Code (USC n.d.), Title 42, Chapter 85, the EPA's "History of the Clean Air Act" (EPA 2008a) and "The Plain English Guide to the Clean Air Act" web pages (EPA 2008b).

1.2 Early Clean Air Act Legislation (1963 – 1967)

The Clean Air Act (CAA), similar to other environmental legislation, has continuously evolved. The federal government's first major efforts in regulating air emissions began in 1955 with the Air Pollution Control Act. This Act provided funds for federal research in air pollution. These efforts were enhanced over the next 15 years through a series of enactments, including the CAA. The CAA of 1963 was the first U.S. attempt to **control** air pollution and for the first time recognized pollution hazards from mobile source (cars, trucks, etc) emissions as well as stationary (industry, fireplaces, etc.) sources. The 1963 CAA also authorized research into techniques to minimize air pollution.

The CAA was amended in 1965 to establish motor vehicle emission standards and to promote research into the problem of transboundary pollution into Canada and Mexico. Amendments to the CAA in 1967, called the Air Quality Act (AQA), divided the nation into Air Quality Control Regions for monitoring and enforcement proceedings were initiated in areas subject to interstate air pollution transport. As part of these proceedings, the federal government for the first time conducted extensive ambient monitoring studies and stationary source inspections. The AQA also authorized expanded studies of air pollutant emission inventories, ambient monitoring techniques, and control techniques.

1.3 1970 and 1977 Clean Air Act (CAA) and Amendments

The Clean Air Act of 1970 (1970 CAA) resulted in a major shift in the federal government's role in air pollution control. It authorized the development of Federal and State regulations to limit emissions for both stationary and mobile sources. It created four different programs for controlling and preventing air pollution:

- The National Ambient Air Quality Standard (NAAQS),
- State Implementation Plans (SIP),
- New Source Performance Standards (NSPS),
- And National Emissions Standard for Hazardous Air Pollutants (NESHAPs).

These amendments occurred around the same time as the National Environmental Policy Act (NEPA), which established the EPA in May of 1971. The EPA was established to implement the requirements of the 1970 CAA.

The CAA lists four overarching goals or purposes for the legislation:

1. To protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population;
2. To initiate and accelerate a national research and development program to achieve the prevention and control of air pollution;

3. To provide technical and financial assistance to State and local governments in connection with the development and execution of their air pollution prevention and control programs; and
4. To encourage and assist the development and operation of regional air pollution prevention and control programs.

The CAA requires regulation of emissions of hazardous air pollutants (HAPs) from a published list of industrial sources referred to as "source categories." HAPs, also known as toxic air pollutants or air toxics, are those pollutants that cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects. This initial CAA recognized two types of stationary sources that generate routine emissions of HAPs:

- "Major" sources are defined as sources that emit 10 tons per year of any of the listed toxic air pollutants, or 25 tons per year of a mixture of air toxics. These sources may release air toxics from equipment leaks, when materials are transferred from one location to another, or during discharge through emission stacks or vents.
- "Area" sources consist of smaller-size facilities that release lesser quantities of toxic pollutants into the air. Area sources are defined as sources that emit less than 10 tons per year of a single air toxic, or less than 25 tons per year of a combination of air toxics. Though emissions from individual area sources are often relatively small, collectively their emissions can be of concern - particularly where large numbers of sources are located in heavily populated areas.

As required under the Act, both mobile and stationary source categories must meet control technology requirements for these HAPs. Development of regulations (also known as rules or standards) is required for all industries that emit one or more of the pollutants in significant quantities.

Amendments to the 1970 CAA occurred in 1977. These amendments authorized provisions related to the Prevention of Significant Deterioration and to areas which are non-attainment with respect to the NAAQS.

1.3.1 National Ambient Air Quality Standards

The 1970 CAAA required EPA to set NAAQS for wide-spread pollutants from numerous and diverse sources considered harmful to public health and the environment. The Clean Air Act established two types of national air quality standards. Primary standards set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. Secondary standards set limits to protect public welfare, including protection against visibility impairment, damage to animals, crops, vegetation, and buildings. The CAA requires periodic review of the science upon which the standards are based and the standards themselves.

EPA has set NAAQS for six principal pollutants, which are called "criteria" pollutants. They are carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO_2), ozone (O_3), particulate matter (PM), and sulfur dioxide (SO_2). On November 12, 2008 EPA substantially strengthened the NAAQS for lead, which is thus far the only metal regulated through the NAAQS. EPA revised the level of the primary (health-based) standard from 1.5 micrograms per cubic meter ($\mu g/m^3$) to 0.15

μg/m^3, measured as total suspended particles (TSP) and revised the secondary (welfare-based) standard to be identical in all respects to the primary standard.

1.3.2 State Implementation Plans

As written in Section 107 of the 1970 CAAA, "Each State shall have the primary responsibility for assuring air quality within the entire geographic area comprising such State by submitting an implementation plan for such State which will specify the manner in which national primary and secondary ambient air quality standards will be achieved and maintained within each air quality control region in such State." The State Implementation Plan (SIP) is a plan for each State which identifies how that State will attain and/or maintain the primary and secondary NAAQS set forth in the CAA and which includes federally-enforceable requirements. Each State is required to have a SIP which contains control measures and strategies which demonstrate how each area will attain and maintain the NAAQS.

1.3.3 New Source Performance Standards

New Source Performance Standards (NSPS) are pollution control standards issued by the EPA. The term is used in the CAAA of 1970 to refer to air pollution emission standards and in the Clean Water Act (CWA) referring to standards for discharges of industrial wastewater to surface waters. NSPS dictate the level of pollution that a new stationary source may produce. An NSPS has been established for a number of individual industrial or source categories, such as landfills, boilers, petroleum refineries, and turbines.

An example describing the need for NSPS comes from the implementation of the CAAA in Ohio. Between the dates of 1970 and 1977, a rule in the CAA required a reduction in the measured SO_2 emitted by coal fired power plants into the air. Ohio decreased the SO_2 emitted by such plants by increasing the height of the smokestacks on the plants. The result was that the SO_2 was carried in the wind out of the state and there was a reduction in the locally measured SO_2. These kinds of exploits in the Clean Air Act were solved in the 1977 revision of the Clean Air Act, when the NSPS were introduced. NSPS measures the concentration and amount of pollution put into the air, thus making a taller smoke stack useless under the new standard.

1.3.4 National Emission Standards for Hazardous Air Pollutants

NESHAPS are stationary source standards for HAPs, which are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. NESHAPs are found in 40 CFR Part 61 (resulting from the CAAA of 1970) and 40 CFR Part 63 (resulting from the CAAA of 1990, see Section 1.4.1). Part 61 NESHAPs regulate only 7 hazardous air pollutants:

- Asbestos
- Beryllium
- Mercury
- Vinyl chloride
- Benzene
- Arsenic
- Radon/radionuclides

1.4 1990 Clean Air Act (CAA) Amendments

Another set of major amendments to the Clean Air Act occurred in 1990 (1990 CAAA). The 1990 CAAA substantially increased the authority and responsibility of the federal government. New regulatory programs were authorized for control of acid deposition (acid rain) and for the issuance of stationary source operating permits. The NESHAPs were incorporated into a greatly expanded program for controlling toxic air pollutants. The provisions for attainment and maintenance of NAAQS were substantially modified and expanded. Other revisions included provisions regarding stratospheric ozone protection, increased enforcement authority, and expanded research programs.

The 1990 CAA amendments required the EPA to regulate hazardous air pollutants through three inter-related programs: Maximum Achievable Control Technology (MACT) standards also known as NESHAPs, the Urban Air Toxics Strategy, and residual risk standards. The MACT rules establish performance-based standards for industrial sources to measure and control HAPs. Under the Urban Air Toxics strategy, smaller industrial sources of HAPs are regulated with MACT standards. Finally, EPA must review MACT standards for a source category at least every 8 years following promulgation and determine if there is any residual risk that requires the standards to be strengthened in order to protect public health. This ongoing process is comprehensively evaluated through National Air Toxics Assessments (NATA). Thus far, EPA has completed three assessments that characterize the nationwide chronic cancer risk estimates and noncancer hazards from inhaling air toxics. The latest NATA in 2002 was made available to the public in June of 2009 (EPA, EPA Technology Transfer Network (TTN) 2010).

1.4.1 Maximum Achievable Control Technology (MACT)

The NESHAPs promulgated after the 1990 CAAA are found in 40 CFR Part 63. These standards require application of technology- and performance-based emissions standards referred to as MACT. Consequently, these post-1990 NESHAPs are also referred to as MACT standards. MACT standards are designed to reduce HAP emissions to a maximum achievable degree, taking into consideration the cost of reductions and other factors. After the EPA adopts a MACT standard at the federal level, the Regulatory and Compliance Support Unit proposes the same standard for adoption at the state level by the Air Quality Control Division on a semi-annual basis.

When developing a MACT standard for a particular source category, the EPA looks at the current level of emissions achieved by best-performing similar sources through clean processes, control devices, work practices, or other methods. These emissions levels set a baseline, often referred to as the "MACT floor" for the new standard. At a minimum, a MACT standard must achieve, throughout the industry, a level of emissions control that is at least equivalent to the MACT floor. The EPA can establish a more stringent standard when it makes economic, environmental, and public health sense to do so.

The MACT floor differs for existing sources and new sources.

- For existing sources, the MACT floor must equal the average current emissions limitations achieved by the best-performing 12 percent of sources in the source category, if there are 30 or more existing sources. If there are fewer than 30 existing sources, the MACT floor must equal the average current emissions limitation achieved by the best-performing five sources in the category.

- For new sources, the MACT floor must equal the current level of emissions control achieved by the best-controlled similar source.

Wherever feasible, the EPA writes the final MACT standard as an emissions limit, i.e. a percent reduction in emissions or a concentration limit that regulated sources must achieve. Emissions limits provide flexibility for industries to determine the most effective ways to comply with the standards.

The NESHAPs are delegated to the states, but both EPA and the states implement and enforce these standards. Under the 1990 amendments, the state is required to develop regulations for all sources that emit significant quantities of one or more of the pollutants. In addition, the 1990 CAAA expanded the regulated HAPs from 7 to 191. Four chemicals, methyl ethyl ketone, caprolactam, glycol ethers, and hydrogen sulfide, have since been removed from the HAPs list. To date, EPA has compiled a list of 187 HAPs which include the following metals and metal compounds:

Antimony Compounds
Arsenic Compounds (inorganic including arsine)
Beryllium Compounds
Cadmium Compounds
Chromium Compounds
Cobalt Compounds
Lead Compounds
Manganese Compounds
Mercury Compounds
Nickel Compounds
Selenium Compounds

For all listings which contain the word "compounds" these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical's infrastructure.

HAPs in urban areas are of special concern because of the large number of people and the variety of pollution sources e.g., cars, trucks, large factories, gasoline stations, and dry cleaners (EPA, Technology Transfer Network (TTN) 2003). Eight of the above metals and their compounds (arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, and nickel) are included in EPA's list of 33 HAPs, i.e. Urban Air Toxics, identified as posing the greatest potential environmental health threat in urban areas. Table C-1 presents federal agency, regional EPA, and selected state health limits.

Table C-1. Community Metals Concentrations of Concern (µg/m^3)

Metal	Typical U.S. National Ambient Air Concentrations[c]			EPA				ATSDR MRL			State Regulations			International
				IRIS		Region IX RSL					Oregon RBC	California REL		
	Rural	Urban	Industrial[d]	RfC	(10^{-6} cancer)	Cancer TR	Noncancer HI	Acute	Inter-mediate	Chronic	Residential	Acute	Chronic	European Union AQS
Antimony[a]	<0.001	0.032	**0.55**	0.2		-	0.21							
Arsenic[a]	**0.002**	**0.02**	**7.6**	0.03[e]	0.0002	0.00057	0.016				0.00057	0.2	0.015	0.006
Beryllium[a]	0.0001	**0.002**	**0.01**	0.02	0.0004	0.001	0.021				0.021		0.007	
Cadmium[a]	0.001	**0.008**	**0.6**	0.01	0.0006	0.0014	0.01	0.03		0.01	0.0014			0.005
Chromium[a]	0.002	0.02	**0.4**				0.01		0.1[h] (5[i])				0.2	
Chromium VI[a]	0.0001	**0.0016**	**0.0153**	0.008[f] (0.1[g])	0.00008	0.000011			0.005[f] (0.3[g])	0.005[f]	0.000029			
Cobalt[a]	0.0001	**0.0005**	**0.61**			0.00027	0.0063			0.1				
Copper	0.01	0.29	0.87									100		
Iron	0.3	1.6	7.0											
Lead [a,b]	0.02	**0.04**	**0.76**			0.03					(>Pv)			0.5
Manganese[a]	0.001	0.02	**0.3**	0.05			0.052			0.3	0.052		0.09	
Mercury[a]	0.0001	0.014	**0.041**	0.3			0.31			0.2	0.31	0.6	0.03	
Nickel[a]	0.006	**0.02**	**0.17**	0.05[e]	0.004[j] (0.002)[k]	0.01	0.052		0.2	0.09	0.0094	6	0.05	0.02
Selenium[a]	0.0001	0.015	0.03				21							
Silver	0.0005	0.004	0.037									5	20	
Vanadium	0.0008	**0.065**	**0.5**			0.1[l]	0.0073	0.8		0.1		30		
Zinc	0.006	0.103	5.0											

[a]Metals designated as Hazardous Air Pollutants by the EPA.

[b] National Ambient Air Quality Standard for lead is 0.15 µm/m^3 as a rolling three month average.

[c]Typical Urban Ambient Air Concentrations procured from the EPA, the ATSDR, the Hazardous Substances Database (HSDB), and/or the World Health Organization (WHO). The majority of the values are based on PM10 measurements taken in the 1980's and 1990's, but may include TSP or PM2.5 and/or more recent (post-2000) measurements. These values are not absolute; they are intended to represent typical concentrations found in urban environments.

[d] Industrial values are concentrations found in ambient air in the vicinity of factories and industry that emit metals; some values may be measurements collected near a particular factory rather than an average of all industrial vicinity ambient air concentrations.

[e] These values are calculated by California EPA

[f] Value for aerosols and mists

[g] Value for particulates

[h] Soluble particulate matter

[i] Insoluble particulate matter

[j] Value for Nickel refinery dust

[k] Value for Nickel subsulfide

[l]Value for metallic V, vanadium pentoxide value is 0.00029

Bold ambient air values exceed one or more of the regulatory health limits for that metal.

EPA = Environmental Protection Agency
IRIS = Integrated Risk Information System
10^{-6} Cancer = Dose at which risk of cancer is one in one million people (Based on the Inhalation Unit Risk)
RfC = Reference Concentration (noncancer)
RSL = Regional Screening Level
Cancer TR = Cancer target risk (1 in one million)
Noncancer HI = Noncancer hazard index
ATSDR = Association of Toxic Substances and Disease Registry
MRL = Minimal Risk Levels
RBC = Risk-based Concentration for residential receptors
REL = Reference Exposure Level
AQS = Air Quality Standard (Averaging period = 1 year)
>Pv = The air concentration reported for the RBC exceeds the vapor pressure of the pure chemical. It can be assumed that this constituent cannot create an unacceptable risk by this pathway.

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1.4.2 Urban Air Toxics

In addition to MACT rules for major sources, 1990 Clean Air Act Amendments required the EPA to develop an Air Toxics Strategy that identifies 33 HAP of particular concern to urban areas, eight of which are metals and metal compounds (see Section 1.4.1). As required by the amendments, the EPA must identify and regulate the area source categories that represent 90% of the 33 HAP emissions. A total of 70 area source categories that contribute these HAP emissions had been identified and, as of June 2007, rules have been promulgated for 28 of them. Under the Urban Air Toxics Strategy, area sources in the following metal-specific categories were regulated with MACT rules:

Hazardous Waste Incineration
Medical Waste Incinerators
Municipal Waste Combustors
Other Solid Waste Incineration
Chromic Acid Anodizing
Decorative Chromium Electroplating
Hard Chromium Electroplating
Portland Cement Manufacturing
Secondary Aluminum Production
Secondary Lead Smelting
Mercury Cell Chlor-Alkali Plants
Primary Nonferrous Metal Production
Primary Copper Smelting
Secondary Copper Smelting
Chemical Manufacturing: Chromium Compounds
Lead Acid Battery Manufacturing

1.4.3 Residual Risk

Under the 1990 CAA Amendments, the EPA was required to submit a report to Congress regarding public health risks remaining following the implementation of the MACT standards, known as residual risks, and recommended legislation to reduce residual risks. This report, the Residual Risk Report to Congress, was submitted in March of 1999 (EPA, Office of Air Quality Planning and Standards 1999). The EPA is required to conduct risk assessments on each source category subject to MACT standards and determine if additional MACT standards called residual risk standards, i.e., lowered health limits "to protect the public health with an ample margin of safety or to prevent an adverse environmental effect," are necessary to reduce residual risk. As part of the residual risk requirements, EPA must review MACT standards for a source category at least every eight years following promulgation. To assess residual risk of HAPs, the EPA uses the following steps:

- Assessment of the public's exposure level
- Assessment of type and severity of adverse effects
- Dose-Response Assessment
- Overall Risk Characterization

Thus far, none of the residual risk standards involve sources that monitor metals or metal compounds; however, petroleum refineries and primary aluminum smelters are two source categories regulated for metals that are in the next group to undergo residual risk standard promulgation (National Lime Association v US EPA 2000).

1.5 Hazardous Waste Combustor Rule

The hazardous waste combustor rule was promulgated on October 12, 2005 and established national emission standards for HAPs for sources that burn hazardous waste, such as commercial and onsite incinerators, cement kilns, lightweight aggregate kilns, boilers, and hydrochloric acid production furnaces. The October 2005 rule limits emissions of:

- Dioxins and furans,
- Mercury,
- Semivolatile metals (cadmium and lead),
- Low volatile metals (arsenic, beryllium, and chromium),
- Particulate matter, as a surrogate for non-mercury metal, HAPs, including
    - Antimony
    - Manganese
    - Selenium
    - Nickel
    - Cobalt
- Hydrogen chloride and chlorine gas, and
- Organic HAPs

EPA estimated that hazardous waste combustors annually emit approximately 12,650 tons of HAPs (metals, total chlorine, organics, and dioxins/furans) and PM. Depending on the total number of facilities that comply, the total reduction of HAP and PM for existing sources was estimated to be between approximately 2,260 and 3,380 tons per year. EPA found that this rule will also protect human health and the environment by reducing PM in conjunction with the air toxics reductions (EPA 2009).

1.6 OSHA/NIOSH Worker Exposure Limits

The Occupational Safety and Health Act of 1970 was the first comprehensive industrial safety legislation passed at the federal level. The act was passed, in part, due to the rise in the number of work-related fatalities in the 1960s, and particularly the Farmington, West Virginia, mine disaster of 1968, in which 78 miners were killed. The Occupational Safety and Health Act was distinguished by its emphasis on the prevention of, rather than compensation for, industrial accidents and illnesses. The legislation provided for the establishment of the Occupational Safety and Health Administration (OSHA) and the National Institute of Occupational Safety and Health (NIOSH). Among the key provisions of the act were the development of mandatory safety and health standards, the enforcement of these standards, and standardized record-keeping and reporting procedures for businesses.

OSHA and NIOSH developed exposure limits designed to protect a worker through both acute and chronic exposure scenarios. The NIOSH recommended exposure limits (RELs) indicates a time-weighted average (TWA) concentration for up to a 10-hour workday during a 40-hour workweek. A short-term exposure limit (STEL) is a 15-minute TWA exposure that should not be exceeded at any time during a workday. A ceiling REL should not be exceeded at any time. TWA concentrations for OSHA permissible exposure limits (PELs) must not be exceeded during

any 8-hour work shift of a 40-hour workweek. An additional screening value used to protect workers is the Immediately Dangerous to Life and Health (IDLH) concentration. IDLH exposure conditions are defined as "conditions that pose an immediate threat to life or health, or conditions that pose an immediate threat of severe exposure to contaminants, such as radioactive materials, which are likely to have adverse cumulative or delayed effects on health." The IDLH is considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection should be permitted (NIOSH 2007).

Occupational exposure limits for HAP metals and those metals of concern to human health are listed in Table C-2. Definitions of the various exposure limits presented in Tables C-1 and C-2 are provided in Table C-3.

1.7 Consent Decrees and Surrogates

A consent decree is a judicial decree expressing a voluntary agreement between parties to a suit, especially an agreement by a defendant to cease activities alleged by the government to be illegal in return for an end to the charges. Many EPA standards and rules are promulgated as a result of consent decrees. For example, the Not-To-Exceed (NTE) standard promulgated by the United States Environmental Protection Agency (EPA) ensures that heavy-duty engine emissions are controlled over the full range of speed and load combinations commonly experienced in use. NTE standards were created by the EPA as a result of a consent decree between the EPA and several major diesel engine manufacturers. As part of the resulting consent decree settlement with the EPA, these manufacturers were assessed heavy fines and were subjected to new emissions standards which included NTE (EPA, Office of Transportation and Air Quality 2005).

For many source categories, the EPA requires measurement and control of particulate matter (PM) as a surrogate for metal HAP. Reasons for use of PM as a surrogate for metal HAP include:

1. Metal HAP emitted from combustion sources are incorporated in the fly-ash PM and therefore the same techniques used to measure and control PM are effective for metal HAP.
2. Since different fuels generally all emit PM but vary in the type and amount of metal HAP they emit, using PM as a standard eliminates the need for many different standards based on fuel changes.
3. Using PM as a surrogate eliminates the need for performance testing of numerous standards for individual metals and therefore reduces costs.

U.S. courts allow EPA to use PM as a surrogate for metals if a “Three-Part Test” consisting of the following is passed:

1. If HAP metals are “invariably present” in stack emissions.
2. If PM control technology “indiscriminately captures HAP metals along with other particulates.”
3. If PM control technology is the only method facilities use to reduce HAP emissions.

PM measurement methods are not discussed here but may be found on the EPA’s Emission Measurement Center’s web site (EPA, Technology Transfer Network 2010).

Table C-2. Occupational/Industrial Limits for Metals of Concern (µg/m^3)

Metal	Carcinogen?	IDLH	NIOSH REL (10-hr TWA)	OSHA PEL (8-hr TWA)
Antimony [a]	No	50,000	500	500
Arsenic [a,b]	Yes	500	2[b]	10
Beryllium [a,c]	Yes	400	0.5	2
Bismuth [d]	No	N.D.	5	5
Cadmium [a]	Yes	900	N.E.	0.005
Chromium [a]	No	250,000	0.5	1
Chromium III [a]	No	2,500	0.5	0.5
Chromium VI [a]	Yes		0.001	0.005
Cobalt [a]	No	20,000	0.05	0.1
Copper [e]	No	100,000	1	1
Lead [a,f]	No	100,000	50	50
Manganese [a,g]	No	500,000	1000	5,000
Mercury [a,h]	No	10,000	0.1	100
Nickel [a,i]	Yes	10,000	15	1000
Selenium [a,j]	No	100	200	200
Silver	No	10,000	10	10
Vanadium [k]	No	35,000	50	50

IDLH = Immediately Detrimental to Life and Health
NIOSH = National Institute of Occupational Safety and Health
REL = Recommended Exposure Limit
OSHA = Occupational Safety and Health Administration
PEL = Permissible Exposure Limit
[a] Metals designated as Hazardous Air Pollutants by the EPA.
[b] NIOSH REL for arsenic is a 15-minute ceiling
[c] OSHA PEL for beryllium has a 30-minute ceiling of 5 µg/m^3
[d] REL and PEL for bismuth is a respiratory limit, the total REL is 10 µg/m^3 and total PEL is
[e] Additional REL of 0.1 and PEL of 0.1 for copper fume
[f] NIOSH REL for lead is an 8-hour TWA standard
[g] NIOSH short term exposure limit (STEL) for manganese is 3,000 µg/m^3 and the PEL is a
[h] NIOSH REL for mercury for skin is 50 µg/m3 and the REL is a ceiling
[i] Nickel as $Ni(CO)_4$ has an IDLH of 14,000 µg/m^3 and an REL and PEL of 7 µg/m^3
[j] Selenium as SeF_6 has an IDLH of 2000 µg/m^3 and an REL and PEL of 400 µg/m^3
[k] NIOSH REL for vanadium is a 15-minute limit

Table C-3. Definition of Risk Levels

Regulatory or Risk Level	Acronym	Agency	Definition
Residential			
Reference Concentration	RfC	EPA - IRIS	A RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from a no adverse effect level (NOAEL), low adverse effect level (LOAEL), or benchmark concentration, with uncertainty factors generally applied to reflect limitations of the data used. Generally used in EPA's noncancer health assessments.
10^{-6} Cancer Risk	10^{-6} Cancer	EPA - IRIS	This dose concentration is based on Inhalation Unit Risk (IUR), which is the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 $\mu g/m^3$ in air. The interpretation of inhalation unit risk would be as follows: if unit risk = 2 × 10-6 per $\mu g/m^3$, 2 excess cancer cases (upper bound estimate) are expected to develop per 1,000,000 people if exposed daily for a lifetime to 1 µg of the chemical per m^3 of air.
Regional Screening Level	RSL	EPA (Region IX)	The residential RSLs (for air) consider human exposure to individual contaminants in air. Generic screening levels are calculated for multiple exposure pathways and for chemicals with both carcinogenic and noncarcinogenic effects. Cancer target risk (TR) is based on one in a million cancer risk and the noncancerous hazard index (HI) is based on a Hazard Quotient (HQ) of 1.
Minimal Risk Level	MRL	ATSDR	An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure. MRLs are derived when reliable and sufficient data are available to identify target organs of effect, or the most sensitive health effects for acute (1-14 days), intermediate (15-364 days), and chronic (365 days or longer) exposure durations and for the oral and inhalation routes of exposure (only noncancer effects considered). These substance specific estimates, which are intended to serve as screening levels, are used by ATSDR health assessors and other responders to identify contaminants and potential health effects that may be of concern at hazardous waste sites. It is important to note that MRLs are not intended to define clean up or action levels for ATSDR or other Agencies.
Risk-Based Concentration	RBC	Oregon DEQ	The RBCs are listed separately for each possible pathway (air inhalation, groundwater ingestion, soil ingestion, etc) to human exposure. If any constituent concentrations exceed the minimum RBC for a given exposure pathway that exposure pathway must be explored and eliminated from concern.
Reference Exposure Level	REL	CalEPA/OEHHA*	The concentration level at or below which no adverse health effects are anticipated for a specified exposure duration is termed the reference exposure level (REL). RELs are based on the most sensitive, relevant, adverse health effect reported in the medical and toxicological literature. RELs are designed to protect the most sensitive individuals in the population by the inclusion of margins of safety. Since margins of safety are incorporated to address data gaps and uncertainties, exceeding the REL does not automatically indicate an adverse health impact. The acute REL is calculated for a one-hour exposure period; the chronic REL is intended to be protective for individuals exposed continuously over an entire lifetime. From a practical standpoint, chronic exposure for humans is considered to be greater than 12% of a lifetime of 70 years, thus, human exposures of greater than 8 years are considered chronic exposures and are not adjusted either in their calculation or application.
Air Quality Standard	AQS	European Union	The European Union has developed an extensive body of legislation which establishes health based standards and objectives for a number of pollutants in air. The standards apply over differing periods of time because the observed health impacts associated with the various pollutants occur over different exposure times. Member States should undertake assessments of air pollution levels using measurements and modelling and other empirical techniques. Where levels are elevated, the Member States should prepare an air quality plan or program to ensure compliance with the limit value before the date when the limit value formally enters into force.
Occupational			
Immediately Dangerous to Life and Health	IDLH	NIOSH/OSHA	The IDLH is considered a maximum concentration above which only a highly reliable breathing apparatus providing maximum worker protection should be permitted. In determining IDLH values, NIOSH considered the ability of a worker to escape without loss of life or irreversible health effects along with certain transient effects, such as severe eye or respiratory irritation, disorientation, and incoordination, which could prevent escape. As a safety margin, IDLH values are based on effects that might occur as a consequence of a 30-minute exposure. However, the 30-minute period was NOT meant to imply that workers should stay in the work environment any longer than necessary; in fact, EVERY EFFORT SHOULD BE MADE TO EXIT IMMEDIATELY!
Recommended Exposure Limit	REL	NIOSH	The REL is a level that NIOSH believes would be protective of worker safety and health over a working lifetime if used in combination with engineering and work practice controls, exposure and medical monitoring, posting and labeling of hazards, worker training and personal protective equipment. For NIOSH RELs, "TWA" indicates a time-weighted average concentration for up to a 10-hour workday during a 40-hour workweek.
Permissible Exposure Limit	PEL	OSHA	The PEL is a legal limit in the United States for exposure of an employee to a chemical substance or physical agent. TWA concentrations for OSHA PELs must not be exceeded during any 8-hour workshift of a 40-hour workweek
Short-Term Exposure Limit	STEL	NIOSH/OSHA	The STEL is a 15-minute TWA exposure that should not be exceeded at any time during a workday
Ceiling	C	NIOSH/OSHA	A ceiling REL or PEL is designated by "C" preceding the value; unless noted otherwise, the ceiling value should not be exceeded at any time

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For industrial sources that use PM as a surrogate for metals, emissions of individual metals are not estimated at all, and the concentration of metals emitted from the source is therefore unknown. Metals are present in PM in trace quantities, i.e., metals are typically measured in the micrograms per dry standard cubic meter (µg/dscm) and PM is measured in mg/dscm. The concentration of metals in PM can therefore change considerably, e.g., by a factor of 2 or more, without impacting the overall bulk concentration of PM. Concentrations of metals in PM can change with different fuels and therefore do not remain in constant proportion to the PM. Clearly, using PM as a surrogate for metals allows for substantial uncertainty in actual metal emissions. The EPA accepts the substitution of PM for metals because it is simpler and cheaper than creating standards and conducting performance tests for individual metals, and because the EPA assumes that the same techniques used to measure and control PM are effective for metal HAPs. With current scientific knowledge pointing towards metal components of PM as a significant contributor to adverse human health effects, the speciation of PM is important in protecting human health and the environment. In addition, technology currently exists that is capable of cost-effectively assessing the metals components of PM (see Guide for Developing a Multi-Metals Fence Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors, Cooper Environmental Services, 2010).

1.8 State Guidelines and Goals

State Implementation Plans (SIP), as created in the 1970 CAAA, requires states to monitor and control air pollutants. Air quality guidelines are available both as Regional EPA standards and state-by-state guidelines for both chronic and acute health effects, as well as for residential and occupational/industrial receptors. The SIP consists of narrative, rules, technical documentation, and agreements that an individual state will use to clean up polluted areas. SIPs also include special control strategies for nonattainment areas, i.e. areas that are not meeting the NAAQS. These control strategies often include items such as vehicle inspection and maintenance, lower gasoline vapor pressures, gas pump vapor recovery, and other reasonably available control technologies (RACT). Finally, SIPs include preconstruction permit requirements for projects that may result in emission increases (EPA, State Implementation Plan 2010). Examples of state exposure limits are presented in Table C-1.

1.9 Summary of Non-US Standards and Limits

Air pollution does not recognize state or international boundaries; international air standards have been developed for countries across all continents. The U.S. EPA, NOAA, NPS, tribal, state, and local agencies developed the AIRNow web site (www.AIRnow.gov) to provide the public with easy access to national air quality information. The Web site offers daily air quality index (AQI) forecasts, as well as real-time AQI conditions for over 300 cities across the US, and provides links to more detailed state and local air quality web sites. In addition, the AIRNow web site includes links to international air quality web sites from Australia and Asia to Europe and South America. An additional source of compiled international guidelines, International Toxicity Estimates for Risk (ITER), is available through the U.S. National Library of Medicine's Toxicology Data Network (ITER 2009). This database includes risk information for over 600 chemicals from authoritative groups worldwide.

The United Kingdom government established nationwide air quality measurement networks in the late 1970s. Metals in the air had been considered a problem with records describing diseases caused by breathing emissions from metal smelters from as far back as 1750 (Brown

2008). In 1996, the European Union (EU) published the Air Quality Framework Directive followed by a series of Daughter Directives (DD) that limited the concentrations of a range of metallic, inorganic, and organic pollutants in ambient air across EU member states. The first DD sets a limit value for the concentration of lead in the PM_{10} fraction of particulate matter, whilst the fourth DD sets target values for the concentrations of nickel, arsenic, and cadmium in the PM_{10} fraction of particulate matter, and the concentration of total gaseous mercury in ambient air. The concentration of particulate phase mercury is not explicitly covered by the 4th DD. The DDs limit the allowable concentrations at individual monitoring sites.

The EU has developed occupational exposure limits similar to those found in the US. Frequently, international air quality objectives are often based, in part, on US standards and research. Air quality standards were found to be divided into two subsections – those standards developed to protect populations as a whole and standards developed to protect humans in the workplace. A comparison of air quality standards for occupational and residential scenarios between the United States, Australia, European Union, and Denmark showed that international limits were either similar or less stringent than those implemented in the United States (TOXNET 2010).

1.10 Expected Future Regulations

New knowledge concerning health effects of metals and their compounds is continuously uncovered. As new discoveries are made, available standards may be raised or lowered in keeping with current knowledge. A summary of contemporary research is included in Chapter 3 of this document.

The CISWI and Boiler MACT Rules

On July 8, 2007, the Court of Appeals for the District of Columbia vacated both the Commercial and Industrial Solid Waste Incinerators MACT rule (CISWI MACT) and the Industrial, Commercial and Institutional Boilers and Process Heaters MACT rule (Boiler MACT). The Court determined that the EPA improperly excluded commercial incinerators that recapture energy from the CISWI source category. Instead, the EPA classified these sources under the less stringent Boiler MACT Rule. The Court ruling requires EPA to rewrite the CISWI MACT to incorporate all commercial incinerators, including many of those formerly listed under the Boiler MACT. As a result, a large group of sources will no longer be regulated under the Boiler MACT and the Court has thus also required the EPA to rewrite the Boiler MACT rule. In the interim, the EPA has stated that it will apply MACT rules to boilers on a case-by-case basis. In addition, several states have their own Boiler MACT rules that will also apply.

Additional MACT Rules for Area Sources

Under the Urban Air Toxics Strategy, 28 rules have already been promulgated and additional rules for area sources "are under development or will be developed in the future" according to the EPA. The following list contains area source categories that are scheduled to be regulated in the future and may involve control and measurement of metal HAPs:

Sewage Sludge Incinerator Units
Pressed and Blown Glass Manufacturing
Secondary Nonferrous Metals
Stainless and Non-stainless Steel Manufacturing (EAFs)
Steel Foundries

Iron Foundries
Fabricated Metal Products, Electrical and Electronic Equipment - Finishing Op.
Fabricated Metal Products, Fabricated Metal Products, nec
Fabricated Metal Products, Fabricated Plate Work (Boiler Shops)
Fabricated Metal Products, Fabricated Structural Metal Manufacturing
Fabricated Metal Products, Heating Equipment, Except Electric
Fabricated Metal Products, Industrial Machinery and Equipment - Finishing Operations
Fabricated Metal Products, Iron and Steel Forging
Fabricated Metal Products, Primary Metal Products Manufacturing
Fabricated Metal Products, Valves and Pipe Fittings
Plating and Polishing
Ferroalloys Production: Ferromanganese and Silicomanganese
Industrial Inorganic Chemical Manufacturing
Inorganic Pigment Manufacturing
Misc. Organic Chemical Manufacturing (MON)
Brick and Structural Clay Products
Copper Foundries
Industrial Boilers Institutional/Commercial Boilers
Nonferrous Foundries

2.0 Overview of Airborne Metals Health Effects and Exposure Limits

2.1 Metals Overview

A metal is a chemical element that is a good conductor of both electricity and heat and that readily lose electrons to form cations and ionic bonds with non-metals. Metals occupy the bulk of the periodic table, while non-metallic elements can only be found on the right-hand-side of the Periodic Table of the Elements (Figure 1, below). A diagonal line, drawn from boron (B) to astatine (At), separates the metals from the nonmetals. Most elements on this line are metalloids, sometimes called semiconductors. This is because these elements exhibit electrical properties common to both conductors and insulators. Elements to the lower left of this division line are called metals, while elements to the upper right of the division line are called non-metals. Metals on the Periodic Table are further divided into alkali, alkaline earth, transitional, and post-transitional metals, as well as lathanoids and actinoids.

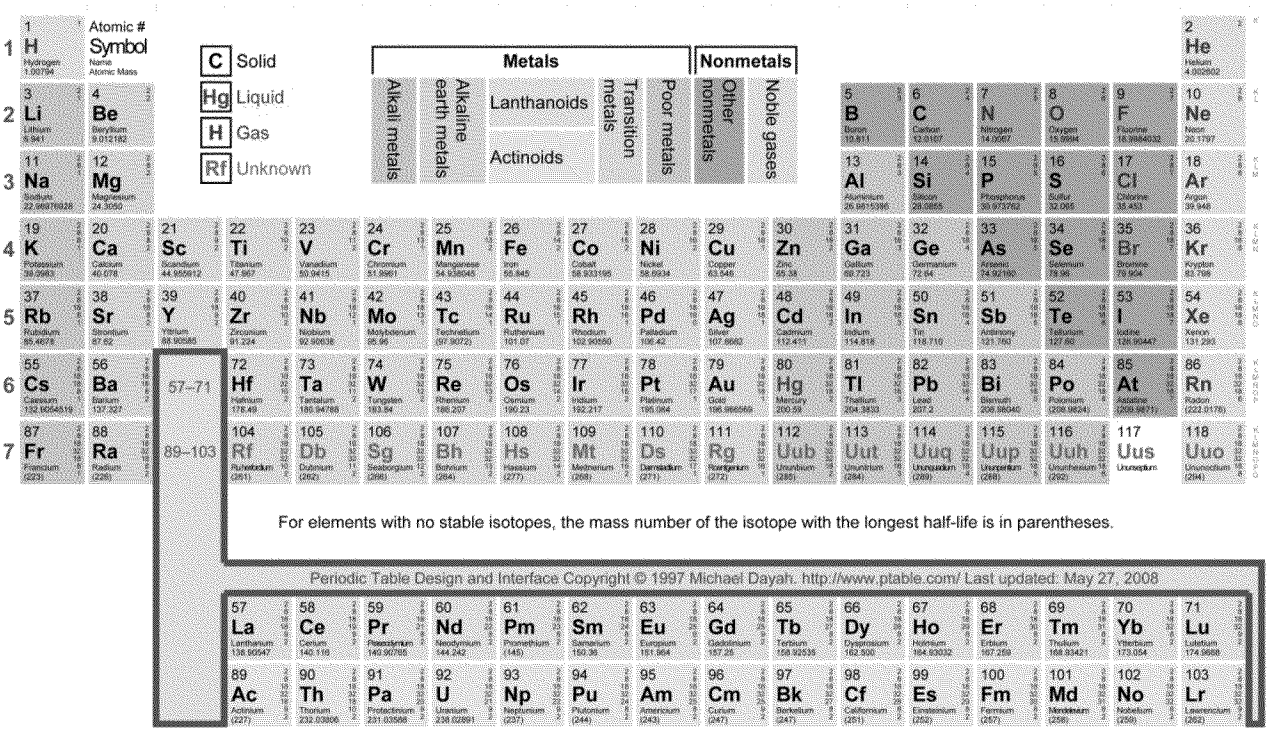

Figure C-1: Periodic Table Showing Metal, Metalloid, and Non-Metal Elements

Metals are found naturally in the environment at low-levels and some are essential nutrients for humans; however, certain types of metals and metals at high concentrations can have detrimental effects on human health and the environment. Because they cannot be degraded or destroyed, metals are persistent in all parts of the environment. Human activity affects the natural geological and biological redistribution of metals through pollution of the air, water, and soil. The primary anthropogenic sources of metals are point sources, such as mines, foundries, smelters, and coal-burning power plants, as well as diffuse sources, such as combustion by-products and vehicle emissions. Humans also affect the natural geological and biological

redistribution of metals by altering the chemical form of metals released to the environment. Such alterations often affect a metal's toxicity by allowing it to bioaccumulate in plants and animals, bioconcentrate in the food chain, or attack specific organs of the body. Monitoring and control of metal compounds in industrial emissions are thus critical for reducing exposure pathways and protecting human health and the environment.

Assessing risk for metals in ambient air is difficult for a variety of reasons. Because organisms have always been exposed to metals, unlike synthetic organic substances, organisms have developed various means of responding to metals. There are major differences between the persistence of metals or inorganic metal compounds in the body and the persistence of organic compounds. Metals are neither created nor destroyed by biological and chemical processes, but may be biotransformed from one chemical species to another. That is, the metal ion thought to be responsible for the toxicity of a metal may persist in the body regardless of how the metal is metabolized. Some metals are considered essential for normal metabolic function, which is one of the primary factors that differentiate risk assessment for metals and metal compounds from that of synthetic organic chemicals (Janssen 2001). Trace elements can be divided into three groups:

- Those known to be essential.
- Those that have beneficial metabolic effects but have not been shown to be essential.
- Those that occur widely in living organisms but seem to be only incidental contaminants, and are not known to be beneficial.

Several elements (e.g. sodium, potassium, magnesium, and calcium) occur in large concentrations in organisms. A second set of metals, termed trace metals, occurs at much lower concentrations (normally < 0.01%) in organisms. Some metals, such as iron, manganese, zinc, copper, cobalt, and molybdenum, have been identified as essential for all living organisms, while the essentiality of other metals, such as nickel, vanadium, iodine, chromium, and selenium, has only been established for a limited number of species.

Table C-4 classifies the metals addressed in this framework by their known essentiality to organisms.

Table C-4. Classification of Metals Based on Characteristics of Health Effects

Nutritionally Essential Metals	Metals with Possible Beneficial Effects	Metals with No Known Beneficial Effects
Cobalt Chromium III Copper Iron Manganese Molybdenum Selenium Zinc	Boron Nickel Silicon Vanadium Iodine	Aluminum Antimony Arsenic Barium Beryllium Cadmium Lead Mercury Silver Strontium Thallium

For those metals considered essential, toxicity can occur when the optimal concentration is exceeded; therefore, all metals are potentially toxic at a high enough dose. Figure 1 below depicts the dependence of biologic function on the tissue concentration of an essential trace element as modified by dietary intake.

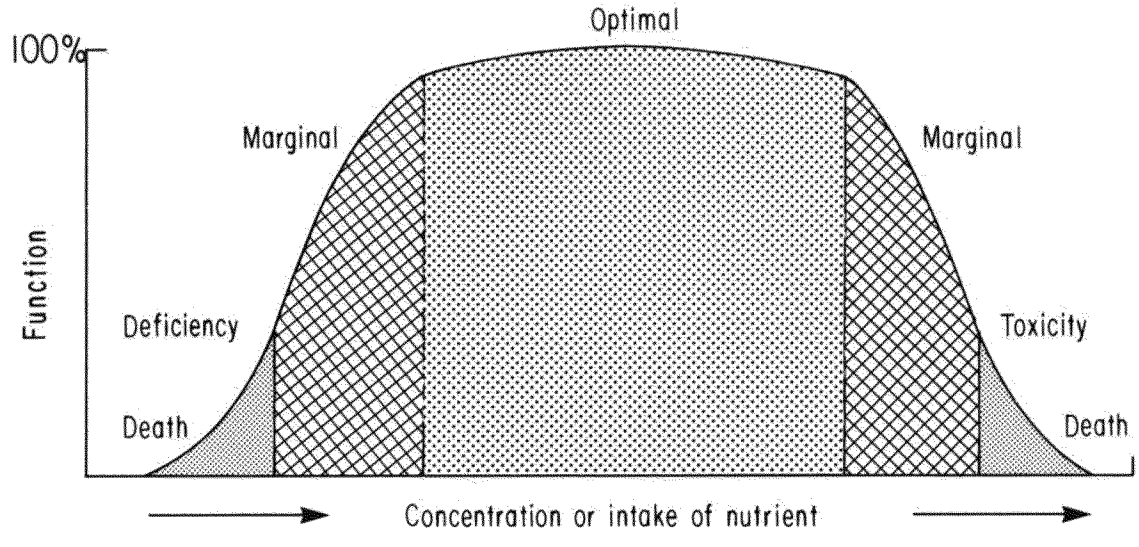

Figure C-2. Dependence of Biologic Function on the Tissue Concentration of Essential Trace Elements

Metals have been associated with a wide range of environmental and health effects including respiratory and pulmonary disorders (Prieditis 2001), neurotoxicity, and cancer (Monn 1999). High concentrations of metals in the environment, especially near industrial facilities, are thus a cause for concern. For example, in 2001, the Missouri Department of Health and Human

Services found that 28% of the town's children ages 6 and under had lead poisoning due to emissions from Doe Run's Herculaneum lead smelter (Missouri DHSS 2002). Within one-quarter of a mile of the smelter, lead poisoning occurred in 56% of children in this age group; suggesting that a closer proximity to the smelter led to a higher probability for lead poisoning. Negative health effects from lead poisoning include learning disabilities, behavioral problems, and, at very high levels, seizures, coma, and even death (US DHHS 2007). In addition to their potential health effects, metals are especially hazardous because they will not biodegrade; once released into the environment, they will always be available for re-introduction into the air, water and food chain. Exposure pathways include: breathing contaminated air, eating contaminated food products, drinking contaminated water, ingesting contaminated soil, and touching contaminated soil, dust, or water.

2.2 Air Exposure Pathways

The major pathways for human intakes of metals in which air serves as the primary medium of contact are inhalation and dermal. Exposure assessment depends on ambient and anthropogenic concentrations and multiple routes of exposure. People are exposed to toxic air pollutants in many ways that can pose health risks, such as by:

- Breathing contaminated air.
- Eating contaminated food products, such as fish from contaminated waters; meat, milk, or eggs from animals that fed on contaminated plants; and fruits and vegetables grown in contaminated soil on which air toxics have been deposited.
- Drinking water contaminated by toxic air pollutants.
- Ingesting contaminated soil. Young children are especially vulnerable because they often ingest soil from their hands or from objects they place in their mouths.
- Touching (making skin contact with) contaminated soil, dust, or water (for example, during recreational use of contaminated water bodies).

Other indirect pathways in which air serves as a medium include:

- Deposition of metals to surface dusts and intake from ingestion, inhalation, or dermal contact;
- Deposition to surface water and sediment and intake from ingestion and dermal contact; and
- Uptake of deposited metals into aquatic and/or terrestrial biota, entrance into the human food chain, and intake from ingestion.

Although, in most instances in which airborne metals have resulted in environmental contamination, ingestion of surface dust tends to be the dominant contributor to human health risk, this may not always be the case. Bioavailability of inhaled metals can be much higher than for other routes of intake. This can result in relatively high internal doses from inhalation even when inhalation intakes are similar to intakes from other routes. An example of this is the large contribution made by cigarette smoking to the body burden of cadmium (Newman 2004). Infants and children can be particularly vulnerable to airborne metal particulates because differences in airway geometry and airstream velocities tend to result in higher deposition fractions of inhaled particulates in infants and children than in adults at similar exposure levels. In addition, research shows that particle pollution may significantly reduce lung function growth in children (C. EPA 2004).

Human exposures to airborne metals are usually to metal-bearing particulates, which necessitates measurements of particle sizes in the breathing zone of receptors of concern to achieve accurate estimates of deposition rates in the respiratory tract. Exceptions to this are exposures to mercury vapor or other gaseous forms of metals, such as arsine gas. In most applications, monitoring of metals for use in environmental risk assessment consists of measuring total metal (i.e., unspeciated) captured in the PM_{10} fraction (the fraction of particles that are less than or equal to 10 microns [µm] in diameter) of samples collected in stationary samplers.

The fate of inhaled particulates deposited in the respiratory tract is substantially affected by particle size, below a diameter of 10 µm (James 1994). For example, a substantial fraction of the inhaled particles larger than 1 µm can be expected to be deposited in the upper respiratory tract and subsequently transferred by mucociliary transport to the gastrointestinal tract, where fractional absorption is likely much different from that of particles absorbed from the respiratory tract. Measurement of unspeciated metals introduces uncertainties into risk estimates for inhaled metals because the physiological solubility of a metal affects the mechanisms, rate, and extent of absorption of metals from the respiratory tract (Newman 2004). Lack of information about the particle sizes, chemical form, and solubility of the airborne metals in the breathing zone of receptors of concern can have important implications for accurate modeling of rates of absorption, internal dose of inhaled metal particulates, and risk (Khoury 2003).

An important risk-assessment concept in evaluating levels of airborne metals is the background concentration. Background concentrations are a function of regional geology and local soil and sediment conditions. It is the regional concentration in a medium that has not been increased by a local source of contamination; furthermore, it is the concentration of a metal in a medium (e.g. soil, air, water) as it existed before being affected by human activity. Occasionally, background metal concentrations can exceed environmental quality criteria at some sites (Langmiur 2004).

2.3 Designated HAP Metals

The following subsections summarize potential health effects, sources, and exposure pathways for 11 different metals as described in EPA's Health Effects Notebook for Hazardous Air Pollutants (EPA, Health Effects Notebook for HAPs 2010) and also for an additional six metals of concern that are not designated as HAPs. The information provided herein is intended as a general overview and not an exhaustive reference for health effects of metals. Metals information and data presented in the following subsections comes from current air research data as well as the Technology Transfer Network (TTN) Air Toxics Web Site (ATW) (EPA, Technology Transfer Network 2010), including data from the Agency for Toxic Substances and Disease Registry (ATSDR 2010), integrated risk information system (IRIS 2010), and the EPA. Other sources of health effect information include the American Conference of Industrial Hygienists (ACGIH 2010), the hazardous substances database (HSDB 2010), and the California Office of Environmental Health Hazard Assessment (OEHHA 2008). A selection of applicable regulatory human health limits for industrial and residential populations are available in Tables C-1 and C-2; the standards are defined in Table C-3. Table C-1 also provides as typical air concentrations for metals in rural, urban, and source-oriented scenarios.

2.3.1 Antimony (Sb)

General: Antimony is a silvery-white metal that is found in the earth's crust. Antimony ores are mined and then either changed into antimony metal or combined with oxygen to form antimony oxide. Antimony may be used in grid metal for lead acid storage batteries, solder, sheet and pipe, bearing metals, castings, type metal, and fire retardants for plastics, textiles, rubber, adhesives, pigments, and paper.

Exposure: Antimony is found naturally in the environment at very low levels, e.g., food contains low amounts of antimony. The most likely exposure pathway to higher than background levels of antimony is inhalation. People can be exposed through breathing air or dust near factories that convert antimony ores into metal, ingesting or touching contaminated soil near hazardous waste sites or antimony-processing sites.

Ambient Air Concentrations: The EPA's TTN ATW site lists ambient air concentrations of Antimony ranging from less than 1 ng/m^3 to about 170 ng/m^3; it may be present at levels up to 1,000 ng/m^3 near factories that convert antimony ores into metal or make antimony oxide.

Short-term Health Effects: Skin and eye effects can occur from inhalation and gastrointestinal effects from ingestion. In animals, high acute exposure has resulted in respiratory effects, such as significant decrease in ventilatory function, congestion, edema, and hemorrhage, as well as effects on the cardiovascular system, and liver.

Long-term Health Effects: Chronic inhalation can result in respiratory effects, e.g., inflammation of the lungs, chronic bronchitis, and chronic emphysema. Specific respiratory effects include antimony pneumoconiosis (inflammation of the lung), alteration in pulmonary function, chronic bronchitis, chronic emphysema, inactive tuberculosis, pleural adhesions, and irritation. Cardiovascular effects have also been reported.

Cancer Risk: Animal studies have linked antimony inhalation exposure with lung tumors, but no conclusive link between cancer and antimony has been found for humans. EPA has not classified antimony for carcinogenicity.

2.3.2 Arsenic (As)

General: Aside from occurring naturally in the environment, arsenic can be released in larger quantities through volcanic activity, erosion of rocks, forest fires, and human activity. The wood preserving industry uses about 90% of the industrial arsenic in the U.S. Arsenic is also found in paints, dyes, metals, drugs, soaps and semi-conductors. Animal feeding operations and certain fertilizers and pesticides can release high amounts of arsenic to the environment as can industry practices such as copper or lead smelting, mining, and coal burning. Arsenic is also used in veterinary medicine. Inorganic arsenic solutions were used to treat diseases such as syphilis and psoriasis up until the 1940s. Arsine, a short-lived, extremely toxic gas, is used in the microelectronics industry and in semiconductor manufacture.

Exposure: Inorganic arsenic is found in low levels throughout the environment. The most common exposure pathway for inorganic arsenic is through food ingestion with lower amounts coming from drinking water and air. Inhalation may occur near metal smelters and by burning wood treated with an arsenic wood preservative. Exposure to arsine occurs through inhalation.

Ambient Air Concentrations: The average concentration of arsenic compounds in the air measured at 13 cities across the U.S. was 2 ng/m3 (Chen and Lippmann 2009). The ToxGuide for arsenic lists environmental levels in air ranging from 1 to 3 ng/m^3 in remote locations and 20-100 ng/m^3 in urban areas *(ATSDR., ToxGuide for Arsenic 2007)*. Workers in metal smelters and nearby residents may be exposed to above-average inorganic arsenic levels.

Short-term Health Effects: Arsenic is odorless and tasteless. Gastrointestinal effects (nausea, diarrhea, abdominal pain) and central and peripheral nervous system disorders can occur from acute inorganic arsenic inhalation and ingestion. Acute oral exposure to inorganic arsenic can result in death. Arsine is extremely toxic and can result in headaches, vomiting, and abdominal pains occurring within a few hours of exposure. Acute exposure to high levels of arsine can also result in death. Lower level exposure can cause decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and a sensation of "pins and needles" in hands and feet.

Long-term Health Effects: Inhalation of inorganic arsenic can result in skin and mucous membrane irritation. Gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, hyperpigmentation, and liver or kidney damage can occur with long-term oral exposure. Long-term low level exposure can cause darkening of the skin and the appearance of small corns or warts on the palms, soles, and torso. Inhalation of inorganic arsenic is strongly associated with lung cancer and oral exposure has been linked to a form of skin cancer and also to bladder, liver, and lung cancer. Women who work in, or live near, metal smelters may have higher than normal spontaneous abortion rates and their children may exhibit lower than normal birth weights.

Cancer Risk: Human inhalation studies have reported inorganic arsenic exposure to be strongly associated with lung cancer. Inorganic arsenic is classified by the EPA as a Group A human carcinogen and can cause cancer of the skin, lungs, liver, and bladder.

2.3.3 Beryllium (Be)

General: Pure beryllium is a hard gray metal that does not occur naturally but does occur as a chemical component of certain kinds of rocks, coal and oil, soil, and volcanic dust. It is also present in a variety of compounds, such as beryllium fluoride, beryllium chloride, beryllium sulfate, beryllium oxide, and beryllium phosphate. Beryllium is used in electrical components, tools, and structural components for aircraft, missiles, satellites, some metal-fabrication, televisions, calculators, personal computers, and other consumer products.

Exposure: The greatest exposure to Beryllium occurs in or near facilities where it is mined, processed, or converted into alloys and chemicals. Individuals may also be exposed through inhalation of beryllium dust or fumes from burning coal, burning fuel oil, or smoking tobacco. Beryllium can also be ingested from fruits, vegetables, and water, as well as soil via hand-to-mouth.

Ambient Air Concentrations: The average concentration of Beryllium measured in the air in the United States during the 1980s was 0.03 ng/m^3. Ambient concentrations measured in 50 cities between 1977 and 1981 were 0.1-0.4 ng/m^3.

Short-term Health Effects: Short-term exposure to high levels of beryllium via inhalation may cause inflammation of the lungs or acute pneumonitis (reddening and swelling of the lungs). Symptoms may be reversible after exposure ceases. Acute animal tests have demonstrated

beryllium compounds to vary in acute toxicity, ranging from high to extreme acute toxicity from oral exposure.

Long-term Health Effects: Long-term exposure to beryllium can result in chronic beryllium disease (berylliosis), in which granulomatous lesions (noncancerous) develop in the lung. Symptoms of chronic beryllium disease include irritation of the mucous membranes, reduced lung capacity, shortness of breath, fatigue, anorexia, dyspnea, malaise, and weight loss. Chronic inhalation exposure has caused immunological effects in humans and animals. Additional chronic effects include chronic pneumonitis, conjunctivitis, and skin allergies.

Cancer Risk: Beryllium is suspected to cause cancer; human studies have shown a causal relationship between beryllium exposure and an increased risk of lung cancer, and animal studies have linked inhalation of beryllium to lung cancer. Beryllium has been classified by the EPA as Group B1, probable human carcinogen.

2.3.4 Cadmium (Cd)

General: Cadmium is a soft silver-white metal that is usually found in combination with other elements. Cadmium is most commonly a byproduct from the smelting of zinc, lead, or copper ores. Cadmium is also used in manufacturing (pigments and batteries), metal-plating, and in the plastics industry.

Exposure: Inhalation and ingestion of contaminated food are the two major exposure pathways. Cadmium is emitted into the air from burning fossil fuels, from incineration of municipal waste materials, and from zinc, lead, and copper smelters. Smoking cigarettes is another source of airborne cadmium; smokers have about twice the amount of cadmium in their bodies as do nonsmokers. Cadmium can occur in food as a result of the application of phosphate fertilizers or sewage sludge to farm fields.

Ambient Air Concentrations: Ambient air cadmium concentrations have generally been estimated to range from 0.1 to 5 ng/m^3 in rural areas, from 2 to 15 ng/m^3 in urban areas, and from 15 to 150 ng/m^3 in industrialized areas (ICdA 2009). Cadmium has been measured in air as high as 600 ng/m^3.

Short-term Health Effects: The short-term effects of cadmium inhalation include lung effects such as bronchial and pulmonary irritation. A single acute exposure to high levels of cadmium can result in long-lasting impairment of lung. Animal tests have shown high acute toxicity for cadmium.

Long-term Health Effects: Long-term effects of cadmium inhalation and ingestion can result in cadmium build-up in the kidneys and can have effects on the liver, lung, bone, immune system, blood, and nervous system. Animal studies have demonstrated fetal malformations and other developmental effects as a result of cadmium exposure, although no conclusive evidence exists in humans. *Itai-itai disease* is caused by cadmium poisoning due to mining in Toyama Prefecture Japan. The cadmium poisoning caused softening of the bones (brittle bones) and kidney failure.

Cancer Risk: Cadmium exposure has been tentatively linked to an increased risk of lung cancer. Cadmium is classified by the EPA as a Group B1, probable human carcinogen.

2.3.5 Chromium (Cr)

General: The metal, chromium, is a steel-gray solid with a high melting point. Chromium is used to make steel and other alloys, and its compounds either in the form of chromium (III) or chromium (VI), are used in chrome plating, manufacturing dyes and pigments, preserving leather and wood, and treating water in cooling towers. It is used in small amounts in drilling mud, textiles, and toner for printers/copying machines. Chromium (III) is an essential element in humans.

Exposure: Chromium occurs naturally in the environment, predominantly either as chromium (III) or chromium (VI). Chromium (VI) is more commonly produced by industrial processes. Exposure to high levels of chromium occurs mainly by inhalation of airborne chromium from ferrochrome production, ore refining, chemical and refractory processing, cement-producing plants, automobile brake lining and catalytic converters for automobiles, leather tanneries, and chrome pigments. Chromium exposure also occurs through food and drinking water. Touching products that contain chromium, e.g., wood treated with copper dichromate or leather tanned with chromic sulfate is also an exposure pathway.

Ambient Air Concentrations: Average daily intake from air is estimated to be less than 200 to 400 nanograms; average air concentration is 3 ng/m^3 measured at 13 cities across the U.S. (AIRS sites) (Chen and Lippmann 2009). People who live in the vicinity of chromium waste disposal sites or chromium manufacturing and processing plants have a greater probability of elevated chromium exposure than the general population. The maximum chromium level measured in ambient air near a chromate manufacturing plant in Corpus, Christi, Texas was 5,500 ng/m^3 with an annual average concentration in ambient air of 400 ng/m^3. Chromium VI concentrations range from 0.013 ng/m^3 to 15.3 ng/m^3 (HSDB 2010).

Short-term Health Effects: The short-term effects of chromium (VI) inhalation include shortness of breath, coughing, wheezing, and other effects on the respiratory tract. Chromium (VI) is much more toxic that chromium (III) and both inhalation and ingestion may also cause gastrointestinal effects including abdominal pain, vomiting, and hemorrhage.

Long-term Health Effects: Long-term effects of chromium (VI) inhalation exposure include effects on the respiratory tract including perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, and pneumonia. Asthma, nasal itching, and soreness have been reported; chromium exposure may also produce effects on the liver, kidney, gastrointestinal and immune systems, and possibly the blood. Chromium (VI) exposure may result in complications during pregnancy and childbirth.

Cancer Risk: Inhaled chromium (VI) is clearly linked to an increased risk of lung cancer; animal studies have shown chromium (VI) to cause lung tumors. Chromium (VI) classified by the EPA as a Group A, known human carcinogen by inhalation route of exposure.

2.3.6 Cobalt (Co)

General: Cobalt is a steel-gray, shiny, hard metal that is insoluble in water and usually occurs in the environment in association with other metals such as copper, nickel, manganese, and arsenic. Cobalt is used in superalloys, alloys that maintain their strength at high temperatures approaching their melting points, and pigment manufacture. Cobalt is an essential element in humans and is used as a treatment for anemia, because it stimulates red blood cell production.

Exposure: Cobalt is found naturally throughout the environment. The general population may be exposed to cobalt in the air, drinking water, and food. Higher-than-normal exposure levels for cobalt can occur in the air and water near industrial areas, particularly near hard metal industrial sites.

Ambient Air Concentrations: Average concentration in ambient air in the U.S. is approximately 0.4 ng/m^3; however, in one industrial area, levels of 610 ng/m^3 were measured.

Short-term Health Effects: The short-term effects of cobalt inhalation include respiratory effects such as a significant decrease in ventilatory function, congestion, edema, and hemorrhage of the lung. Acute animal tests in rats have shown cobalt to have extreme toxicity from inhalation exposure.

Long-term Health Effects: Long-term effects of cobalt inhalation include respiratory irritation, wheezing, asthma, pneumonia, and fibrosis. Cardiac effects, congestion of the liver, kidneys, and conjunctiva, and immunological effects that include cobalt sensitization are also potential effects from chronic exposure. Animal studies have reported respiratory, cardiovascular, and CNS effects, decreased body weight, necrosis of the thymus, and effects on the blood, liver, and kidneys from inhalation exposure to cobalt.

Cancer Risk: No conclusive link between cancer and cobalt has been determined. EPA has not classified cobalt for carcinogenicity, as limited data is available on carcinogenic effects of cobalt.

2.3.7 Lead (Pb)

General: Lead is a naturally occurring, bluish-gray metal that is found in small quantities in the earth's crust. Pure lead is insoluble in water; however, the lead compounds vary in solubility. The primary use of lead is in manufacturing batteries. Lead is also used in the production of metal products, including sheet lead, solder, and pipes, and in ceramic glazes, paint, ammunition, cable covering, and other products. Tetraethyl lead was used in gasoline to increase the octane rating until lead additives were phased out and eventually banned from use in gasoline in the U.S. by the EPA by 1996.

Exposure: The largest source of lead in the atmosphere has been from leaded gasoline combustion; however, air lead levels have decreased considerably with the phase-down of lead in gasoline. Exposure to lead can occur by inhalation of airborne lead from combustion of solid waste, coal, and oils, emissions from iron and steel production and lead smelters, and tobacco smoke. Ingestion of lead in food and soil are also common pathways. The hand-to-mouth pathway is common in children (i.e., they commonly put hands, toys, and other items that may come in contact with lead-contaminated soil and dust in their mouths), therefore this group is especially at risk to lead exposure. Lead in paint products is major pathway for exposure in children as a result. Drinking water and food sources are also pathways of due to the presence of lead in old pipes, solder, and fixtures as well as its environmental persistence and potential for bioaccumulation.

Ambient Air Concentrations: Nationwide, average concentrations of lead in the air have dropped nearly 94 percent between 1980 and 2007. Average lead concentration measured in 13 cities across the U.S. (AIRS sites) is 6 ng/m^3 (Chen and Lippmann 2009). The average concentration of lead in air samples in 2002 is less than 50 ng/m^3 (ATSDR., ToxGuide for Lead 2007). Urban

concentrations of lead average 1,100 ng/m^3 of lead, non-urban concentrations average 210 ng/m^3, and remote areas average 20 ng/m^3 (HSDB 2010).

Short-term Health Effects: Lead is very toxic in low doses and can cause death in children with high lead blood levels. Short-term exposure to lead can also lead to brain damage, kidney damage, and gastrointestinal distress.

Long-term Health Effects: Long-term effects of lead exposure can lead to problems with the blood, CNS, blood pressure, kidneys, and Vitamin D metabolism. Neurological symptoms have been reported in workers, and slowed nerve conduction in peripheral nerves in adults. Chronic lead exposure can cause loss of IQ, slowed cognitive development, reduced growth, hearing loss, and other developmental effects in children. Additional effects of lead exposure can include reproductive effects e.g., decreased sperm count, spontaneous abortions, low birth weight, slowed postnatal neurobehavioral development.

Cancer Risk: EPA considers lead to be a Group B2, probable human carcinogen; human studies are inconclusive regarding lead exposure and increased cancer risk.

2.3.8 Manganese (Mn)

General: Manganese is a silver-colored metal that forms compounds in the environment with chemicals such as oxygen, sulfur, and chlorine. Manganese is used in the production of steel, carbon steel, stainless steel, and high-temperature steel, cast iron, superalloys, dry-cell batteries, matches, and fireworks. Manganese chloride is used in the chlorination of organic compounds, in animal feed, and in dry-cell batteries. Manganese sulfate is used as a fertilizer, livestock nutritional supplement, in glazes and varnishes, and in ceramics, and potassium permanganate is used for water purification. Manganese is an essential nutritional element in humans.

Exposure: Manganese is a naturally occurring element found in low levels in water air, soil, and food. Elevated levels of manganese can occur in the air near iron and steel production plants, power plants, and coke ovens. The most common route of exposure to high doses of manganese is through inhalation of contaminated air.

Ambient Air Concentrations: Average air levels are approximately 20 ng/m^3 as reported in the ATSDR Toxicological Profile. Average manganese concentration measured in 13 cities across the U.S. (AIRS sites) is 6 ng/m^3 (Chen and Lippmann 2009).

Short-term Health Effects: No short-term effects for acute manganese exposure have been reported in humans; however, contemporary researchers are evaluating manganese health effects. Some tests in animals have shown effects on the lungs via inhalation. Manganese is considered to have moderate acute toxicity based on the short-term tests in rats.

Long-term Health Effects: Long-term exposure to manganese leads primarily to effects on the CNS, including slowed visual reaction time, hand steadiness, and eye-hand coordination. Inhalation exposure specifically can cause respiratory effects. Chronic exposure to high levels can also result in a syndrome called manganism, which typically begins with feelings of weakness and lethargy, tremors, a mask-like face, psychological disturbances, and can involve impotence and loss of libido.

Cancer Risk: EPA has classified manganese as a Group D, not classifiable as to carcinogenicity in humans.

2.3.9 Mercury (Hg)

General: There are three forms of mercury, all of which are toxic to humans: elemental mercury, inorganic mercury, and organic mercury. Elemental mercury is used in thermometers, barometers, other pressure-sensing devices, batteries, lamps, industrial processes, refining, lubrication oils, and dental amalgams. Most uses of inorganic mercury have been discontinued (e.g., use of mercury in paint, laxatives, skin-lightening creams, and soaps) in the U.S.; however, mercuric chloride is still used as a disinfectant and pesticide. Organic mercury such as methyl mercury is formed in the environment from the methylation of the inorganic mercury ion.

Exposure: Inhalation in occupational settings is a major exposure pathway for elemental mercury. Ingestion of methyl mercury through consumption of contaminated foods such as fish is also a major route to exposure; mercury is very persistent in the environment and has great bioaccumulation potential. Exposure to inorganic mercury can occur though the use of old paint (made with mercury before the ban).

Ambient Air Concentrations: Elemental mercury vapor (Hg^0) is present globally in ambient air at concentrations on the order of 1.5 -2.0 ng/m^3 (NCDENR 2009). The EPA reports that the average atmospheric concentration of total mercury ranges from 2 to 10 ng/m^3. Total mercury in the air is normally found to be less than 0.1 ng/m^3 in regions unaffected by local sources and at or above 41 ng/m^3 in more industrialized urban environments (HSDB 2010).

Short-term Health Effects: For high levels of elemental mercury, short-term exposure can result in CNS effects such as tremors, mood changes, and slowed sensory and motor nerve function. Short-term exposure to inorganic mercury can cause nausea, vomiting, and severe abdominal pain via the oral ingestion route. Methyl mercury acute exposure can cause blindness, deafness, and impaired level of consciousness in humans

Long-term Health Effects: Long-term exposure to elemental mercury can cause effects on the CNS including erethism (increased excitability), irritability, excessive shyness, and tremors. For inorganic mercury, long-term exposure can lead to kidney damage; alterations in testicular tissue, increased resorption rates, and abnormalities of development have been reported in animals as well. Long-term exposure to methyl mercury can cause CNS effects with symptoms such as paresthesia (a sensation of pricking on the skin), blurred vision, malaise, speech difficulties, and constriction of the visual field. Ingestion of methyl mercury can lead to developmental effects in infants such as mental retardation, ataxia, constriction of the visual field, blindness, and cerebral palsy.

Cancer Risk: Elemental mercury has not been conclusively linked to cancer, so is classified as Group D, not a human carcinogen. The EPA has classified inorganic and methyl mercury as a Group C, possible human carcinogen.

2.3.10 Nickel (Ni)

General: Nickel is used in alloys, electroplating, batteries, coins, industrial plumbing, spark plugs, machinery parts, stainless-steel, nickel-chrome resistance wires, and catalysts. Nickel carbonyl is used in nickel refining, but its use is severely limited.

Exposure: Nickel is found naturally throughout the environment and occurs in small amounts in food, water, soil, and air. The major exposure pathway for nickel is ingestion of food. Exposure can also occur though touching everyday items such as nickel-containing jewelry, stainless steel cooking and eating utensils, as well as smoking tobacco. Inhalation of nickel is a pathway for those in the vicinity of nickel production, processing, and use, and releases from oil and coal combustion, nickel metal refining, sewage sludge incineration, manufacturing facilities, etc. Exposure to nickel carbonyl is very rare.

Ambient Air Concentrations: Typical average levels of airborne nickel are: 0.01 - 3 ng/m^3 in remote areas; 3 - 30 ng/m^3 in urban areas having no metallurgical industry; 70 - 770 ng/m^3 in nickel processing areas (HSDB 2010). Average nickel concentration measured in 13 cities across the U.S. (AIRS sites) is 3 ng/m^3 (Chen and Lippmann 2009).

Short-term Health Effects: One case of short-term exposure to a high level of nickel via inhalation showed damage to the lungs and kidneys. Effects of ingestion through drinking water can include gastrointestinal distress (e.g., nausea, vomiting, and diarrhea) and neurological effects. Nickel carbonyl exposure can cause pulmonary fibrosis and renal edema. Current research is showing that Nickel at ambient levels is capable of causing acute changes in heart rate and other health effects, partially due to its ability to create reactive oxygen species (ROS) (Zelikoff 2002). Reduced mortality in humans is associated with longer-term Nickel concentrations extending from 19 ng/m^3 to a national average of 1.9 ng/m^3 (Lippmann et al. 2006).

Long-term Health Effects: Long-term exposure via skin contact can result in nickel dermatitis, consisting of itching of the fingers, hands, and forearms. Inhalation exposure can have respiratory effects and has been linked to an increased risk of lung and nasal cancers.

Cancer Risk: Nickel inhalation in animals has been linked to lung tumors; human studies have reported an increase risk of lung and nasal cancers among nickel refinery workers exposed to nickel refinery dust. Nickel refinery dust and nickel subsulfide are classified by the EPA as Group A human carcinogens, and nickel carbonyl is classified as a Group B2 probable human carcinogen.

2.3.11 Selenium (Se)

General: Selenium is used in the electronics industry, the glass industry, pharmaceutical preparation, antidandruff shampoos, fungicides, pesticide formulations, and in pigments used in plastics, paints, enamels, inks, and rubber. It is also a nutritional feed additive for poultry and livestock.

Exposure: Selenium is found naturally in the environment and is a nutritionally essential element. A major pathway for selenium exposure is ingestion of food. Air and drinking water also have low levels of selenium. Exposure to high levels of selenium can occur via inhalation in the vicinity of metal industries, selenium-recovery processes, painting, and special trades.

Ambient Air Concentrations: An average ambient air selenium concentration is estimated to be below 10 ng/m^3. Concentration ranges of selenium associated with particulate matter in urban atmospheres were 0.2 to 30 ng/m^3 in the U.S. (HSDB 2010).

Short-term Health Effects: Acute exposure of humans via inhalation to selenium compounds, such as selenium dioxide, hydrogen selenide, results primarily in respiratory effects. Short-term exposure to elemental selenium dust via inhalation can cause irritation of the mucous membranes in the nose and throat, nosebleeds, dyspnea, bronchial spasms, bronchitis, and chemical pneumonia. Acute animal tests have shown hydrogen selenide to have extreme toxicity via oral exposure.

Long-term Health Effects: Long-term exposure to high selenium levels via ingestion can result in discoloration of the skin, pathological deformation and loss of nails, loss of hair, excessive tooth decay and discoloration, garlic odor in breath and urine, lack of mental alertness, and listlessness.

Cancer Risk: EPA has classified elemental selenium as Group D, not classifiable as to human carcinogenicity. Ingestion of selenium sulfide may result in an increase of liver and lung tumors; therefore, EPA has classified selenium sulfide as Group B2, a probable human carcinogen.

2.4 Non-Designated HAP Metals

2.4.1 Copper (Cu)

General: Copper is used to make wire, plumbing pipes, and sheet metal. U.S. pennies made before 1982 are made of copper, while those made after 1982 are only coated with copper. Copper is also combined with other metals to make brass and bronze pipes and faucets. Copper compounds are commonly used in agriculture to treat plant diseases like mildew, for water treatment and, as preservatives for wood, leather, and fabrics. Copper is also used in contraception as intrauterine devices.

Exposure: Copper is a metal that occurs naturally throughout the environment, in rocks, soil, water, and air. Copper is an essential element in plants and animals (including humans). Plants and animals absorb some copper from eating, drinking, and breathing. In general the soluble ionized salts of copper are much more toxic than the insoluble or slightly dissociated compounds. Sources of exposure are from fume, from copper ore smelting and related metallurgic operations, from welding, and from dusts of copper metal and salts.

Ambient Air Concentrations: Atmospheric levels of copper in the United States have been reported to vary from 10-570 ng/m^3, the highest values being found in urban areas (HSDB 2010).[26] Average copper concentration measured in 13 cities across the U.S. (AIRS sites) is 3 ng/m^3 (Chen and Lippmann 2009).

Short-term Health Effects: Inhalation of dust, fumes, and mists of copper salts can result in irritation of nasal mucous membranes, eye irritation, upper respiratory tract irritation; metallic taste, nausea, and metal fume fever. Acute copper poisoning can cause liver injury, methemoglobinemia, and hemolytic anemia. Effects of single exposure following suicidal or accidental oral exposure have been reported as metallic taste, epigastric pain, headache, nausea, dizziness, vomiting and diarrhea, tachycardia, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding, liver and kidney failure, and death.

Long-term Health Effects: Mammals have efficient mechanisms to regulate copper stores such that they are generally protected from excess dietary copper levels; however, at high enough

levels, chronic overexposure to copper can damage the liver and kidneys. Chronic exposure may also result in an anemia. Vineyard sprayer's lung disease, a lung and liver disease, occurs in individuals exposed to copper sulfate spray for 2 to 15 years. Wilson's disease is inherited, genetic disorders in which copper builds up in the liver; symptoms include liver toxicity (jaundice, swelling, pain) usually do not appear until adolescence.

Cancer Risk: Although some studies of workers exposed to copper have shown increased cancer risks, they were also exposed to other potentially carcinogenic chemicals. Copper is currently categorized as Group D, not classifiable as to carcinogenicity in humans.

2.4.2 Iron (Fe)

General: Iron is the second most abundant metal and the fourth most abundant element in the earth's crust, comprising 5.1% (by weight) of the earth's crust. Hydrous iron(II) oxides are generally red-brown gels and are the major constituents of soil. Iron is an essential element that is required by all forms of life. Iron is a natural constituent of all foods of plant or animal origin, and occurs in foods as iron oxides, inorganic and organic salts, and organic complexes, such as hemoglobin. Iron is the most widely used of all the metals, accounting for 95% of worldwide metal production. Its low cost and high strength make it indispensable in engineering applications such as the construction of machinery and machine tools, automobiles, the hulls of large ships, and structural components for buildings. Since pure iron is quite soft, it is most commonly used in the form of steel.

Exposure: The production and use of iron compounds as catalysts, pigments, drugs, as well as their use in agriculture, nutrition, metallurgy, and leather tanning may result in their release to the environment through various waste streams. The mining and processing of iron ores also may result in the release of iron compounds to the environment. The iron and steel industries are also likely sources of emissions of iron compounds to the environment. Occupational exposure to iron compounds may occur through inhalation and dermal contact with these compounds at workplaces where iron compounds are produced or used.

Ambient Air Concentrations: The average vanadium concentration measured in 13 cities across the U.S. (AIRS sites) is 108 ng/m^3 (Chen and Lippmann 2009). An average iron concentration in urban air of 1.6 µg/m^3 has been reported; other sources provide a range of atmospheric iron concentration s of 0.9 to 1.2 µg/m^3, as particular ferric oxide. In a study monitoring air in nonproduction departments of 147 pulp and paper mills in 11 countries mean concentration s for iron, iron oxide, and iron oxide fumes in maintenance, construction, cleaning areas were reported to be 914, 260, and 260 µg/m^3, respectively.

Short-term Health Effects: Toxicity occurring with acute iron overdose results from a combination of the corrosive effects on the gastrointestinal mucosa and the metabolic and hemodynamic effects caused by the presence of excessive elemental iron. Inhalation of ferric salts as dusts & mists is irritating to the respiratory tract. Ferric salts are regarded as skin irritants. Early symptoms of acute iron toxicity include diarrhea, sometimes containing blood; fever; nausea, severe; stomach pain or cramping, sharp; vomiting, severe, sometimes containing blood. Late symptoms of acute iron toxicity include bluish-colored lips, fingernails, palms of hands; drowsiness; pale, clammy skin; seizures; unusual tiredness or weakness; weak and fast heartbeat. Pulmonary siderosis results from inhalation of iron dust or fumes.

Long-term Health Effects: The corrosive effect of iron results in stomach and intestinal erosions and ulceration (i.e., hemorrhagic gastritis and enteritis with blood loss); however, there is a lack

of correlation between the severity of intestinal damage and death. Large chronic doses of iron may so interfere with assimilation of phosphorus as to cause severe rickets in infants.

Cancer Risk: Free iron is a pro-oxidant and can induce oxidative stress and DNA damage. The carcinogenicity of iron has been demonstrated in animal models, and epidemiologic studies have shown associations with several human cancers.

2.4.3 Silver (Ag)

General: The principal use of silver is as a precious metal and its halide salts, especially silver nitrate, are also widely used in photography. The major outlets are photography, the electrical and electronic industries and for domestic uses as cutlery, jewelry and mirrors. Silver is also employed in the electrical industry: printed circuits are made using silver paints, and computer keyboards use silver electrical contacts. Other applications are as a catalyst in oxidation reactions, in dentistry, and in high-capacity zinc long-life batteries. Silver has also been used in lozenges and chewing gum to help people stop smoking. Silver is often found as a by-product during the retrieval of copper, lead, zinc, and gold ores.

Exposure: Silver is a naturally occurring element. It is found in the environment combined with other elements such as sulfide, chloride, and nitrate.

Ambient Air Concentrations: Ambient air concentrations of silver are in the low ng/m^3 range. Atmospheric concentration of silver varied little from non-industrial to industrial cities with values ranging from 0.04 to 10.5 ng/m^3. Chadron, Nebraska (1973), which has a population of 6,000 in a sparsely inhabited region, and San Francisco (1970) had the same average ambient air concentration of silver in 0.15 ng/m^3 (HSDB 2010).

Short-term Health Effects: Exposure to high concentrations of vapors may cause dizziness, breathing difficulty, headaches or respiratory irritation. Extremely high concentrations may cause drowsiness, staggering, confusion, unconsciousness, coma or death. Acute symptoms of overexposure also include decreased blood pressure, diarrhea, stomach irritation and decreased respiration. Exposure to high levels of silver in the air has resulted in breathing problems, lung and throat irritation, and stomach pains. Skin contact with silver can cause mild allergic reactions such as rash, swelling, and inflammation in some people.

Long-term Health Effects: Chronic exposure to silver compounds includes fatty degeneration of the liver and kidneys and changes in blood cells. Long-term inhalation of soluble silver compounds or colloidal silver may cause argyria and/or argyrosis (a permanent bluish-gray discoloration of the skin or eyes). Soluble silver compounds are also capable of accumulating in small amounts in the brain and muscles.

Cancer Risk: Silver in any form is not thought to be carcinogenic.

2.4.4 Thallium (Tl)

General: According to the EPA, man-made sources of thallium pollution include gaseous emission of cement factories, coal burning power plants, and metal sewers. The main source of elevated thallium concentrations in water is the leaching of thallium from ore processing operations. The major source of thallium for practical purposes is the trace amount that is found in copper, lead, zinc, and other heavy-metal-sulfide ores. Approximately 60–70% of thallium production is used in the electronics industry, and the rest is used in the pharmaceutical industry

and in glass manufacturing. It is also used in infrared detectors. Thallium is highly toxic and was used in rat poisons and insecticides. Its use has been cut back or eliminated in many countries because of its nonselective toxicity.

Exposure: Thallium and its compounds are extremely toxic, and should be handled with great care. Contact with skin is dangerous, and adequate ventilation should be provided when melting this metal. Thallium compounds have a high aqueous solubility and are readily absorbed through the skin. Exposure to them should not exceed 0.1 mg per m^2 of skin in an 8-hour time-weighted average (40-hour work week).

Ambient Air Concentrations: Data on thallium concentrations in ambient air are limited. One study reported a mean value of 0.22 ng/m^3 for North America. A study of six large cities in the United States reported a range of <0.04 to 0.1 ng/m^3. The thallium concentration near a coal-burning power plant was estimated to be 700 ng/m^3 by the EPA in 1988.

Short-term Health Effects: The human body absorbs thallium very effectively, especially through the skin, the breathing organs and the digestive tract. Thallium poisoning, mainly caused by accidental uptake of rat poison, causes stomachaches and nervous system damage, with consequences such as trembling, paralyses and behavioral changes will remain possible death. With unborn children thallium poisoning can cause congenital disorders. Studies in people who ingested large amounts of thallium over a short time have reported vomiting, diarrhea, temporary hair loss, and effects on the nervous system, lungs, heart, liver, and kidneys. It has caused death.

Long-term Health Effects: Due to accumulation of thallium in the bodies of humans, chronic effects consist, such as tiredness, headaches, depression, lack of appetite, leg pains, hair loss, and sight disturbances. Further effects that can be related to thallium poisoning are nerve pains and joint pains. These are consequences of thallium uptake through food. A study on workers exposed on the job over several years reported nervous system effects, such as numbness of fingers and toes, from breathing thallium. It is not known if breathing or ingesting thallium affects human reproduction. Studies showed that rats that ingested thallium for several weeks had some adverse reproductive effects. Animal data suggest that the male reproductive system may be susceptible to damage by low levels of thallium.

Cancer Risk: Thallium is a suspected human carcinogen; however, the EPA has not classified thallium as to its human carcinogenicity.

2.4.5 Vanadium (V)

General: Vanadium is a compound that occurs in nature as a white-to-gray metal, and is often found as crystals. Pure vanadium has no smell. It usually combines with other elements such as oxygen, sodium, sulfur, or chloride. Vanadium and vanadium compounds can be found in the earth's crust and in rocks, some iron ores, and crude petroleum deposits. Vanadium is mostly combined with other metals to make special metal mixtures called alloys. Vanadium in the form of vanadium oxide is a component in special kinds of steel that is used for automobile parts, springs, and ball bearings. Most of the vanadium used in the United States is used to make steel. Vanadium oxide is a yellow-orange powder, dark-gray flakes, or yellow crystals. Vanadium is also mixed with iron to make important parts for aircraft engines. Small amounts of vanadium are used in making rubber, plastics, ceramics, and other chemicals.

Exposure: Vanadium exposure can occur through eating foods containing vanadium, higher levels are found in seafood; breathing air near an industry that burns fuel oil or coal; these industries release vanadium oxide into the air; working in industries that process it or make products containing it; breathing contaminated air or drinking contaminated water near waste sites or landfills containing vanadium. Vanadium is not readily absorbed by the body from the stomach, gut, or contact with the skin.

Ambient Air Concentrations: The average vanadium concentration measured in 13 cities across the U.S. (AIRS sites) is 3 ng/m^3 (Chen and Lippmann 2009). Small amounts of vanadium compounds are found in air where there is no known anthropogenic source; such concentrations are found to be in the range from 0.02 to 2.0 ng/m^3. Urban sites may have vanadium levels as high as 164 ng/m^3, while industrialized urban centers with a high consumption of residual fuel oil may have maximum levels up to 1,300 ng/m^3 (range of 450-1,300 ng/m^3). Occupational exposure to vanadium may involve exposure to levels in the order of milligrams per cubic meter (mg/m^3) of vanadium, or roughly 106 times typical background levels (HSDB 2010).

Short-term Health Effects: Breathing high levels of vanadium may cause lung irritation, chest pain, coughing, and other effects. Vanadium is considered a metal of concern, particularly due to its ability to produce reactive oxygen species (Chen and Lippmann 2009). High level acute exposures may result in CNS effects including paralysis, respiratory depression, convulsions, and death. Since vanadium is poorly absorbed from the gastrointestinal tract, inhalation exposures potentially pose the greatest risk. Vanadium intoxication (i.e., rhinorrhea, sneezing, lacrimation, and sore throat) has been reported in workers exposed to concentrations of V_2O_5 during the workshift ranging from 10 to 33 mg/m^3. Concentrations of V_2O_5 exceeding 56 mg V/m^3 have resulted in local respiratory effects; other workers exposed intermittently to 56 mg V/m^3 showed no evidence of intoxication.

Long-term Health Effects: Workers exposed to a range of vanadium pentoxide dust levels for as little as 1 day or as long as ≥6 years show mild respiratory distress, such as cough, wheezing, chest pain, runny nose, or sore throat. One study of chronically-exposed workers showed increased neutrophils in the nasal mucosa.

Cancer Risk: The International Agency for Research on Cancer (IARC) has classified vanadium pentoxide as possibly carcinogenic to humans based on evidence of lung cancer in exposed mice. The US Department of Health and Human Services (DHHS), IARC, and EPA have not classified vanadium as to its human carcinogenicity.

2.4.6 Zinc (Zn)

General: Zinc is one of the most common elements in the earth's crust. It is found in air, soil, and water, and is present in all foods. Pure zinc is a bluish-white shiny metal. Zinc has many commercial uses, such as coatings to prevent rust, in dry cell batteries, and mixed with other metals to make alloys like brass, and bronze. A zinc and copper alloy is used to make pennies in the United States. Common zinc compounds found at hazardous waste sites include zinc chloride, zinc oxide, zinc sulfate, and zinc sulfide. Zinc compounds are widely used in industry to make paint, rubber, dyes, wood preservatives, and ointments. Many alloys contain zinc, including brass, an alloy of zinc and copper. Zinc is the fourth most common metal in use, trailing only iron, aluminum, and copper with an annual production of about 10 megatons. The

production for sulfidic zinc ores produces large amounts of sulfur dioxide and cadmium vapor. Smelter slag and other residues of process also contain significant amounts of metals.

Exposure: Zinc is an essential trace element, necessary for plants, animals, and microorganisms. Zinc is found in nearly 100 specific enzymes (other sources say 300). It is typically the second most abundant transition metal in organisms after iron and it is the only metal which appears in all enzyme classes. Some zinc is released into the environment by natural processes, but most comes from human activities like mining, steel production, coal burning, and burning of waste. It attaches to soil, sediments, and dust particles in the air. Rain and snow remove zinc dust particles from the air. Depending on the type of soil, some zinc compounds can move into the groundwater and into lakes, streams, and rivers. Most of the zinc in soil stays bound to soil particles and does not dissolve in water. It builds up in fish and other organisms, but it does not build up in plants. Ingesting small amounts present in your food and water. Humans are exposed to zinc through drinking contaminated water or a beverage that has been stored in metal containers or flows through pipes that have been coated with zinc to resist rust; eating too many dietary supplements that contain zinc; and working in any of the following jobs: construction, painting, automobile mechanics, mining, smelting, and welding; manufacture of brass, bronze, or other zinc-containing alloys; manufacture of galvanized metals; and manufacture of machine parts, rubber, paint, linoleum, oilcloths, batteries, some kind of glass, ceramics, and dyes.

Ambient Air Concentrations: The average vanadium concentration measured in 13 cities across the U.S. (AIRS sites) is 15 ng/m^3 (Chen and Lippmann 2009). A mean zinc concentration of 103 ng/m^3 was reported in the aerosol (0.01 to 1.0 µm particle size) collected in Detroit, Michigan in August 1996. The annual mean atmospheric concentration of zinc was 5 µg/m^3 near a lead smelter in Kellogg, Idaho, and the 24-hour values ranged from 0.27 to 15.7 µg/m^3.

Short-term Health Effects: Zinc is an essential element in our diet. Too little zinc can cause problems, but too much zinc is also harmful. Harmful effects generally begin at levels 10-15 times higher than the amount needed for good health. Large doses taken by mouth even for a short time can cause stomach cramps, nausea, and vomiting. Inhaling large amounts of zinc (as dusts or fumes) can cause a specific short-term disease called metal fume fever. Acute exposure to zinc oxide can result in coughing, substernal pain, upper respiratory tract irritation, rales, chills, fever, nausea, and vomiting. Zinc chloride fume is an irritant of the eyes, skin, mucous membranes, and lungs in humans. The signs and symptoms of acute exposure to zinc chloride fume include conjunctivitis, irritation of the nose and throat, hoarseness, cough, dyspnea, wheezing, rales, rhonchi, chest tightness and/or pain, nausea, vomiting, epigastric pain, listlessness, lightheadedness, and a metallic taste in the mouth.

Long-term Health Effects: Excessive concentrations of zinc taken on a long-term basis can cause anemia and decrease the levels of good cholesterol. Chronic exposure to zinc oxide by skin contact may result in papular-pustular skin eruptions in the axilla, inner thigh, inner arm, scrotum and pubic areas. Excessive absorption of zinc suppresses copper and iron absorption. The U.S. Food and Drug Administration (FDA) has stated that zinc damages nerve receptors in the nose, which can cause anosmia (loss of sense of smell).

Cancer Risk: Epidemiologic studies of zinc refinery workers found no correlation between industrial zinc exposures and lung or other types of cancer. Based on incomplete information from human and animal studies, the EPA has determined that zinc is not classifiable as to its human carcinogenicity.

3.0 Summary of Contemporary Research on Airborne Metals Health Effects

3.1 Ambient Air Health Effects

Numerous epidemiological events led to the development of the United States NAAQS for particulate matter. Initially, PM was evaluated as total suspended particulates (TSP); however, this included larger, noninhalable particles. By 1987, the importance of the inhalable fraction less than 10 μm became the focus of new ambient air standards. More stringent PM NAAQS led to not only a reduction of overall ambient air PM, but also saved lives (Laden 2006). Research was clearly beginning to show that particulate pollution was associated with respiratory system episodes, whereas no connection was apparent for other air components such as ozone and sulfur dioxide (Braun-Fahrlander 1992). Clearly, epidemiological data demonstrates a significant increase in pneumonia, chronic obstructive pulmonary disease, and other respiratory-inflammation-induced deaths associated with high air pollution days (Schwartz and Dockery 1992). However, according to Morton Lippmann, of New York University's (NYU) School of Environmental Medicine, sharpening the focus of the PM NAAQS by particle-size characteristics has gone as far as is reasonable to go. He states that to serve the public needs, the EPA and the scientific community need to generate data to provide a sufficient basis for chemical component-specific PM NAAQS that will target the PM components and/or sources that are most directly responsible for the adverse effects associated with PM mass concentrations (Lippmann 2010).

Exposure to metals in the air is capable of causing a myriad of human health effects, ranging from cardiovascular and pulmonary inflammation to cancer and damage of vital organs (Utsunomiya 2004). Contemporary research into air pollution is revealing that the metals components of particulate matter (PM) are contributing significantly to adverse health effects, even at the low levels found in ambient air (Pope et al. 1995). The EPA set health-based standards for fine particulates in 1997, but the standards do not take into account new research on the composition of the particulate matter or the toxicity of its components (Konkel 2009). The toxicity of particulate matter, in particular the fine and ultrafine particles (those particles smaller than 2.5 μm, has been proven to cause severe mortality and morbidity in humans over the past 25 years; however, in the past decade, emerging research is providing evidence that the metallic particles may be more dangerous than other PM components (Konkel 2009). In addition, current evidence is showing that mass concentration of PM alone may not be the best indices for associating health effects with exposure to PM (Costa and Dreher 1997)(Carter 1997).

The most recently published U.S. Census presents that approximately 80% of the U.S. population lives in urban areas (U.S. Bureau of the Census, 2000). Accordingly, a majority of the U.S. population is exposed to typical ambient metals concentrations found in urban environments. Furthermore, a significant segment of this population also lives in the vicinity of metals sources, such as waste incinerators, metal processors, metal fabrication, welding, etc., where they may be exposed to airborne metals greatly in excess of the typical ambient concentrations. Recent monitoring data in East St. Louis, Illinois depicts levels of metal HAPs in the general community and near schools that not only exceed residential regulatory limits, but reach levels above guidelines set for exposure in an occupational setting (arsenic, measured at approximately 2,340 ng/m^3; occupational short-term exposure limit is 2,000 ng/m^3)(Pettersen 2010). Levels such as these would prompt wearing respiratory personal protective equipment in

an industrial setting, yet these levels were found near not only unprotected members of the general public, but children, who are more sensitive to elevated airborne metals.

3.1.1 Metals in Particulate Matter

As mentioned in Section 2.0, trace metals are released to the atmosphere by the combustion of fossil fuels and wood, high temperature industrial activities and waste incinerations. Natural emissions are mainly from volcanism, wind erosion, as well as from forests fires and the oceans (Nordberg 2007). Specifically, the combustion of fossil fuels constitutes the principal anthropogenic source for beryllium, cobalt, mercury, molybdenum, nickel, antimony, selenium, tin and vanadium. Fossil fuel combustion also contributes to anthropogenic release of arsenic, chromium, copper, manganese and zinc. In addition, a large percentage of arsenic, cadmium, copper, nickel and zinc are emitted from industrial metallurgical processes. Exhaust emissions from gasoline formerly contained variable quantities of Lead, Copper, Zinc, Nickel and Cadmium. Zinc emission is also associated with tire rubber abrasion (Councell 2004).

Several independent groups of investigators have shown that the sizes of the airborne particles determine the potential to elicit inflammatory injury, oxidative damage, and other biological effects (Costa and Dreher, 1997; Lippmann, 2006; Ghio et al. 2002; Sangani et al, 2010; Utsonomiya et al., 2004). The particle size distribution of an aerosol will also determine the deposited fraction of inhaled particles in the various regions of the respiratory tract (Oller 2010). PM is a complex mixture of extremely small particles and liquid droplets and is made up of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals, and soil or dust particles. The EPA is concerned about particles that are 10 μm in diameter or smaller, because those are the particles that generally pass through the throat and nose and enter the lungs. Once inhaled, these particles can affect the heart and lungs, travel throughout the body, deposit in organs, penetrate cell membranes, and cause serious health effects (Adachi and Buseck 2010). EPA groups particle pollution into two categories:

- "Inhalable coarse particles," such as those found near roadways and dusty industries, are larger than 2.5 μm and smaller than 10 μm in diameter.
- "Fine particles," such as those found in smoke and haze, are 2.5 μm in diameter and smaller. These particles can be directly emitted from sources such as forest fires, or they can form when gases emitted from power plants, industries and automobiles react in the air.

These particles can be further defined with reference to relevant health effects for various regions, as described by Nieboer et al. (2005):

- The Inhalable aerosol fraction" is the fraction of total airborne particles that enters the body through the nose and/or mouth during breathing. This fraction corresponding to particles with aerodynamic diameter (d_{ae}) > 100 μm is relevant to health effects throughout the respiratory tract such as rhinitis, nasal, bronchial effects, and lung cancer. This fraction is also relevant for systemic effects.
- The "thoracic aerosol fraction" is a subfraction of the inhalable fraction [d_{ae} < 30 μm] composed of particles that can penetrate into the tracheo-alveolar region of the lung and is important for asthma, bronchitis, and lung cancer.

- The "respirable aerosol fraction" (or alveolar fraction) is the subfraction of the inhaled particles [d_{ae} < 10 μm] that penetrates into the alveolar region of the lung (i.e., includes the respiratory bronchioles, the alveolar ducts and sacs) and is pertinent to the development of such chronic diseases as pneumoconiosis and emphysema.

3.1.2 Characteristics of Fine Particulate Matter

The World Health Organization states that 2.4 million people die each year from causes directly attributable to air pollution (WHO 2002), particularly to fine particles (K. M. Ravindra 2001). According to current human health research, we now know that free radicals similar to those in cigarettes are also found in airborne fine particles and potentially can cause many of the same life-threatening conditions (Dollemore 2008).

In a study of trace metals in PM performed in the Detroit urban atmosphere, Utsonomiya et al. postulates that if toxic trace elements are homogenously dispersed as impurities in insoluble larger-size particles, risks to human health and the environment are less than if they occur as major constituents in individual, trace-metal, nanoscale particles (2004). Generally, the evaluation of most studies shows that the smaller the size and solubility of the PM, the higher the toxicity through mechanisms of oxidative stress and inflammation (Valavandis 2008). A study of $PM_{2.5}$ in 2010 showed that metals were the important source for cellular oxidant generation and subsequent health effects (Maciejczyk 2010). Health effects are stronger for fine (1 to 2.5 μm) and ultrafine (0.1 to 1 μm) particles for a variety of reasons:

1. The studies of the size distribution of metals show that most of the toxic metals accumulate in the smallest particles ($PM_{2.5}$ or less) (K. M. Ravindra 2008).
2. This size fraction can penetrate deeper into the airways of the respiratory tract and predominantly deposits in the alveolar region of the lungs, where the adsorption efficiency for trace elements varies from 60–80% (Pope and Dockery 2006).
3. A metallic particle in contact with lung tissue/cells involves the release of metal ions into the biological system (Midander 2007).
4. Fine and ultrafine particulate matter have the longest residence time in the atmosphere (~100 days), which allows for a large geographic distribution (Utsunomiya 2004).
5. Ultrafine particles are known to have increased solubility, as compared to larger size particles of the same composition because of the increased surface-to-volume ratio for smaller particle sizes (Navrotsky 2001).
6. Recent studies have shown that the metals component in fine and ultrafine PM is particularly toxic and are the primary contributors to negative human health (Magari et al. 2002).
7. Furthermore, these particles also play a significant role in global climate change and can be transported over long distances by prevailing winds (WHO. 2007).

These consequences demand to give priority to the chemical characterization of the fine and ultrafine fraction of airborne particles to understand their possible implication to health effects (K. M. Ravindra 2008). The size of PM with associated ability to penetrate the nasal, throat, and pulmonary boundaries can be seen below in Figure 3 (Particulate Danger 2008).

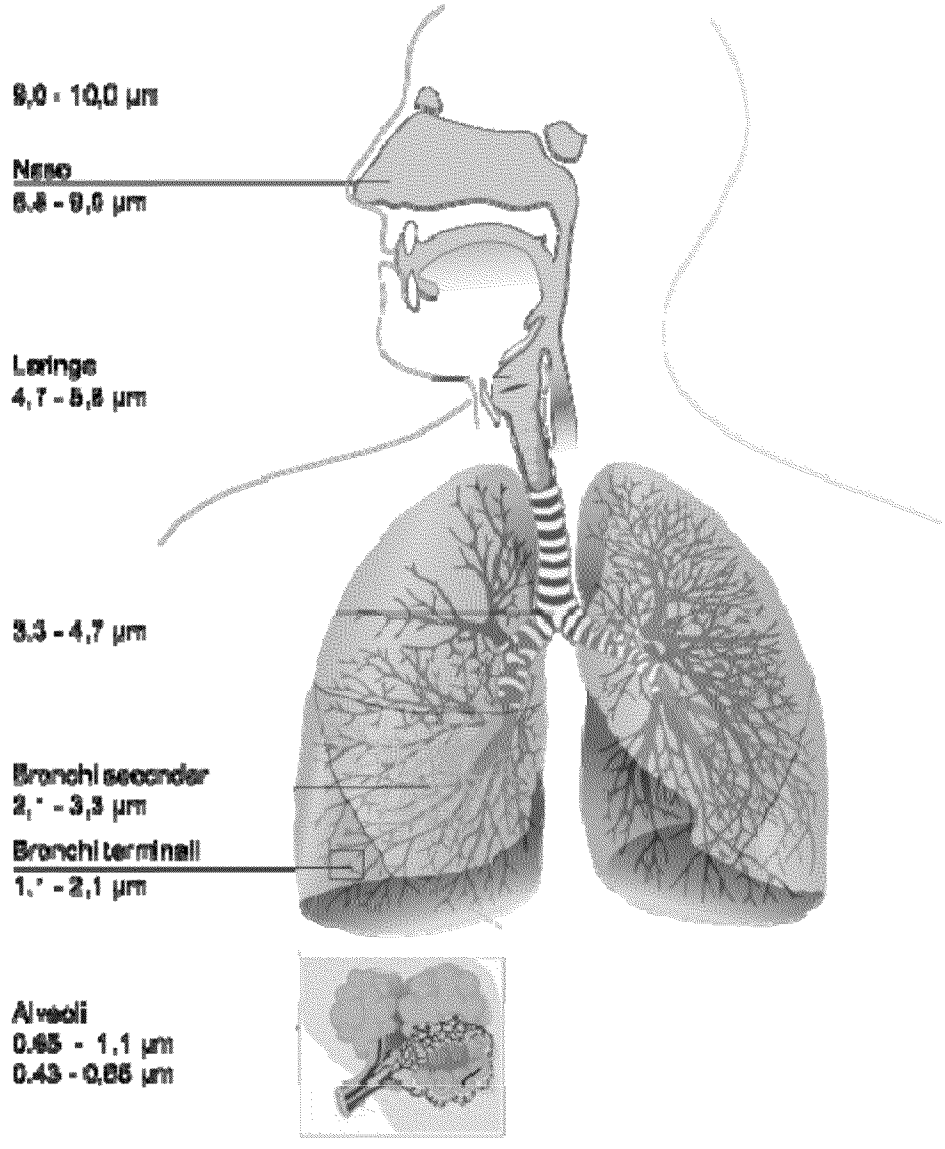

Figure C-3. Particulate size with associated depth of lung deposition

3.1.3 Bioavailable Transition Metals

In-vitro and *in-vivo* studies have identified generation of ROS and increased oxidative stress as a primary biological process that may contribute to produce such a variety of diverse health effects (Hou et al. 2010). Ionic forms of metals will be most bioavailable and therefore most likely to affect cells and organs beyond their deposition sites in the lung airways (Lippmann 2010). Bioavailability has been defined as the fraction of a compound in a matrix that is released from that matrix and absorbed into the body's blood plasma (Spear et al. 1998). An influential study by Daniel Costa and Kevin Dreher in 1997 evaluated the relative importance of bioavailable metal to that of the mass dose of PM. Their results indicated that the lung dose of bioavailable transition metal, not instilled PM mass, was the primary determinant of the acute inflammatory response for both the combustion source and ambient PM samples (Costa and Dreher 1997). Transition metals, such as iron, vanadium, nickel, chromium, copper, and zinc,

have been particularly cited a most likely to be toxic on the basis of their ability to support electron exchange (Ghio 1996) and catalyze and generate ROS in biological tissues (Chen and Lippmann 2009). ROS, such as hydroxyl radicals (OH·), are thought to be involved in various forms of lung injury and are considered to be both genotoxic and carcinogenic (Knaapen et al. 2004).

A study in the Utah Valley looked at the effect of metal, in particular transition metal, removal on the toxicity of airborne particulate matter (Molinelli et al. 2002). This study was prompted by human health data discovered following the closure of an open-hearth steel mill over a year in1987 (Pope 1989); respiratory disease and related hospital admissions were reduced significantly and increased upon reopening (Dye et al. 2001). In a subsequent study of PM effects, metals were removed from an aqueous extract of PM collected in the Utah Valley during the operation of the steel mill. The treated (i.e. metals removed) and untreated (i.e. including original transition metal content) PM samples were exposed to human airway epithelial cells and to rats *in vivo*. Cells that were incubated with the untreated extract (the extract containing metals) showed a significant concentration-dependent increase in the inflammatory mediator interleukin-8 (IL-8) when compared to the control cells. It was also found that significant increases in lactate dehydrogenase (LDH) and total protein occurred in the rats exposed to the untreated extract effects. Generally speaking, the extracts that were stripped of their transition metal content lost their potency to elicit inflammatory responses in the lung. Taken together, this research supports a role for transition metal involvement in PM-associated increases in morbidity and mortality (NHEERL 2010).

A similar effect was found in Redcar, England when a steel plant was closed temporarily. The total metal content of PM_{10} collected before and during the closure period were similar, but on reopening of the steel plant there was a significant 3-fold increase ($p < 0.05$) compared with the closure and pre-closure samples. Of metals analyzed, iron was most abundant in the total and acid extract, while zinc was the most prevalent metal in the water-soluble fraction. Conclusions of the study found that PM_{10}-induced inflammation in the rat lung was related to the concentration of metals in the PM_{10} samples tested, and activity was found in both the soluble and insoluble fractions of the particulate pollutant (Hutchison et al. 2005).

Recent work at NYU's Department of Environmental Medicine looked at daily exposure of concentrated ambient particulate matter (CAPs) to ApoE mice. After exposure, significant increases in heart rate and heart rate variability were found on 14 of the 103 days. A back trajectory analysis of the weather patterns on all 14 of these days demonstrated a wind from the northwest. In addition, trace metal analyses found significant increases in nickel, chromium, and iron, even though the CAPs concentration was markedly reduced on those days. It was then discovered that the air mass passed by the largest nickel refinery plant in North America, located in Sudbury, Ontario, thus suggesting a source for the observed changes in heart rate and heart rate variability. The CAPs inhalation studies at NYU suggest that CAPs overall, and nickel in particular, yields evidence that current levels of ambient air concentrations produce health effects of interest in terms of public health (Lippmann et al. 2006).

Metals in the water-soluble fraction of air pollution particles decrease whole-blood coagulation time. A 1999 study of pulmonary toxicity of PM found that the pulmonary response and cell injury following exposure to this urban dust is related to soluble material, probably metal ions, rather than to the number or composition of the insoluble particles (Adamson 1999). These metals can potentially contribute to procoagulative effects observed following human exposures to air pollution particles (Sangani et al. 2010). Transition metals are also being shown to have involvement in the immunotoxicity of inhaled ambient PM. Iron and Nickel reduced the

clearance of bacteria from the lungs of infected rats, demonstrating that inhaled ambient metals can worsen the outcome of pulmonary infection (Zelikoff et al. 2002).

Additional data not only extrapolates animal toxicity testing to humans, but also provides evidence linking transition metals directly to human health effects. Groups of particular interest include the elderly, pregnant women, those with heart and lung disorders, and young children. A study performed by researchers at the Columbia University's Center for Children's Environmental Health followed more than 700 children between birth and two years of age living in northern Manhattan and the south Bronx. New York City, NY has the highest average ambient air concentration of Nickel at 19 ng/m^3 (versus the national average of 1.9 ng/m^3; (Lippmann et al. 2006)). Researchers found that children exposed to nickel and vanadium in the air were more likely to wheeze. Michelle Bell, a Yale University environmental health scientist, looked at respiratory and cardiovascular hospital admissions of patients 65 years or older and found that counties with higher nickel, vanadium, and elemental carbon were found to have higher risk of hospitalizations associated with short-term particulate exposure (Konkel 2009).

Evidence points towards genotoxicity of inhaled transition metals as well. Mitochondria are the major intracellular source and primary target of ROS, which are generated under normal conditions as by-products of aerobic metabolism in animal and human cells. Compared with nuclear DNA, mitochondrial DNA lacks protective histones and has diminished DNA repair capacity, and is therefore particularly susceptible to ROS-induced damage. Cells challenged with ROS have been shown to synthesize more copies of their mitochondrial DNA and increase their mitochondrial abundance to compensate for damage and meet the increased respiratory demand required for ROS clearance. At the same time, ROS are also generated from the increased mitochondria in these cells and thus cause additional oxidative damage to mitochondria and other intracellular constituents including DNA, RNA, proteins, and lipids. In a study by Hou et al., increased mitochondrial DNA in circulating blood leukocytes was positively correlated with blood markers of oxidative stress. Mitochondrial damage and dysfunction, as reflected in increased mitochondrial DNA copies, may thus represent a biological effect along the path linking PM inhalation to its health effects (Hou et al. 2010).

Table C-5 presents a chronological summary of studies that implicate metals as significant contributors to human health effects.

3.1.4 Vanadium and Nickel producing ROS

Current research is providing strong evidence that nickel and vanadium are accounting for a large portion of adverse human health effects. A majority of *in vitro* and animal model investigations support the postulation that transition metals, which are present in such substances as residual oil fly ash (ROFA), participate in Fenton-like chemical reactions to produce ROS (Ghio et al. 2002). In the Fenton reaction, iron reacts with naturally present hydrogen peroxide to form free radicals, such as hydroxyl radicals (OH·). Research shows that special attention must be taken with Ni and other transition metal concentrations, because of their high potential bioavailability. Nickel is important, in particular, mainly due to the high solubility of the chemical forms of Ni in the finest particles (Fernandez-Espinosa 2004).

Table C-5. Chronological Summary of Studies Implicating Metals

Date	Type	Corresponding Author	Relevant Key Conclusions
1971	R	EPA	NAAQS for total suspended particles (TSP) include larger, noninhalable particles
1987	R	EPA	Regulatory focus on combination of fine (<2.5 µm) and coarse (<10 µm) particulate matter (PM), all of which can be inhaled into the respiratory tract.
1989	E, H	Pope A.C. III	"Closure of an open-hearth steel mill in the Utah Valley over the winter of 1987 was associated with reductions in respiratory disease and hospital admissions in valley residents; effects were a result of reduction in PM levels."
1992	H, E	Braun-Fahrlander et al.	"Particulate pollution (TSP) was associated with incidence and duration of respiratory symptom episodes. No such associations were observed with $S0_2$ or ozone."
1992	H, E	Schwartz and Dockery	"A 100 µg/m^3 increase in TSP was associated with an increase in mortality due to COPD, pneumonia, and cardiovascular disease equal to 19, 11, and 10%, respectively. On high pollution days, COPD, pneumonia, and dead-on-arrival deaths were disproportionately increased."
1995	R	Pope, Bates, and Raizenne	"...Respirable particulate air pollution is likely an important contributing factor to respiratory disease."
			"Observed (PM) health effects include increased respiratory symptoms, decreased lung function, increased hospitalizations and other health care visits for respiratory and cardio-vascular disease, increased respiratory morbidity as measured by absenteeism from work or school or other restrictions in activity, and increased cardiopulmonary disease mortality. "
			"These (PM) health effects are observed at levels common to many U.S. cities including levels below current U.S. National Ambient Air Quality Standards for particulate air pollution."
1996	T	Ghio et al.	"Transition metals have the capacity to support electron exchange and catalyze free radical production."
1997	T	Carter et al.	"Free radicals can induce alterations in host pulmonary defense, inflammation, and lung injury."
1997	T, A	Costa and Dreher	"..The lung dose of bioavailable transition metal, not instilled PM mass, was the primary determinant of the acute inflammatory response for both the combustion source and ambient PM samples."
			"...Soluble metals from PM mediate the array of PM-associated injuries to the cardiopulmonary system of the healthy and at-risk compromised host."
1999	T, A	Adamson et al.	"This (study) suggests that the pulmonary response and cell injury following exposure to this urban dust is related to soluble material, probably metal ions, rather than to the number or composition of the insoluble particles."
2001	E, H, T	California Air Resources Board	"Groundbreaking long-term studies of children's health conducted in California have demonstrated that particle pollution may significantly reduce lung function growth in children."
2001	R	Ravindra et al.	"Data on daily mortality show that, on a global scale, 4% to 8% of premature deaths may occur due to the exposure of suspended particulate matter (SPM) and especially of fine particles ($PM_{2.5}$) in the ambient and indoor environment."
2002	R	California Air Resources Board	"Premature deaths linked to particulate matter or "PM" are now at levels comparable to deaths from traffic accidents and second-hand smoke. "
2002	H, T	Magari et al.	"The metals component in fine and ultrafine PM is particularly toxic and are the primary contributors to negative human health."
			"…Results of this study suggests an association between exposure to airborne metals (vanadium, nickel, chromium, lead, copper, and manganese) and significant alterations in cardiac autonomic function."
2002	R	Ghio et al.	"…Transition metals present in ROFA (especially vanadium) participate in Fenton-like chemical reactions to produce reactive oxygen species (ROS)."
2002	T, A	Zelikoff et al.	"…Both iron and nickel (inhaled) reduced pulmonary bacterial clearance in previously infected rats."
2002	T, A	Molinelli et al.	"…Ambient air particles in the Utah Valley induce their health effects in part by delivering transition metals to the airway epithelium in a catalytically-active form."
			"Results (*in vivo* and *in vitro*) support a role for transition metal involvement in PM-associated increases in morbidity and mortality."
2004	T, H	Fernandez-Espinosa and Ternero-Rodriguez	"Physical speciation of lead showed that the major risk for health was from fine particles less than 2.7 µm, because particles between 2.7 and 0.6 µm were the size fractions of the TSP with the major mass abundance of lead (mainly particles between 2.7 and 1.3 µm) and because particles less than 0.6 µm were the fraction of the airborne particles most abundant in the urban air."
			"Chemical speciation results showed that special attention must be taken with Ni and Cd concentrations because of their high potential bioavailability, mainly a result of the high solubility of the chemical forms of Ni in the finest particles."
2004	T	Utsonomiya et al.	"If toxic trace elements are homogenously dispersed as impurities in insoluble larger-size particles, risks to human health and the environment are less than if they occur as major constituents in individual, trace-metal, nanoscale particles "
			"Fine and ultrafine particulate matter have the longest residence time in the atmosphere (~100 days), which allows for a large geographic distribution"
			"Ultrafine particles…have increased solubility as compared to larger size particles of the same composition because of the increased surface-to-volume ratio for smaller particles."
2005	R, E	Thurston et al.	"…treating all particles that contribute to mass concentration (of PM) equally in the regulatory process may lead to inefficient protection of public health. A potentially more effective approach would be to address the individual types of particles independently, focusing control efforts on the most toxic categories."
2006	E, H, T	Karthikeyan et al.	"Daily Respiratory Uptake (DRU) values were significantly higher for several metals, including Zn, Cu, and Fe, during bushfires. ...Measurements showed that the particulate samples collected during bush fires generate more toxic hydroxyl radicals (OH·) than those in the background air, due to the presence of more soluble iron ions."
			"As a result (of increased metals from bushfires), people seeking treatment for respiratory-tract infections went up 25% and asthma cases went up 29%."
2006	T, A	Lippmann et al.	"Nickel appears to be the component (of fine particulate matter) most likely to cause acute cardiac responses."
2006	T, A	Pope and Dockery	"The fine PM less than 2.5 µm fraction predominantly deposits in the alveolar region of the lungs, where the adsorption efficiency for trace elements varies from 60–80%."

Table C-5. Chronological Summary of Studies Implicating Metals

Date	Type	Corresponding Author	Relevant Key Conclusions
2007	E	WHO	"Fine particles also play a significant role in global climate change and can be transported over long distances by prevailing winds."
2008	O,T	Ravindra et al.	"The studies of size distribution of metals show that most of the toxic metals accumulate in the smallest particles ($PM_{2.5}$ or less)."
			"Variations in natural/anthropogenic fractions of $PM_{2.5}$ were…found to be a function of meteorological conditions as well as of long-range transport of air masses from industrialized regions…"
2008	R	Dollemore	"Epidemiological studies suggest that more than 50,000 Americans die each year from cardiopulmonary disease linked to breathing fine particle air pollution."
			"According to current human health research, we now know that free radicals similar to those in cigarettes are also found in airborne fine particles and potentially can cause many of the same life-threatening conditions."
2008	T	Valavandidis et al.	The smaller the size of the PM, the higher the toxicity through mechanisms of oxidative stress and inflammation
			Recent data emphasize the importance of water-soluble constituents, such as transition metals..known to be adsorbed onto the surface cavities of the PM and can be released in the lung alveoli and deposited in the lung parenchyma.
			Toxicological studies in vivo and in vitro showed that PM have the ability to generate continuously high reactive ROS, which contribute to the genotoxic and cytotoxic mechanisms of PM.
2009	MA	Konkel	"(There is)…evidence linking nickel, vanadium, and elemental carbon in the air to wheeze and cough in inner city children."
			"Total levels of particulates were not significantly associated with wheeze or cough, suggesting that individual ingredients - not fine particles as a whole - may be harmful."
2009	R	Chen and Lippmann	"Residual Oil Fly Ash (ROFA), which is…notably high in vanadium and nickel, were more toxic than other source-related mixtures that have been tested in laboratory animals in vivo or in cell in vitro."
			"…Concentrations of nickel and vanadium in ambient air PM were associated with significant differences in mortality rates, while other measured PM components were not."
			"Ambient air fine particulate matter toxicity may vary depending on its source and chemical composition."
			"...Reduction of metals in PM associated with a year-long closure of a steel mill was associated with improved health conditions in the local population. The role of metals was further confirmed by later studies using human clinical as well as animal toxicology studies."
2010	T,H	Maciejczyk et al.	"Metals in PM2.5 (especially nickel) were the important source for cellular oxidant generation and may be responsible for subsequent health effects associate with particle air pollution."
			"Three metals (nickel, barium, and manganese)… appear to be much more influential on lung cell responses than black carbon and sulfate ions that are present at much higher mass concentrations."
2010	R	EPA	"...Recent studies have shown that extracts stripped of transition metals lose their potency and that solutions of pure transition metals in the ratios and concentrations found in the particles can induce similar effects in animals as the complete extracts. This conformed to a theory of particle toxicity emphasizing the ability of metals on fine particulates to induce toxic oxygen radical species and subsequent inflammatory response in the lung."
			"While particle size does matter, particle composition seems also to be extremely important in the pulmonary inflammatory response to particulate air pollution."
2010	T	Sangani et al.	"Metals in the water-soluble fraction of air pollution particles decrease whole-blood coagulation time."
2010	MA	Lippmann	"...The EPA and the scientific community need to generate data to provide an adequate basis for chemical component-specific PM NAAQS that will target the PM components and/or sources that are most directly responsible for the adverse effects associated with PM mass concentrations."
			"…The lack of daily data on concentrations makes it all but impossible to accurately study acute responses to peaks in exposure."

Type:
O = Original
A = Animal Study
E = Epidemiological
H = Human Study
T = Toxicological
R = Review
MA = Magazine Article

3.2 Olfactory Risk

Recent studies have found that certain metals can result in olfactory and neurological injury. The olfactory system forms a direct interface between the nervous system and the external environment (Aschner et al. 2005). The olfactory (nasal) neuron can provide a pathway by which foreign materials can reach the brain (Bondier et al. 2008). The metals with potential to

travel through the olfactory nerve are aluminum, cadmium, cobalt, mercury, manganese, nickel, and zinc.

Two metals that have recently been shown to be particularly toxic through the olfactory nerve transportation pathway are cadmium and manganese. As in inhalation studies, results of investigations into particle size uptake of manganese (Fechter et al. 2002) suggested that particle size may influence the delivery of manganese to the rat olfactory bulb because manganese delivery appeared to be smaller for the larger particles (18 µm) and larger for the fine particles (1.3 µm). The addition of methylcyclopentadienyl manganese tricarbonyl (MMT) to gasoline in some countries led to increased levels of manganese in the atmosphere; furthermore, the nervous system is the major target organ of manganese. Manganese species and solubility also have an influence on the brain distribution of Mn in rats (Normandin et al. 2004) and were found in dopamine-rich areas of the brain (Antonini 2010). Bondier et al. recommend that the olfactory route of entry for cadmium should be taken into account as cadmium is able to penetrate the CNS and cause brain injury (2008). Although both metals are considered dangerous via the olfactory route, manganese is also capable of traveling along secondary and tertiary neurons, whereas cadmium is not (Aschner et al. 2005).

3.3 Industrial Health Effects

Occupational exposure to particles has been related to respiratory tract cancer in humans in the past and present time. Most of the epidemiological evidence for this has been gathered from high occupational exposures in the past (Knaapen et al. 2004).

Foundry work has been associated with various adverse health outcomes, including cardiovascular disease, respiratory disease, and lung cancer, that may depend on ROS-induced damage and genotoxicity. Even in modern foundry facilities that adopt state-of-art measures for exposure reduction, workers are still exposed to substantially higher levels of airborne PM compared to those found outdoors. In a study by Hou et al., the association of blood mitochondrial DNA with exposures to airborne PM and its metal components was investigated for foundry workers exposed to a wide range of PM levels (2010). The results of this study showed that PM exposure is associated with damaged mitochondria, which subsequently intensify oxidative-stress production and effects.

As reported by Oller and Oberdorster, even though the issue of particle size distribution differences between animal and human aerosols has been raised before and is well known to inhalation toxicologists, it has not yet been incorporated into Occupational Exposure Limits (OEL) setting frameworks in the European Union or the United States (2010). When comparing the levels considered to adversely affect human health at a community level versus levels permissible in an occupational setting, it is clear that a large discrepancy exists. Although the occupational scenario considers a shorter duration of exposure (i.e. an 8- to 10-hour work day), occupational exposure levels (OELs) are not necessarily keeping pace with current scientific knowledge (Oller and Oberdoerster. 2010). In addition, extreme caution must be exercised with such metals as lead and beryllium as the U.S. National Research Council has been unable to establish any safe level of exposure (NRC 2008).

The advantage of OELs is that they are produced through a very strict process that provides checks and balances, which makes these limits legally enforceable (Meagher 2002). However, when looking at exposure limits for Nickel, the most relevant medical and toxicological literature lists an acute (1-hour) average of 6 $\mu g/m^3$ (as reported in California EPA's reference exposure level (REL), whereas the 8-hour permissible exposure limit (PEL) is 1,000 $\mu g/m^3$ (equaling 125

$\mu g/m^3$ for 1 hour). Even more recent data, such as research being performed by Morton Lippmann and Chi Chen, suggests that nickel at even the lowest ambient levels has the potential to cause adverse health effects (2009).

3.4 International Air Quality

The World Health Organization (WHO) estimates that urban air pollution contributes to approximately 800,000 premature deaths and 4.6 million lost life-years worldwide each year (HEI 2004). PM pollution is estimated to cause 22,000-52,000 premature deaths per year in the United States and 200,000 premature deaths per year in Europe (Mokdad et al. 2004). Emissions from industrial and mobile sources are not bound by country borders. The concentration, composition, and size of suspended particulate matter at any given site are determined by such factors as: meteorological properties of the atmosphere, topographical influences, emission sources, and particulate parameters such as density, shape, and hygroscopicity (Fang et al. 2010). Data on daily mortality show that, on a global scale, 4% - 8% of premature deaths may occur due to the exposure of suspended PM and especially of fine PM in the ambient and indoor environment. The anthropogenic group of metals, such as zinc, lead, sulfur, vanadium, chromium, copper, nickel, and bromine occur in scattered relative abundance in $PM_{2.5}$ samples (K. M. Ravindra 2008). The concentration pattern seems to be related to the changes in meteorological conditions, such as wind speed, wind direction, or, on a larger scale, long range transports, which can cause large differences in the amount of different anthropogenic elements in $PM_{2.5}$.

Countries without the regulatory infrastructure to properly monitor and reduce air toxics are particularly susceptible to elevated levels of airborne metals in ambient air. In fact, in a report by the Health Effects Institute in Boston, Massachusetts, of the 800,000 premature deaths attributable to urban air pollution worldwide, two-thirds of the deaths occur in developing countries in Asia (HEI 2004). Some of these countries do not have high enough amounts of industrial activity to incite human health risks, such as in some African countries; however, other countries, such as Mexico and China, have levels of air toxics introduced by industrial activity far above what would be considered “safe” in more regulated systems. In Shanghai, China, concentrations of trace metals, such as chromium, manganese, nickel, and zinc, in PM are reported far above the human health protection levels listed by the U.S. EPA (Weisheng et al. 2007). These types of modern environmental health hazards are products of rapid development in the absence of health and environmental safeguards, as well as the unsustainable consumption of natural resources (WHO 1997).

Significant health impacts from metal-containing air pollution have been reported in several developing countries. Bushfires in Singapore created significant increases in the concentration of Zn, Fe, and Cu. As a result, people seeking treatment for respiratory-tract infections went up 25% and asthma cases went up 29% (Karthikeyan et al. 2006). Electron paramagnetic resonance (EPR) measurements showed that the particulate samples collected during the bushfires generated more toxic hydroxyl radicals than those in the background air, most likely due to the presence of more soluble iron (and other transition metal) ions. In Africa, an important source of direct human exposure to high levels of mercury is artisanal gold mining and processing. Exposure to vaporized mercury occurs during burning to separate gold from the gold-mercury amalgam. The release of mercury occurs within the breathing zone of workers who are typically not equipped with personal protective equipment (Nweke and Sanders 2009).

A study of metals in traffic pollution performed in Spain found important relationship between Pb and Cu, which supports current research into PM speciation. Physical speciation of lead showed

that the major risk for health was from fine particles less than 2.7 μm, because particles between 2.7 and 0.6 μm were the size fractions of the total suspended particles with the major mass abundance of lead (mainly particles between 2.7 and 1.3 μm) and because particles less than 0.6 μm were the fraction of airborne particles most abundant in the urban air. Chemical speciation results showed that special attention must be taken with nickel and cadmium concentrations, because of their high potential bioavailability, mainly a result of the high solubility of the chemical forms of Ni in the finest particles (Fernandez-Espinosa 2004).

A study of metal nanoparticles, defined in this study as particles smaller than 50 nanometers, in Mexico City revealed that well over half of the 572 metal nanoparticles contained two or more metals. Of these, iron, lead, or zinc occurred in more than 60%. In addition, many of the metal-bearing nanoparticles were attached to or embedded within host particles, which were mainly organic matter and sulfate, both of which are more soluble than most metal-bearing nanoparticles and will dissolve in the deposited region of the body/lung, leaving the metal nanoparticles behind. The findings of this study implied that different physiological areas and effects would result from the inhalation of either free-floating metal nanoparticles or metal nanoparticles carried by host material (Adachi and Buseck 2010).

3.5 Future Research on Metals in Air Pollution

As described in the previous sections, contemporary researchers in the field of airborne metals' health effects are finding that the metals components of PM are quite toxic and cause various significant health effects from pulmonary inflammation (Costa and Dreher 1997) to increased heart rate variability (Lippmann et al. 2006) to decreased immune response (Zelikoff et al. 2002). These effects are not only seen from chronic exposure, but also from short-term peaks in ambient air concentrations (Chen and Lippmann 2009).

When dealing with a community near a single source of HAP metals, a 24 hour integrated average sample taken ever third or sixth day is not likely to provide an adequate indicator of short-term exposure levels. This is due in part to the fact that when a monitor is close to a source, some of the time the wind will move the emissions in the opposite direction of the monitor, and the metal concentration at the monitor will be close to zero. Thus, to achieve the average, the concentrations at shorter time intervals must be substantially greater than the 24 hour average.

Accurate assessment of human exposures to air pollution is an important part of environmental health effects research; however, most air pollution epidemiological studies rely upon imperfect surrogates of personal exposure, such as information based on available central-site outdoor concentration modeling or modeling data. In a 2008 study modeling population exposures to HAPs, results indicated that the total predicted chronic exposure concentration of outdoor HAPs from all sources are lower than the modeled ambient concentrations by about 20% on average for most gaseous HAPs and by about 60% on average for most particulate HAPs (Ozkaynak et al. 2008). These findings highlight the importance of applying exposure-modeling methods, which incorporate information on time-activity, commuting and exposure factors data, in order to accurately determine human exposure to HAPs.

Researchers are calling for further investigation into the characterization of ambient air metals. Terry Gordon of NYU's Department of Environmental Medicine (2007) calls for:

1) Larger numbers of study subjects
2) More frequent time points for response and exposure assessment

3) More precise (time resolution & component speciation) measurements of exposure to account for the temporal-spatial variability in exposure parameters.

As reported by Morton Lippmann, continuous records of PM components such as coarse mode PM, fine PM, and perhaps ultrafine PM would greatly accelerate the accumulation of knowledge on PM component exposure–response relationships that would provide a sound basis for more targeted air quality standards and pollution control measures. He also states that "the lack of daily data on concentrations makes it all but impossible to accurately study acute responses to peaks in exposure" (Lippmann 2010). Furthermore, legislation concerned only with measuring physical PM mass concentrations fails to address potential health effects linked to chemical variations in ambient aerosols (Moreno 2009). Most importantly, equal treatment of all particles that contribute to mass, irrespective of composition, may be leading to less-optimal control strategies to avoid the adverse human health effects of PM. A more effective approach would be to address the types of particles independently, focusing control efforts on the most toxic categories (Thurston 2005).

4.0 Key Source Indicating Metals for Apportionment

The goal of source apportionment is to determine contributions of various pollution sources to a location of interest (e.g. outdoor, indoor, or personal exposure measurement). Accurate size-resolved chemical characterization of emissions from potential sources in each air shed is an essential component in receptor modeling studies. Lack of this source information is currently one of the major, if not most significant, factors limiting further improvements in the accuracy and precision of quantitative source apportionment. Identifying and quantifying a source's contribution relies on a comparison of the chemical and physical features of the ambient aerosol measured at the receptor with the features of an aerosol emitted from a potential source.

Ambient air fine PM is a chemically nonspecific pollutant, and may originate from, or be derived from, various emission source types; thus, fine PM toxicity may well vary, depending on its source and chemical composition. If the fine PM toxicity could be associated with specific source signatures, then health effects research could be better focused on specific FPM components that come from those sources and specific biological mechanisms could be postulated for further consideration by toxicological studies.

Source composition varies according to industrial and other anthropogenic activities, as well as naturally occurring geologic events. Typical source contributions can be characterized in the following categories (Cooper 1999):

a. Geological – soil dust, agricultural tilling, rock crushing; mostly larger, coarse particles
b. Automotive and truck exhaust – fuels, prior use of leaded gasoline, diesel (indicated by high elemental carbon); mostly fine particles
c. Stationary fossil fuel combustion – residual oil, coal, distillate oil, natural gas; fine and coarse particles
d. Primary emissions from industrial point sources – typically fine particles, varies with industrial activity
e. Residential solid fuels (wood and coal) – high levels of pollutants with current technology; fine and coarse particles
f. Secondary aerosols – sulfate, nitrate, hydrocarbons; fine particles
g. Natural sources – pollen, spores, leaf fragments, biomass emissions; mostly coarse particles
h. Miscellaneous sources (galvanizing, boiler cleaners, construction, etc)
i. Background aerosols – marine, continental, material entering an airshed with the prevalent air mass, not subject to control

A study performed in Japan measured concentrations of elements vanadium, calcium, cadmium, iron, barium, magnesium, manganese, lead, strontium, zinc, cobalt and copper in aerosols with ICP-MS. The results showed that calcium, magnesium, manganese, strontium, cobalt, and iron were mainly associated with coarse particles (>2.1 μm), primarily from natural sources. In contrast, the elements zinc, barium, cadmium, vanadium, lead, and copper dominated in fine aerosol particles (<2.1 μm), implying that the anthropogenic origin is the dominant source. Results of the factor analysis on elements with high crust values (>10) showed that emissions from waste combustion in incinerators, oil combustion (involving waste oil burning and oil combustion in both incinerators and electricity generation plants), as well as coal combustion in electricity generation plants were major contributors of anthropogenic metals in the ambient atmosphere in Kanazawa (Wang et al. 2006).

Table C-6: Examples of key indicating elements with associated sources

Source	Indicating Elements
Crustal/Geologic	Na, Mg, Al, Si, K, Ca, Sc, Ti, Mn, Fe, Ga, Rb, Sr, and Zr
Coal Combustion	Crustal plus fine PM such as Ge, As, Se, Sb, Ba, W, U, Hg, and B
Oil Combustion	V, Ni, and Mo (fine PM)
Petroleum Refinery	La, Ce, Nd, and other elements specific to process
Automotive	Br and Pb (fine PM)
Copper, Nickel, and Lead Smelters	Cu, As, Cd, Pb, In, Sn, Sb
Marine Aerosol	Na, Cl
Vegetative Burning	Organic Carbon, Elemental Carbon, K, Cl, Zn
Iron and Steel Industry	Fe, Co, Cr, Ni, and Mg (fine PM)
Na=sodium, Mg=magnesium, Si=silicon, K=potassium, Ca=calcium, Sc=Scandium, Ti= titanium, Mn=manganese, Fe=iron, Ga=gallium, Rb=rubidium, Sr=strontium, Zr=zirconium, Ge=germanium, As=arsenic, Se=selenium, Sb=antimony, Ba=barium, W=tungsten, U=uranium, Hg=mercury, B=boron, V=vanadium, Ni=nickel, Mo=molybdenum, La=lanthanum, Ce=cerium, Nd=neodymium, Br=bromine, Pb=lead, Cu=copper, Cd=cadmium, In=indium, Sn=tin, Cl=chlorine, Zn=zinc, Co=cobalt, Cr=chromium	

Understanding the sources of ambient particulate matter has become increasingly important. While local sources can be monitored and subjected to local control regulations, particulate matter that has been transported into the region cannot be easily monitored or controlled. The commonly identified source categories include: secondary sulfate/coal burning (sometimes over 50 percent of the mass), secondary organic carbon/mobile sources, crustal sources, biomass burning, nitrate, industrial, smelters and metal processing, and sea salt in coastal regions. Frequently, the smaller sources and the mobile sources appear as combinations of sources. The combined sources are usually those that would naturally affect the receptor concurrently, such as a mobile — road dust or road salt combination. The main tools for apportioning the sources rely on variations in source strength to separate the sources; hence, sources acting together cannot be separated. Consequently, while separating the mobile sources into diesel- and gasoline-based emissions is clearly a goal for several of the studies, the success depends on either additional data or analyses.

Airborne PM pollution is presently regulated by the NAAQS using gravimetric mass as the particle metric to assess air quality. However, an enormous number of different chemical species are associated with the various types of ambient particles, depending upon their source origins (e.g., Cooper and Watson 1980). For example, primary particles emitted from coal combustion are characteristically enriched with arsenic and selenium, whereas residual oil combustion particles are more enriched in nickel and vanadium, and soil particles are especially enriched in the crustal elements (e.g., silicon, aluminum). In addition, secondary components of particles (e.g., sulfates, nitrates, and organic compounds) are formed in the atmosphere from gaseous pollutant emissions. These secondary components can either condense on primary particles or form secondary particles that can then collide and coagulate with primary particles. Individual particles in an urban airshed can contain both primary and secondary components,

and the composition of ambient aerosols have been found to reflect source PM emission characteristics differences over space (e.g., between cities) and time (e.g., across seasons) (e.g., Spengler and Thurston 1983). Because the composition of particle types varies greatly, it is probable that some types of particles are more toxic than others. Thus, treating all particles that contribute to the mass concentration equally in the regulatory process may lead to inefficient protection of public health. A potentially more effective regulatory approach would be to address the individual types of particles independently, focusing control efforts on the most toxic categories.

In conclusion, for the effective management of air quality, great importance must be attached to the identification of the sources of suspended PM. Source apportionment provides an estimate on the PM contribution of various sources to the levels at the receptor; it is also a key component necessary for developing and achieving desired air-quality objectives. Source apportionment methods rely on the principle that if a group of chemical constituents have a common origin, they should show a similar variation. The results of source apportionment can be used to evaluate emissions reduction on the PM levels and to devise more efficient emission reduction strategies. Therefore, estimating the airborne PM mass concentration, as well as individual chemical/metal speciation, is very critical not only for comparing with recommended values, but also to identify the major sources that affect a particular area. This knowledge will also help regulators both foresee and prevent threats and risks before they become problems (Abdul-Wahab 2004).

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APPENDIX D

Example Application: Secondary Lead Smelter

DRAFT

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Summary

This hypothetical example illustrates how Guide for Developing a Multi-Metals Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors (Guide) can be applied to quantify and characterize air quality issues associated with stack and fugitive emissions from secondary lead smelters. Secondary lead smelters are relatively prevalent in the United States and are usually located in large urban areas with significant receptor populations and general air quality issues. Lead emissions are a national concern, and lead is the only metal included in the National Ambient Air Quality Standards (NAAQS) promulgated by the United States Environmental Protection Agency (U.S. EPA). Lead is a potent neurotoxin, and has been linked to mental impairment in adults and developmental disabilities in children. The lead NAAQS was recently lowered from 1.5 μg/m³ to 0.15 μg/m³, reflecting new scientific understanding that virtually no level of lead in the blood is safe for human health.

States have five years to achieve compliance with the new standard, and a number of locations near secondary lead smelters are currently out of attainment. For this example, a secondary lead smelter near downtown Los Angeles (The Facility) is developing a lead NAAQS attainment plan. The goal of the plan is to use near-real-time (NRT) multi-metals ambient air monitors to assess potential threats to a local airshed from fugitive and process stack lead emissions, identify major fugitive lead sources within the facility and develop successful engineered emissions controls.

A key to compliance with the lead NAAQS at The Facility is accurate identification of sources within the smelter responsible for measured high lead detection at the NAAQS total suspended particulate (TSP) monitors. Many studies of fugitive emissions at secondary lead smelters show that short-term spikes in concentrations are the major contributors to total monthly lead TSP. As such, this plan incorporates a fence line metals monitor to characterize these expected concentration spikes and correlate the elevated lead concentrations with particle size, wind speed and direction, plant activity, and monitor location. Using this contextual information, fugitive sources can be identified and engineered controls can be developed to curb lead emissions and comply with the lead NAAQS.

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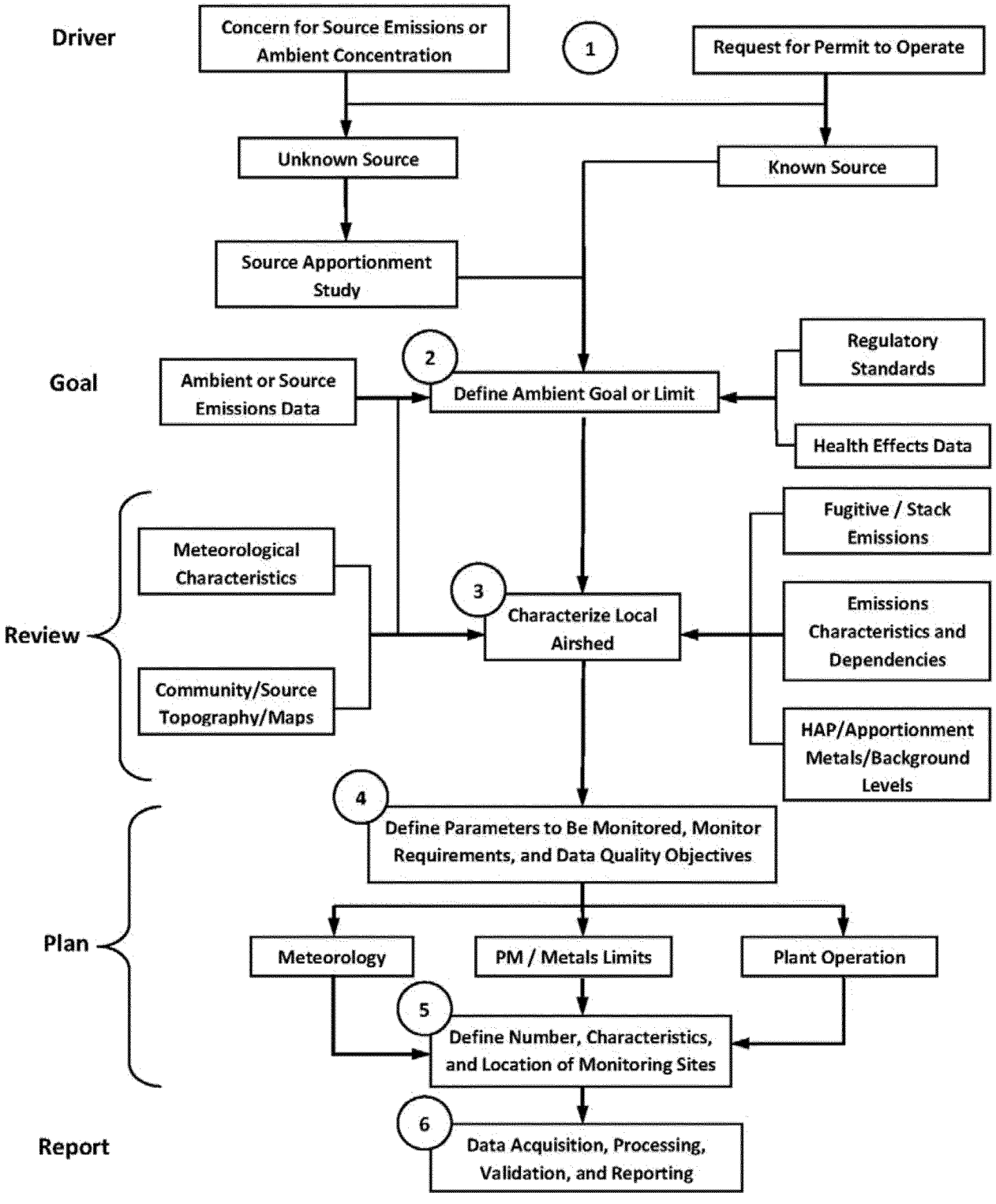

Figure 1. Procedure Flow Diagram

1.0 Driver – Ambient Lead Emissions in an Urban Setting

For this hypothetical example, the Guide is applied to establish a fugitive emissions Hazardous Ambient Metals Compliance Plan (Plan) for a secondary lead smelter located southeast of downtown Los Angeles, California (The Facility). The Facility recycles automobile lead-acid batteries and other lead-bearing material. The Facility is one of the largest secondary lead smelters in the United States (EPA,1998), and is situated on 24 acres of land in a dense industrial/commercial area near a major railway corridor and U.S. Interstate 5. Residential neighborhoods are located to the north, east, and south within a mile radius of the facility.

The secondary lead smelter location has been utilized for various metals fabrication and recovery purposes since 1922, and lead-acid battery recycling has been the primary industrial function of the site since the early 1970s. The facility produces around 100,000 tons of lead annually, which is the equivalent of recycling approximately 11 million automotive batteries, or the entire annual consumption of the state of California. Lead-acid batteries usually represent 60 - 90% of the raw materials at a secondary lead smelter (EPA,1998). Other raw materials include lead pipe, lead covered cable, and scrap solder. At The Facility, lead-acid batteries and other lead-bearing materials arrive via truck or rail car. The batteries are mechanically deconstructed and acid, lead alloys, lead-oxide paste and polypropylene are isolated. The polypropylene is shipped off-site for recycling into additional plastic products. The waste acid is mixed with on-site waste water and storm-water, and managed and treated as a hazardous waste before being discharged into the local sewer. The standard lead recycling process proceeds in a reverberatory or blast furnace as lead sulfate paste and lead alloy is heated, or "sweated" with coke and fluxing agents like soda ash, silica, and limestone. The $PbSO_4$ and PbO are reduced to lead metal (EPA,1998). Blast furnaces produce a relatively hard lead-antimony alloy, and reverberatory furnaces produce a more pure, soft lead metal.

Lead emissions are the primary concern. Cadmium, antimony, arsenic, chromium, nickel, and manganese emissions may also be associated with The Facility. Emissions may occur from process sources, process fugitive sources or from lead dust fugitive sources. Process sources include stack emissions from the blast furnace and the reverberatory furnace. Process fugitive sources include the smelting furnace and dryer charging hoppers, chutes and skip hoists, smelting furnace lead taps and molds during tapping, refining kettles, dryer transition pieces, and agglomerating furnace product taps. Lead dust fugitive sources include toxic dust from facility roadways, storage piles, materials handling transfer points, transport areas, storage areas, process areas, and buildings.

Regulation of emissions from secondary lead smelters is mandated by the Clean Air Act Title 40 CFR 63, National Emission Standards for Hazardous Air Pollutants, subpart X. Specific emissions targets are set by the regulations for both stack and fugitive emissions using the Maximum Achievable Control Technology (MACT) guidelines. Annual performance tests are conducted to determine compliance with standards.

In November 2008 the U.S. EPA revised the NAAQS for lead from 1.5 µg/m³ to 0.15 µg/m³ over a three-month rolling average period. Stricter ambient standards reflect new scientific understanding of the health risks associated with exposure to lead. Recent studies suggest that there is no level of lead in blood that is safe for humans. Well-documented health effects include lower IQ, weakened memory, and learning disabilities in children, and cardiovascular problems, kidney problems and higher blood pressure in adults.

The Facility has been out of compliance with both the historic lead NAAQS and the updated lead NAAQS since December 2007. In the fall of 2007, California's Air Quality Management District (AQMD) received a number of public complaints reporting significant particulate fallout from the plant in the immediately adjacent neighborhood. Subsequent investigations found ambient levels of lead in the neighborhood ranging from 2 – 3 µg/m³. More recent data from September 2010 give lead values ranging from 0.03 µg/m³ - 0.50 µg/m³.

Due to the lead exceedances above the NAAQS, the AQMD revised The Facility's permit, cutting throughput for the facility 50%, and imposing 27 additional conditions designed to reduce the lead emissions from the smelter into the surrounding neighborhood. However, The Facility's progress in implementing the corrective action plan has not yet resulted in compliance with the lead NAAQS.

1.1 Daily Variability in Fugitive Emissions and Real-Time Multi-Metals Monitoring

Secondary lead smelters utilize wet scrubbers and baghouses to control lead concentrations in stack emissions. However previous studies at secondary lead smelters indicated that fugitive lead emissions can be comparable or even higher than stack emissions (Goya, 2005). A significant portion of the ambient lead concentrations found near The Facility are hypothesized to be related to process fugitive sources and fugitive dust sources. Fugitive emissions sources can be particularly difficult to control due to their sporadic nature and the problems identifying the specific source.

Current lead monitors near The Facility collect 24-hour integrated samples and report over this period. However, continuous multi-metals ambient air monitoring devices can sample from a range of one sample every fifteen minutes to one sample every four hours, and can provide more detailed, high resolution data characterizing the variability in lead concentrations throughout the course of the smelter's daily operations. When analyzed with plant process records and meteorological records, near-real-time data can prove invaluable in determining the specific source of ambient lead.

Due to shifting wind conditions and dynamic smelter operations, ambient metals concentrations can range as much as two to three orders of magnitude within a 24-hour sampling period. Detailed concentration plots derived from NRT monitoring can identify the specific times in which ambient lead concentration is elevated, recording the times in which the largest fraction of potential exceedence occurred. Fence line NRT multi-metals monitoring data, when correlated

with plant records and meteorological data, can provide a detailed account of the contribution to lead concentrations from fugitive emissions, help identify fugitive sources, characterize risks to human health, and assist in developing a successful NAAQS compliance plan.

2.0 Goals: Defining Goals and Compliance

The Facility is currently not in attainment with the National Ambient Air Quality Standard for lead. Local workers and residents in the area surrounding the facility are being exposed to lead concentrations that are potentially dangerous to human health. For this example, a hypothetical Hazardous Ambient Metal Compliance Plan (Plan) to monitor local ambient air near the secondary lead 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 sources and develop engineered controls to problematic fugitive emissions; and 3) to aid in enforcing compliance with applicable standards.

Continuous ambient multi-metals monitoring is the appropriate air monitoring approach at The Facility for a number of reasons:

1) The Facility is out of attainment with a nationwide ambient air standard and previous compliance initiatives have not fully succeeded in reducing ambient lead concentrations to acceptable levels.

2) Near-real-time continuous metals monitoring analyzed with facility records and meteorological data can assist regulators and plant management in source apportionment and help to develop an effective corrective action plan.

2.1.0 Source Emissions Data: Primary Element(s) of Health/Regulatory Concern

Lead is the primary element of health and regulatory concern for risks from ambient air near secondary lead smelters. Numerous studies indicate that stack and fugitive lead emissions are the primary pollution issue associated with secondary lead smelters (EPA,1984). Data from a 1984 EPA study titled *Secondary Lead Smelter Test of Area Source Fugitive Emissions for Arsenic, Cadmium, and Lead* showed that fugitive lead emissions are generally greater than arsenic by two orders of magnitude and cadmium by three orders of magnitude.

2.1.1 Source Emissions Data: Secondary Elements of Concern

Secondary elements of concern include antimony, arsenic, and cadmium. Antimony is a component of automobile batteries as an alloy with lead, and therefore can be detected in secondary lead smelter emissions at significant levels. Arsenic and cadmium are present in trace amounts in lead alloys. Arsenic and cadmium both have well-defined chronic and acute exposure health risks.

2.1.2 Source Apportionment: Identifying fugitive sources

Accurate source apportionment is a critical goal of the Hazardous Ambient Metals Compliance Plan. Source apportionment can be analyzed from four basic approaches: 1) particle size; 2) plant activity/time; 3) chemistry; 4) and wind direction and speed.

1) Particle size is a helpful source identifier, as specific size fractions are generally associated with unique operations and processes at the secondary lead smelter. For instance the lead $PM_{2.5}$ (2.5 µg or less) size fraction is generally associated with high-heat smeltering processes. Ambient air samples high in the lead $PM_{2.5}$ fraction will therefore be primarily derived from the melting and refining of the lead, and a successful fugitive emissions corrective action plan should focus on related engineered controls. Larger size fraction samples can be associated with fugitive dust and mechanical smeltering operations such as the storage and processing of raw materials, and corrective action will necessarily address those sources. As the fugitive emissions study proceeds at The Facility, the PM inlet of the ambient metals monitor can be altered as necessary to achieve Plan goals.
2) Plant activity and operations observations are helpful in determining the source of fugitive lead emissions. Near-real-time data, coupled with direct observations and facility records can be utilized to relate elevated concentrations in ambient monitors with specific smelter operations or practices.
3) The chemistry of each sample may also associate an elevated concentration with a specific secondary smelter source. For example, concentrations high in antimony and cadmium can be linked to high heat smeltering operations, as the trace metals and alloys within the ore are released during heating. Alternately, a broad metals fingerprint in a sample may indicate a fugitive dust source.
4) Wind speed and direction can also be utilized to develop simple contaminant transport models and associate high lead concentrations with specific smelter locations.

Near-real-time multi-metals monitors are especially designed for fugitive emissions monitoring, and have unique capabilities that can assist in fugitive source identification.

2.2 Regulatory Standards

The federal Clean Air Act requires the U.S. EPA to establish National Ambient Air Quality Standards for pervasive wide-spread pollutants from diverse sources that are dangerous to human health and the environment. Lead is currently the only metal included in the NAAQS. The NAAQS for lead was updated in 2008 from 1.5µg/m³ to 0.15 µg/m³. Facilities that emit lead in excess of one ton per year are required to monitor points of maximum off-site impact and are given three to five years to comply with the new standard. Specific non-attainment areas surrounding a facility are calculated based off of permitted facility emissions, dispersion models and receptor models. If the facility is not in attainment with NAAQS standards, a state

implementation plan must be developed and implemented within a given time frame to control stack and fugitive emissions and achieve compliance. **Figure 3** illustrates nation-wide areas not in attainment with the new lead NAAQS as of June, 2010.

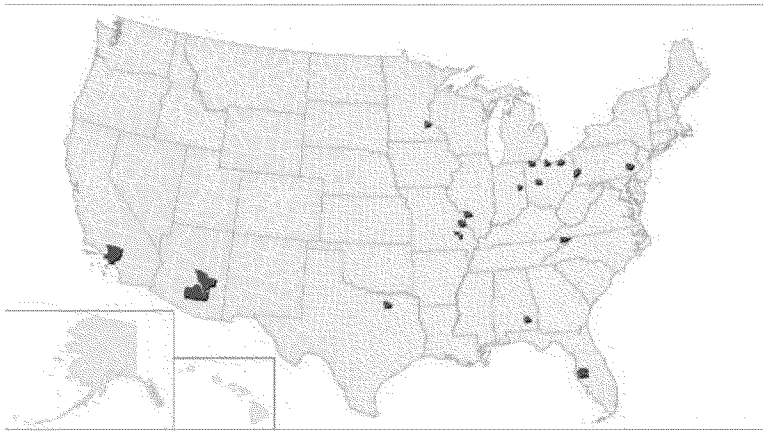

Figure 3. Nation-wide non-attainment areas for lead NAAQS

2.3 Health Effects Data

Health risk to humans from lead exposure is one of the most widely researched topics in environmental and public health. Chronic lead poisoning damages a variety of the body's systems. Common chronic exposure symptoms include a loss of short term memory, depression, nausea, abdominal pain, loss of coordination, and tingling in the extremities. Fatigue, headaches, torpor, slurred speech and sleep disorders may also be present. In children, lead exposure may have more pronounced, immediate health impacts, and include lower IQ, developmental disorders and behavior disorders such as increased aggression. Recent scientific studies strongly suggest that no blood level of lead is safe for humans. However, the normal range is considered to be < 5 µg/dl. A 1996 study of children living near The Facility showed blood lead levels higher than those in the control group, but within the normal range (California DHS, 1996).

Lead is a relatively common environmental pollutant. However, since the phasing out of leaded gasoline in the early 1970s, ambient lead levels in the United States have dropped significantly across the country. The majority of lead emissions and ambient lead exposure today is associated with coal and oil combustion, waste incineration, metals recycling, smelters, and foundries.

2.4 Demonstrating Compliance

The national TSP lead NAAQS set at 0.15 µg/m³ is for a rolling three month average period. However, California's Air Quality Management District has established a stricter, one month

average standard for ambient lead concentrations at The Facility, and is proposing a rule that The Facility be in compliance by January 2012.

Nationwide lead monitoring stations to demonstrate compliance with the lead NAAQS are either non-source oriented or source oriented. Source-oriented ambient metals samplers are located near facilities like The Facility which emit greater than one ton of lead per year. Monitors are located at or near the fence line of the facility in areas of maximum impact to assess compliance with the new standard. **Table 1** details recent lead data from The Facility.

Table 1. July 2010, average lead concentration in µg/m³ in local ambient monitors. See Figure 9 for locations.

NAAQS	Mid East Site	SW Site	New NE Site	New N site	Mid Site
0.15	0.34	0.13	0.64	0.76	0.27

Compliance at The Facility is based upon monthly averages of lead data emerging from the EPA approved Total Suspended Particulate lead monitors on site. The data is compared to the lead NAAQS to determine if the airshed is in attainment with federal and state ambient air standards. If current ambient lead concentrations at the secondary lead smelter persist, The Facility will not be in attainment when the new standard goes into effect in 2012.

While The Facility has implemented some emissions controls, and lead concentrations in specific monitors show declining levels, further corrective action is necessary to reduce ambient lead concentrations to acceptable levels. Fugitive emissions of lead, which generally are comparable to stack emissions in concentration and volume, can be difficult to identify and control. Multi-metals continuous ambient air monitors will help to identify sources and develop engineered controls to reduce problematic fugitive emissions at The Facility.

2.4.1 Lead NAAQS Compliance Plan

In this hypothetical example, a multi-metals continuous monitor will be deployed at The Facility and data will be collected at the initial location for a period of six months. The monitor will: 1) further characterize areas that are not in compliance with the NAAQS; 2) determine the specific times in which the majority of lead emissions occur; and 3) provide a basic source apportionment identifying problematic lead sources.

After the initial six month monitoring period, a corrective action plan will be developed by regulators and The Facility designed to limit process fugitive and lead dust fugitive emissions to acceptable standards.

Figure 4 illustrates the goals of the Lead NAAQS Compliance Plan (Compliance Plan). The long-term goals of the Compliance Plan will be contingent upon successful control on stack, process fugitive and fugitive dust emissions. Successful implementation of the Compliance

Plan will reduce lead concentrations near The Facility to levels below the lead NAAQS. Long-term goals are to lower ambient lead concentrations to near background levels, or less than 0.05 µg/m³, over the following decade.

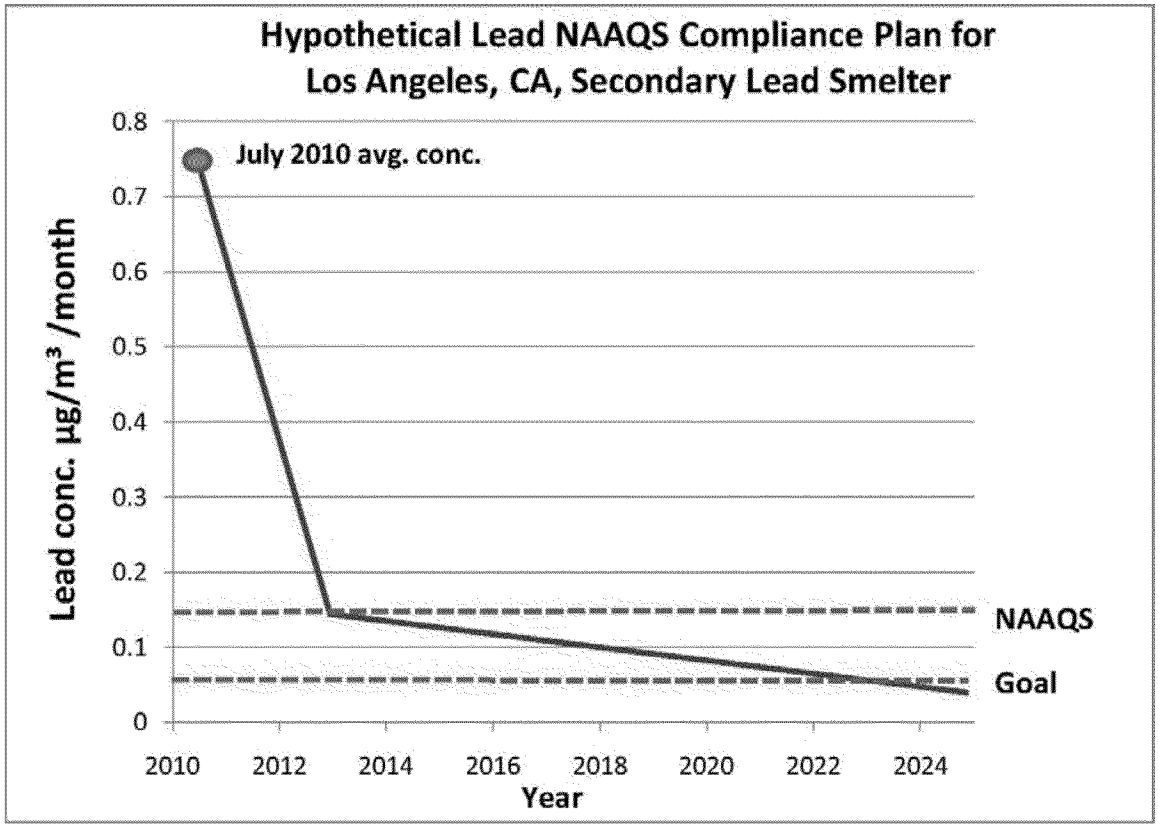

Figure 4. NAAQS Compliance Plan for Secondary Lead Smelter

3.0 Local Airshed Characteristics

3.1 Meteorological Characteristics

The Facility is located in the greater Los Angeles metropolitan area in southern California, U.S.A. and is less than five miles from downtown Los Angeles. The climate of the Los Angeles area is categorized as Sub-Tropical Mediterranean, with warm to hot, dry summers and mild to cool, wet winters. The average yearly temperature is 66° F. The region is relatively dry and receives an average of 35 days of measurable precipitation per year, with total precipitation averaging around 15 inches, occurring primarily between winter and spring.

The Facility lies at about 230 feet above mean sea level in what is known as the Los Angeles Basin. The basin is bounded to the north by the Santa Monica Mountains and to the east and south by the Santa Ana Mountains. The Los Angeles area is well-known for its air pollution problems associated with the basin geography of the region, atmospheric inversion, a significant industrial sector, and a large population heavily reliant upon automobile transportation.

Relatively low annual rainfall also adds to air particulate issues, as rainfall clears smog. While air pollution problems are improving, in 2007 and 2008 the American Lung Association ranked Los Angeles as the most polluted city in the country with elevated levels of short-term and annual air particulate pollution. **Figure 5** shows the location of the secondary lead smelter, and downtown Los Angeles, CA.

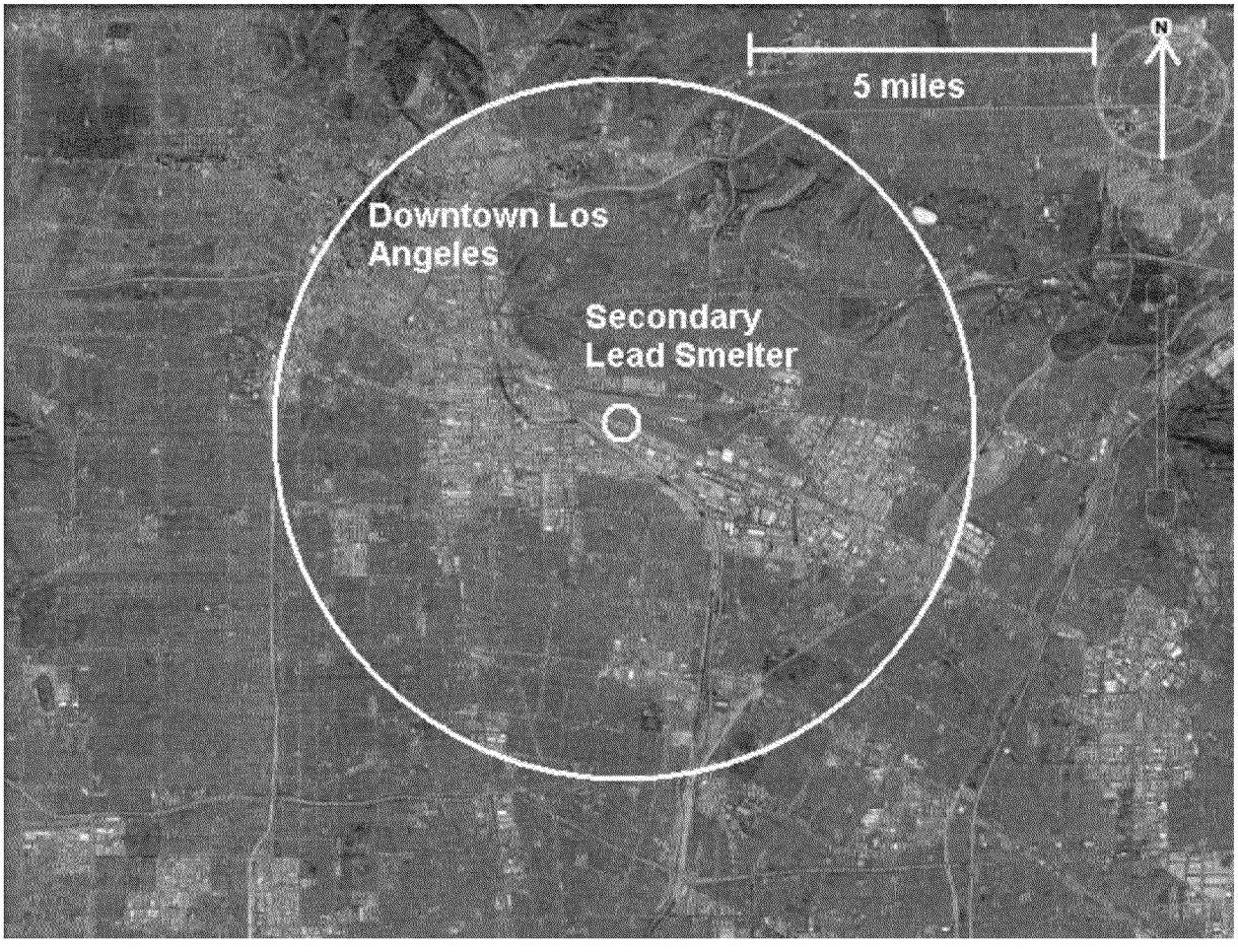

Figure 5. The Facility, secondary lead smelter near downtown Los Angeles.

Typical wind directions in Los Angeles are primarily from the west and west-south-west and average around eight miles per hour. **Figure 6** illustrates average wind speed and direction conditions in the Los Angeles region, averaged over a four year period.

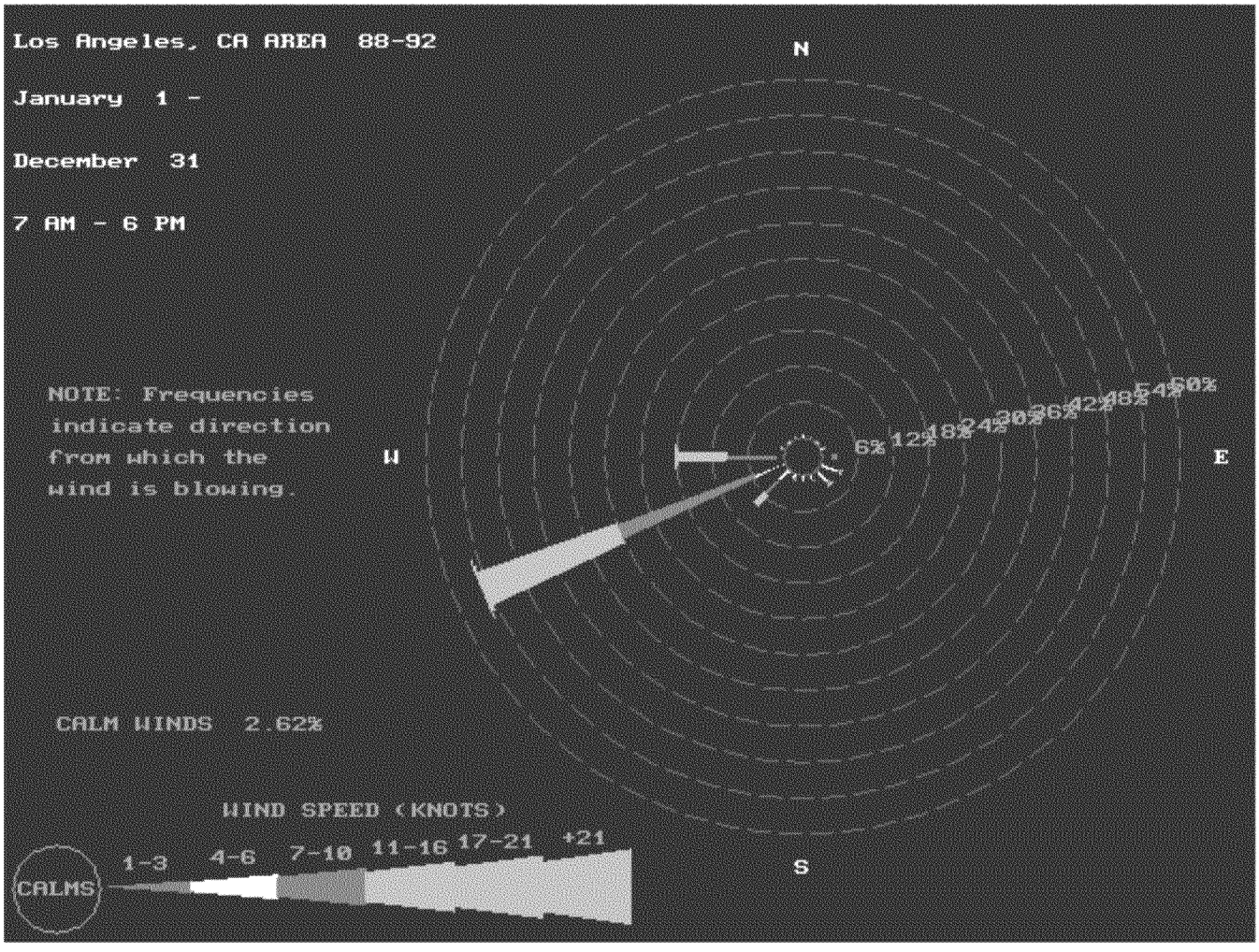

Figure 6. Average Annual Wind Rose for Los Angeles, CA, 1988 – 1992. 1 knot = 1.15 mph

3.2.1 Source Characteristics –Secondary Lead Smelter Maps

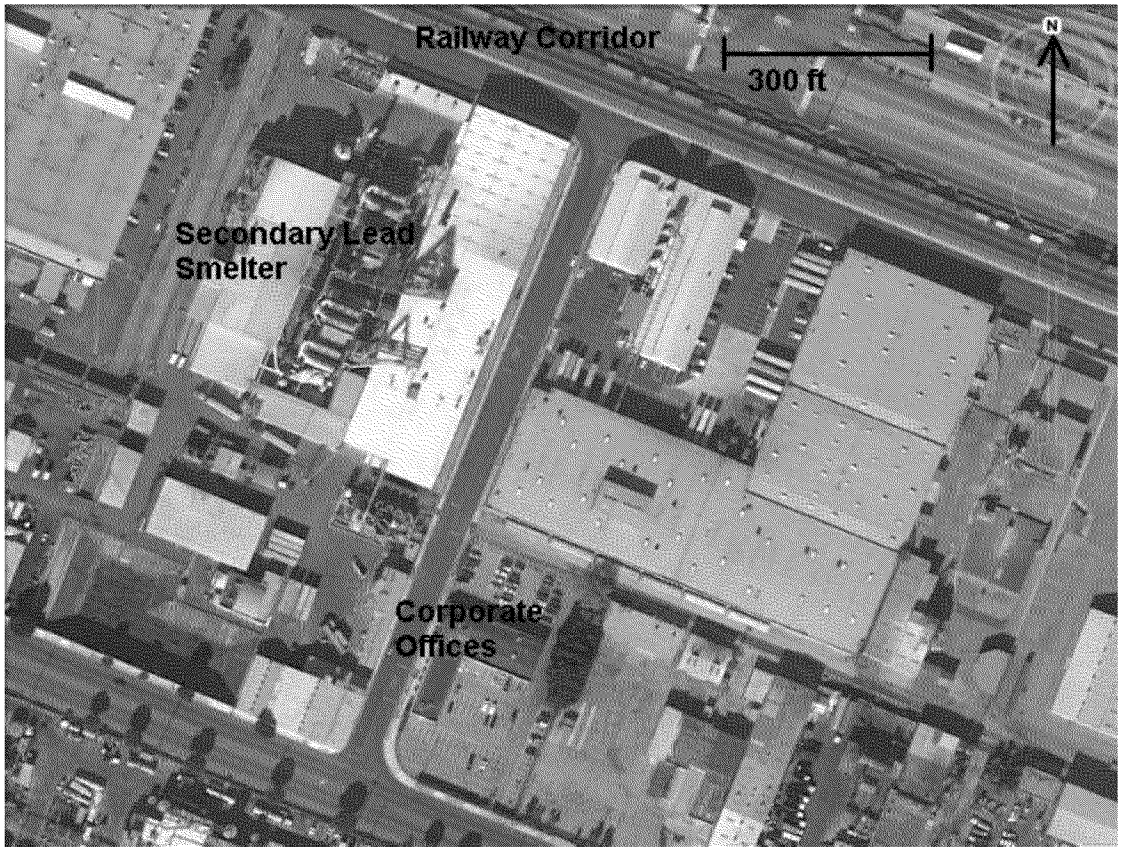

Figure 7. Secondary Lead Smelter Facility Arial Map

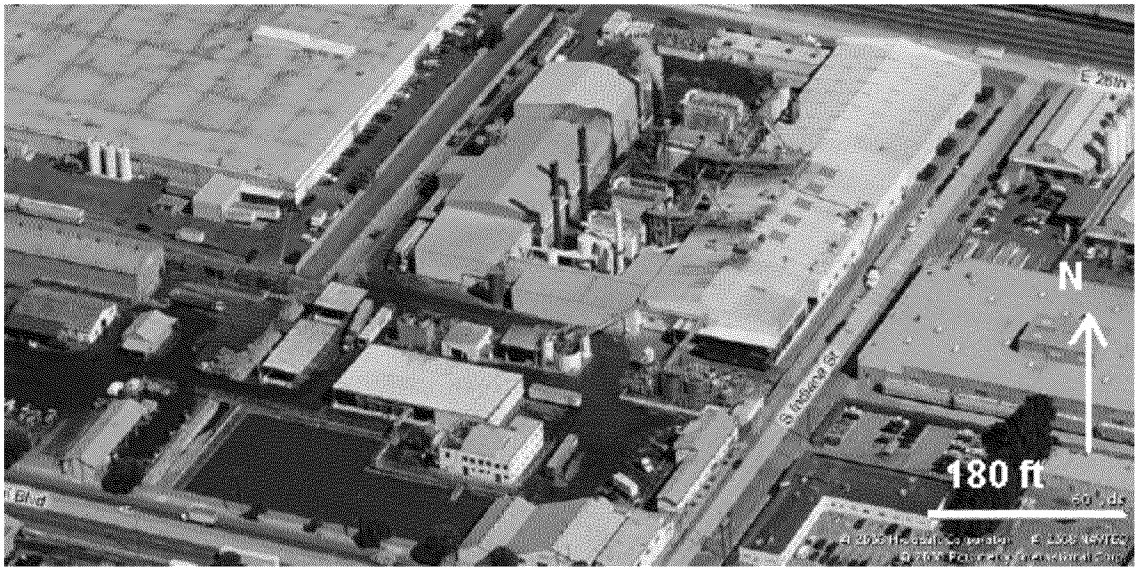

Figure 8. Secondary Lead Smelter Facility Map

3.2.2 Source Characteristics

Lead emissions at secondary lead smelters occur from process sources, process fugitive sources or from lead dust fugitive sources. Process sources include stack emissions from the blast furnace and the reverberatory furnace. The smoke and fumes from the furnace are collected and vented. A baghouse or wet scrubber is installed to reduce lead emissions from the stack. Wet electrostatic precipitators and regenerative thermal oxidizers have also been shown to be effective means to reduce lead stack emissions. The main emission stacks at the secondary lead smelters are around 100 feet or less. **Figure 7** and **Figure 8** depict the secondary lead smelter lead-acid battery recycler in Los Angeles, California.

Total ambient lead concentrations from process fugitive and fugitive dust sources are generally comparable to contributions from stack emissions, especially in facilities with modern stack pollution control technology (EPA, 1984). Process fugitive sources at a secondary lead smelter include the smelting furnace and dryer charging hoppers, smelting furnace lead taps and molds during tapping, as well as refining kettles, dryer transition pieces; and agglomerating furnace product taps. Lead dust fugitive sources include toxic dust from roadways, storage piles, materials handling transfer points, transport areas, storage areas, process areas, and buildings.

Fugitive lead emissions can occur throughout the standard operations of the facility and the smelting process. A study by the U.S. EPA published in March, 1984, entitled Secondary Lead Smelter Test of Area Source Fugitive Emissions for Arsenic, Cadmium, and Lead, found that the majority of fugitive emissions occur from the facility roadway, however if the roadway was kept watered, emissions dropped from 82 grams/hour to 12 grams/hour. The study determined that the second largest source of fugitive lead particulate was the smelting process itself, such as the reverberatory and blast furnace, the dryer charging hoppers, refining kettles, and the lead taps and molds. During charging, tapping, and other furnace procedures, lead particulate matter and fumes escape the hoods and vents that serve as air pollution collection and control devices. The study recorded fugitive lead emissions from the smelting building at 80 grams/hour. The slag dross storage, battery breaking area, and the raw materials storage area, were also relatively large sources of fugitive emissions at the study area. See **Table 2.**

Table 2. 1984 EPA Study of fugitive lead emission rates at a secondary lead smelter

	Smelter Bldg.	**Road (dry)**	**Road (wet)**	**Raw Materials Storage**	**Slag/Dross Storage**	**Battery Breaking Area**
Pb Emission Rate Avg. (range) g/hr	80 (32 -160)	82 (8.3-210)	12 (3.6-19)	67 (12-240)	30 (12-56)	13 (9.3-16)

Ambient lead particle size can be categorized in three ranges; the nuclei mode (<0.1 µm); the accumulation mode (0.1 – 2 µm); and the large particle mode (>2 µm). Urban atmospheric lead is primarily found in the accumulation mode size range, at about 0.2 to 0.3 µm. However, the proximity of the secondary lead smelter source to the air monitor will affect sample particle size. Combustion and smelting releases sub-micron size lead particulate. Lead particles emitted during the smelting process will be significantly smaller (< 1 µm) than lead particles released due to mechanical processes at the site (> 2µm), and can be utilized for source apportionment of the facility's lead emissions.

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 lead concentration data in order to fully characterize potential facility sources. Local meteorological wind and precipitation data will be necessary to characterize potential contaminant transport in the area and will be used in close conjunction with the continuous ambient lead data to analyze potential emissions sources.

4.1.2 Elements, PM and Sampling Frequency

The ambient air FLM devices will monitor for the primary and secondary elements of health and regulatory concern, as well as accompanying metals.

Primary Elements of Health and Regulatory Concern: lead (Pb)

Secondary Elements of Health and Regulatory Concern: cadmium (Cd), arsenic (As), and antimony (Sb)

Accompanying metals: chromium (Cr), copper (Cu), zinc (Zn), silver (Ag), manganese (Mn), selenium (Se) calcium (Ca), scandium (Sc), titanium (Ti), vanadium (V), iron (Fe), cobalt (Co), nickel (Ni), bromine (Br), tin (Sn), and mercury (Hg)

The ambient air metals FLM devices can be fit with TSP, PM_{10}, and $PM_{2.5}$ inlets to limit particle size. A PM_{10} inlet will be the primary inlet utilized by the study in order to measure the full range of coarse and fine particulate fraction of ambient metals near the secondary lead smelter. The $PM_{2.5}$ inlet would be utilized, if necessary, for source apportionment studies.

4.1.3 Plant Processes and Events

Secondary lead smelter operations and processes will be monitored along with ambient lead concentration and meteorology. **Table 2** details the range of emission rates previously recorded from specific fugitive sources at secondary lead smelters. It is highly probable that elevated lead concentrations can be associated with specific smelter events and operations. Detailed

records of secondary lead smelter operations, analyzed with emerging real-time lead data, will provide a comprehensive set of information to identify and reduce fugitive emissions.

4.2 Monitoring Sites

The multi-metals ambient air monitoring device will be located utilizing established site guidelines for siting ambient lead monitors around stationary sources (EPA,1997). The Hazardous Ambient Metal Compliance Plan (Plan) will use existing lead sampling sites established by California's AQMD and The Facility. For this example, four sampling sites for the continuous multi-metals ambient air sampling device have been established and a rotating monitoring plan will be discussed and developed. See **Figure 9** for sampling locations.

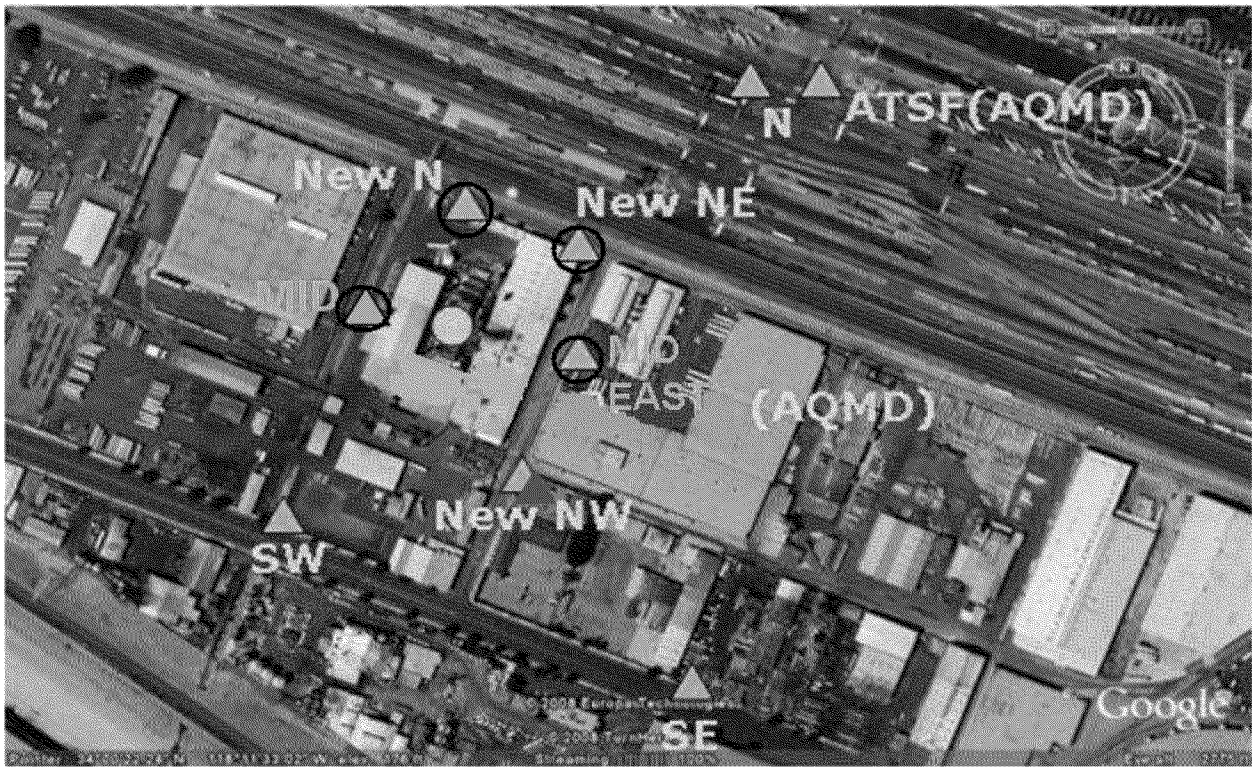

Figure 9. California AQMD and Facility sampling locations. Continuous multi-metals monitoring site in the Hazardous Ambient Metals Compliance Plan are circled.

Based off of recent lead data (**see Table 1**), The New North, Northeast, Mid, and Mid East ambient lead sampling locations are all currently detecting lead in concentrations that exceed the NAAQS. Continuous hourly lead data from these sites will characterize the quantity of the lead emissions, provide data on the specific times in which the majority of lead emissions occur, and aid in fugitive source identification.

4.3 Monitoring Plan

Initially, the continuous multi-metals ambient air sampling device will be located at the NEW N sampling location. This site consistently has the highest ambient lead concentrations, and is the optimal location to study fugitive emissions at The Facility and develop controls. After six months of sampling in which corrective action and fugitive mitigation plans should be developed and applied, the monitor will be re-located to the New Northeast site, followed by the Mid East and Mid sites. However, successful mitigation of lead concentrations at the New N site will reduce over-all lead concentrations, and therefore should be the focus of the fugitive emissions Plan. If an extended sampling period is determined to be necessary to characterize lead emissions and identify sources, then the continuous multi-metals ambient air sampling device would be semi-permanently stationed at the problematic sampling location. As the study progresses, source identification proceeds, and corrective action controls are applied, the continuous multi-metals ambient sampling device may be relocated to the other sampling locales, depending upon the greatest lead impact.

While the sample analysis technology and method of X-Ray fluorescence utilized by the real-time multi-metals sampling devices is mainstream and EPA approved, it is not currently approved for total suspended particulate matter (TSP), which is the required parameter for the lead NAAQS. However the monitor can be fit with a TSP inlet if necessary for correlative data gathering, and can be used in conjunction with local TSP lead monitors to further regulatory goals.

4.3.1 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 sampling once every four hours. Higher time resolution provides more information to regulators and the secondary lead smelter managers to assess and protect worker and public health, and to more fully characterize smelter operations on emissions.

Air samples are collected on a tape medium that is relatively expensive. In this case, where ambient fugitive lead emissions may vary substantially throughout the day, the multi-metals ambient air sampling device will initially be programmed to sample every hour. After a month of ambient air sampling, data can be analyzed to determine how hourly lead data compares to daily averaged lead data. If continuous ambient lead monitoring is prolonged at The Facility, the data can be examined to assess if a decrease in sampling frequency would reduce costs without adversely impacting the source apportionment and other data goals of the project.

Data can be available within two hours of sampling event, streamed via wireless or cabled connection to regulators and smelter managers, 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 by regulators or plant technicians.

The multi-metals continuous ambient air monitors will be protected from weather conditions with a shelter and rain guard. A TSP, PM_{10} or $PM_{2.5}$ inlet will direct size selected particulate to the sampler, and electrical lines and data acquisition cables will run from the shelter to the nearest phone/internet connection.

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 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

The Facility is currently not in attainment with the 2008 lead National Ambient Air Quality Standard. The Facility has five 5 years to achieve attainment status. However, the California AQMD has developed more stringent requirements in Proposed Rule 1420, which requires The Facility to be in attainment by January 2012, submit a compliance plan if ambient air lead concentrations exceed 0.12 $\mu g/m^3$ averaged over a one month period, and implement various other engineered controls to reduce ambient lead emissions.

This hypothetical example utilizes continuous multi-metals ambient air sampling devices as another tool for regulators and Facility operators to achieve compliance with the lead NAAQS. Regulators could potentially recommend the sampling device to the secondary lead smelter as part of a compliance plan, or The Facility itself may want to initiate hourly sampling as a way to achieve compliance. Regardless, the California AQMD will regulate the emissions of The Facility based upon existing rules and regulations including the NAAQS and Proposed Rule 1420.

4.4.3 Plant

Near real-time data emerging from the ambient metals-air monitoring system will be available to The Facility in order to adequately characterize emissions and develop more effective emissions controls.

4.4.4 Internet and Public

Regulators will maintain a public internet location that details appropriate rules and regulations, outlines the ambient lead goals, shows the data emerging from the monitoring location(s), and provides a venue for regulators to answer any questions that the public or industry may have over the monitoring program and attainment with the lead NAAQS. Data on the site will be updated daily to ensure quality assurance of the reported values.

5.0 References

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APPENDIX E

Example Application: Primary Lead Smelter

DRAFT

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

MACTEC Work Order No.: 20081752
MACTEC Project No.: 827008S407

Submitted To:
MACTEC Federal Programs
Research Triangle Park, NC

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Portland, OR

December 9, 2010

Summary

This example describes how the Guide for Developing a Multi-Metals, Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors (Guide) can be applied to develop a fugitive emissions characterization and monitoring plan for a primary lead smelter. Primary lead smelters are large industrial facilities that process ore into lead metal. Hazardous air pollutants (HAP) associated with primary lead smelters include lead, arsenic, and cadmium. Ambient lead pollution is a national concern, and lead is the only metal listed in the National Ambient Air Quality Standards (NAAQS) promulgated by the United States Environmental Protection Agency (U.S. EPA). Lead is a potent neurotoxin, with many documented health effects from exposure including mental impairment in adults and significant developmental disabilities in children. In 2008 the lead NAAQS was reduced from 1.5 μg/m³ to 0.15 μg/m³, which reflected the growing scientific understanding that no blood level of lead is safe for humans.

While ambient levels have fallen dramatically since the phase out of leaded gasoline in the early 1970s, there are still numerous locations in the United States out of attainment with the 2008 lead NAAQS. Most of the areas out of attainment are located near metals fabrication facilities, primary lead smelters and secondary lead smelters. The ambient lead NAAQS functions as a regulatory control as it compels states and facilities to lower lead emissions in order to reach attainment with the national standard.

Fugitive emissions at primary lead smelters are a major contributing source to ambient lead concentrations and NAAQS exceedances. Near-real-time (NRT) lead data from a primary smelter near Herculaneum, Missouri, indicates that a relatively small percentage of monthly samples often contribute a majority of the total monthly Pb mass. Ambient NRT multi-metals monitors can be utilized to identify and apportion fugitive sources and serve as an early lead release warning system to regulators, plant operators and the public, who can then take action to mitigate the lead emissions.

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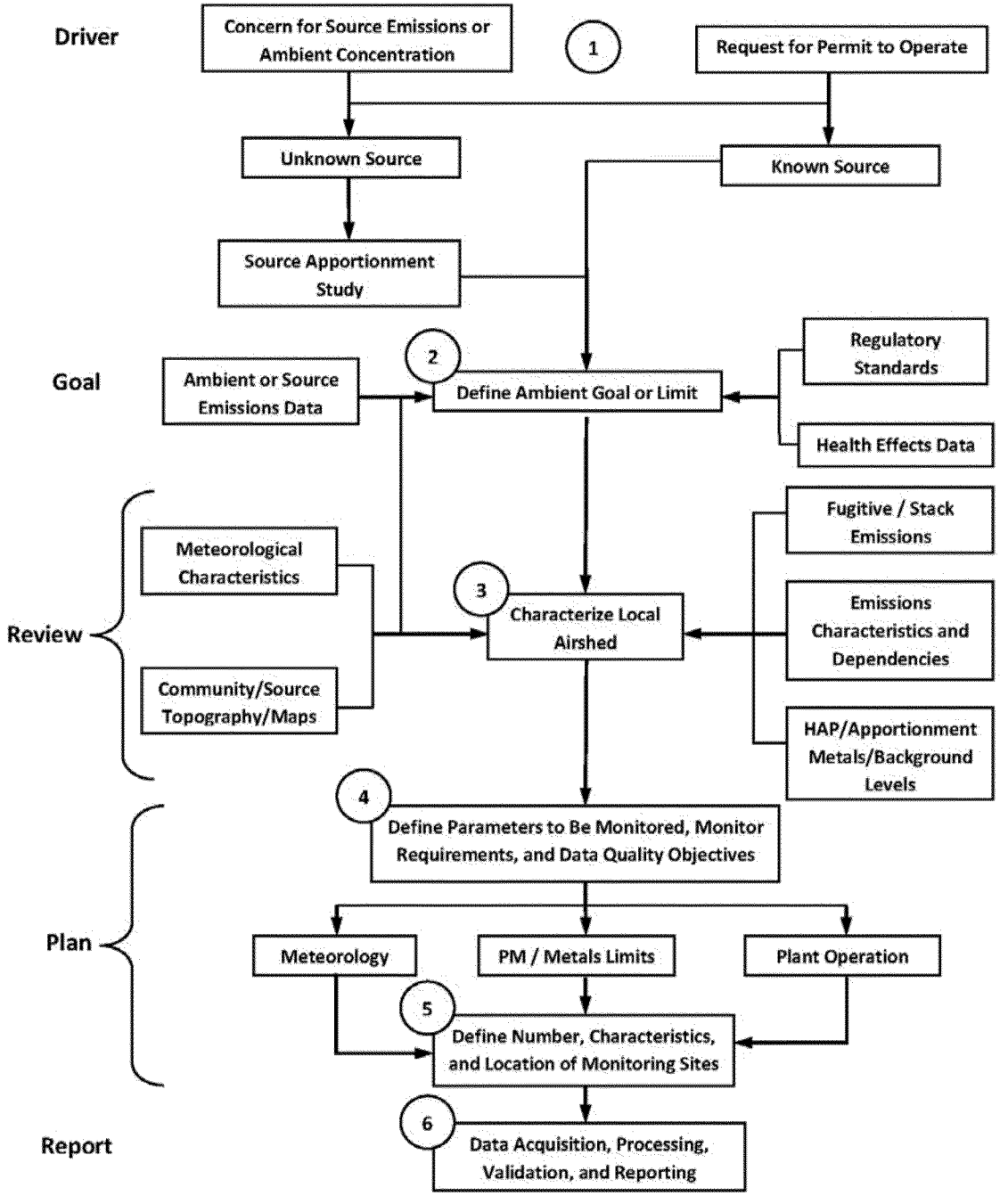

Figure 1. Procedure Flow Diagram

1.0 Driver – Ambient Lead Measurements above NAAQS from Fugitive Source

For this hypothetical example, the Guide procedure will be applied to establish a Fugitive Emissions Hazardous Ambient Metals Compliance Plan for a primary lead smelter (The Facility) in Herculaneum, Missouri. Herculaneum, Missouri, is located approximately 25 miles south of St. Louis on the Mississippi River. The Facility is adjacent to the river, with residential neighborhoods to the north, south, and east. Lead smelting operations and other metals refining have been occurring at the site since as far back as 1892. The primary lead smelter is currently the only active primary lead smelter in the United States and at 52 acres is one of the largest smelters currently in operation globally with an annual production capacity of nearly 250,000 tons of lead.

Lead smelters process lead-rich ore into metallurgical lead using three major steps; sintering, reduction and refining. The process initiates as sulfur and lead-rich minerals such as galena, sphalerite, and chalcopyrite present in carbonate rocks are transported to the smelter via rail car, truck or river barge. After initial sorting of the lead ore, it is fed to the sinter where it is mixed with undersized recycled sinter material, high-lead content sludge, lime rock, and silica. The primary purpose of the sintering process is the reduction of the sulfur content of the feed material. After sintering the material is conveyed to a blast furnace in charge cars with coke, ores, slag, and baghouse dusts for further reduction. The lead-rich ore and charge turns molten in the blast furnace, which allows for the separation of lead from slag. Slag and molten lead differentiate in the furnace and are tapped continuously. The slag cools and is stored or reprocessed and the lead is discharged into refining kettles. After further refining, which involves the removal of trace metals and remaining sulfur, a 99 .99 % pure lead metal is produced, which is then cast into 100 lb pigs for shipment.

Lead metal is the primary hazardous ambient pollutant of concern, but arsenic and cadmium can also be an issue. Lead emissions are associated with a wide variety of smelter processes and can occur as process emissions from the stacks or as fugitive emissions. Fugitive emission sources include dust from the ore crushing load area and other dust or slag storage areas, emission leaks from the sinter and the sinter building, fugitive leaks from the blast furnace, fugitive leaks from tapping the refining kettles and settlers, road dust, and various pouring, skimming, cooling and tapping operations in the dross building.

The facility has been out of compliance with the lead NAAQS since at least 1986. Numerous state implementation plans have been developed since then, but have not had success in lowering ambient lead concentrations near the facility to applicable standards. The U.S. EPA states that the majority of lead emissions from The Facility that contribute to elevated ambient lead concentrations exceeding the NAAQS are fugitive in nature. The facility has attempted to curtail fugitive emissions with various controls on site, including additional site enclosures, improved hood ventilation systems routing to stacks, and installation of pollution control equipment such as baghouses. However The Facility continues to have difficulty achieving the ambient NAAQS.

The lead NAAQS standard was revised in 2008 to 0.15 µg/m³/3 month rolling average, and the facility is currently out of attainment with the new standard. Stricter ambient standards reflect new scientific understanding of the health risks associated with exposure to lead. Recent studies suggest that there is no level of lead in blood that is safe for humans. Well-documented health effects include lower IQ, weakened memory, and learning disabilities in children, and cardiovascular problems, kidney problems and higher blood pressure in adults.

1.1 Fugitive Emissions Daily Variability and Real-Time Multi-Metals Monitoring

Primary lead smelters utilize wet scrubbers and baghouses to control lead concentrations in stack emissions. However the U.S. EPA has noted that a significant portion of lead emissions that contribute to the NAAQS exceedence at the Herculaneum facility are related to fugitive emissions. A source apportionment conducted in 2000 by Cooper Environmental Services reported that 96% of ambient lead concentrations in Herculaneum air monitors were from fugitive sources (CES, 2000). Fugitive emissions sources can be particularly difficult to identify and control because; 1) emissions are often related to a specific plant process and therefore occur sporadically throughout the course of a facility's daily operations; and 2) fugitive emissions control technologies are difficult to apply effectively because of the broad source footprint.

Continuous multi-metals ambient air monitoring devices are much more effective than 24-hour average ambient lead samplers in characterizing fugitive lead emissions and identifying potential sources. Continuous multi-metals ambient air monitoring devices can sample from a range of one sample every fifteen minutes to one sample every 4 hours, and therefore can provide more detailed, high resolution data characterizing the variability in lead concentrations throughout the course of the smelter's work day operations.

Figure 2, derived from 24-hour continuous ambient lead sampling data at the primary lead smelter in Herculaneum, Missouri, illustrates the orders of magnitude variability in ambient lead concentrations throughout the course of a the day. Examining the data, lead concentration at the monitor can be confidently identified with a specific smelter action or facility operation, as lead concentrations spike and wind direction remains steady. Detailed concentration plots such as this derived from real-time monitoring can identify the specific times in which ambient lead concentration is elevated, and record the times in which the largest fraction of lead release occurred. Regulators and plant operators can then compare near-real-time lead data to facility records and direct observation to identify a source and develop and implement a corrective action.

Figure 3 details how a small number of high concentration fugitive lead emission episodes can contribute the majority of PM_{10} lead in a given month. The data suggests that if the major lead release episodes can be mitigated and controlled, a facility such as the primary lead smelter in Herculaneum would be much closer to attainment with the lead NAAQS.

Near-real-time continuous multi-metals monitoring data, analyzed with plant records and meteorological data, can provide a detailed account of the contribution to lead concentrations

from fugitive emissions, help identify fugitive sources, characterize risks to human health, and assist in developing a successful NAAQS compliance plan. A well-designed NRT lead TSP monitoring system also can provide an early warning to plant operators and regulators if lead emissions begin to approach levels that would threaten the NAAQS standard.

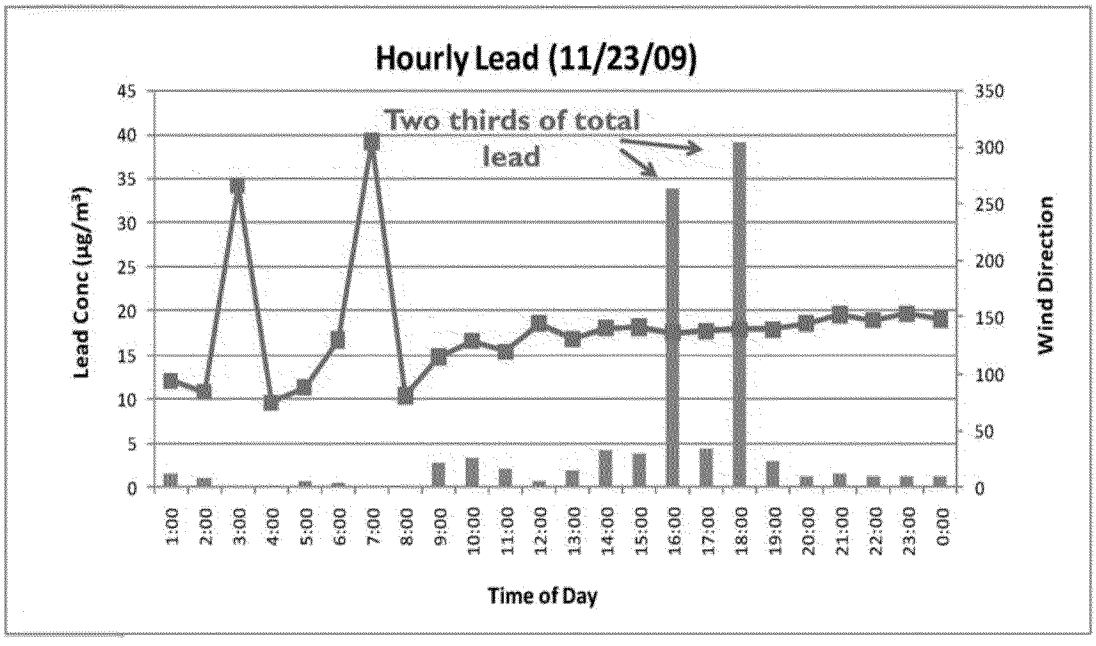

Figure 2. 24-hour Lead conc. in ambient monitor with stable wind conditions.

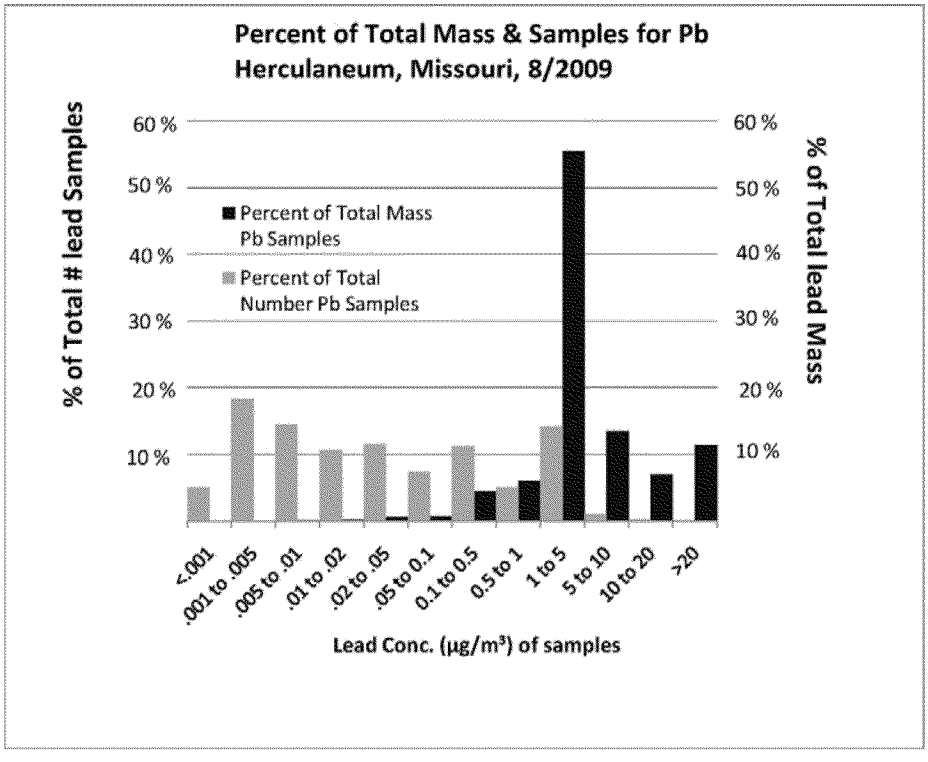

Figure 3. Percent contribution comparison of total lead

2.0 Goals: Defining Goals and Compliance

The Facility is currently not in attainment with the National Ambient Air Quality Standard for lead. Local workers and residents in the area surrounding the facility are being exposed to lead concentrations that pose significant risk to human health. For this example, a hypothetical Hazardous Ambient Metal Compliance Plan (Plan) to monitor local ambient air near the primary lead 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) aid in, and enforce compliance with applicable standards.

Continuous ambient multi-metals monitoring is the appropriate air monitoring approach at the primary lead smelter for a number of reasons:

1) The Facility is out of attainment with the lead NAAQS and previous compliance initiatives have not fully succeeded in reducing ambient lead concentrations to acceptable levels.

2) Real-time continuous metals monitoring analyzed with facility records and meteorological data will assist regulators and The Facility's management in further characterizing the major source(s) of lead contamination and help to develop an effective corrective action plan.

3) Near-real-time data will alert The Facility that a major lead release is occurring and the facility can immediately implement a corrective action.

2.1.0 Source Emissions Data: Primary Element(s) of Health/Regulatory Concern

Lead is the primary element of health and regulatory concern for risks from ambient air near primary lead smelters. Studies show that lead emissions surpass other hazardous air pollutants arsenic, cadmium and mercury by two to four orders of magnitude.

2.1.1 Source Emissions Data: Secondary Elements of Concern

Secondary elements of concern include arsenic, cadmium, and mercury. Arsenic, cadmium, and mercury are present in trace amounts in lead ore. These metals have well-defined chronic and acute exposure health risks.

2.2 Regulatory Standards

Regulation of emissions from primary lead smelters is mandated by the Clean Air Act Title 40 CFR 63, National Emission Standards for Hazardous Air Pollutants, subpart TTT. Lead emissions targets are based upon the quantities of lead produced at the facility. Specifically, the regulations state that no owner or operator of a primary lead smelter facility shall discharge

or cause to be discharged into the atmosphere lead compounds that exceed one (1) pound of lead compounds per one (1) ton of lead produced.

The federal Clean Air Act also requires the U.S. EPA to establish National Ambient Air Quality Standards for pervasive wide-spread pollutants from diverse sources that are dangerous to human health and the environment. Lead is currently the only metal included in the NAAQS. The NAAQS for lead was updated in 2008 from 1.5μg/m³ to 0.15 μg/m³. Facilities that emit lead in excess of 1 ton per year are required to monitor points of maximum off-site impact and are given three to five years to comply with the new standard. For point sources, specific non-attainment areas surrounding a facility are calculated based on permitted facility emissions, dispersion models and receptor models. If the facility is not in attainment with NAAQS, a State Implementation Plan must be developed and implemented within a given time frame to control stack and fugitive emissions and achieve compliance. **Figure 4** illustrates nation-wide areas not in attainment with the new lead NAAQS as of June, 2010.

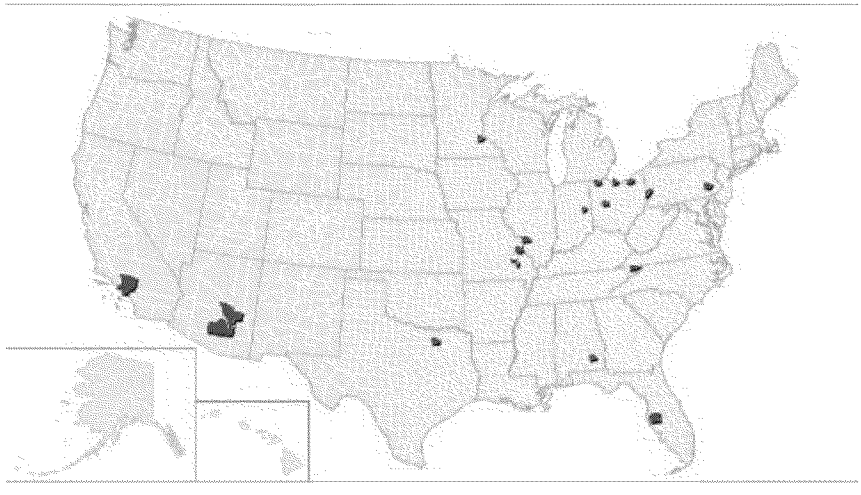

Figure 4. Nation-wide non-attainment areas for lead NAAQS

2.3 Health Effects Data

Health risk to humans from lead exposure is one of the most widely researched topics in environmental and public health. Chronic lead poisoning damages a variety of the body's systems. Common chronic exposure symptoms include a loss of short-term memory, depression, nausea, abdominal pain, loss of coordination, and tingling in the extremities. Fatigue, headaches, torpor, slurred speech and sleep disorders may also be present. In children and fetuses, lead exposure may have more pronounced, immediate health impacts, and include lower IQ, developmental disorders and behavior disorders such as increased aggression. Recent scientific studies strongly suggest that no blood level of lead is safe for humans. However, the normal range is considered to be < 5 μg/dl. A study conducted in 2002

at Herculaneum showed that nearly 28% of children residing in the town had blood lead levels exceeding the federal standard for lead poisoning set at 10 µg/L.

Lead is a relatively common environmental pollutant. However, since the phasing out of leaded gasoline in the early 1970s, ambient lead levels in the United States have dropped significantly across the country. The majority of lead emissions and ambient lead exposure today is associated with coal and oil combustion, waste incineration, metals recycling, smelters, and foundries.

2.4 Demonstrating Compliance

The national lead NAAQS set at 0.15 µg/m³ is for a rolling three (3) month average period. If a state is not in attainment with the new standard, they must submit a State Implementation Plan (SIP) by June, 2013. States are required to develop a SIP that details corrective action measures necessary to achieve attainment with the new standard. States must meet the new NAAQS by January 2017.

Nationwide lead monitoring stations to demonstrate compliance with the lead NAAQS are either non-source oriented or source oriented. Source-oriented ambient metals samplers are located near facilities like the primary lead smelter which emit greater than one (1) ton of lead per year. Monitors are located at or near the fence line of the facility in areas of maximum impact to assess compliance with the new standard. Lead NAAQS compliance monitors measure for total suspended particulate (TSP) lead.

While The Facility has implemented some emissions controls, and lead concentrations at specific monitors show declining levels, further corrective action is necessary to reduce ambient lead concentrations to acceptable levels. Fugitive emissions of lead, which in some cases are comparable to stack emissions in concentration and volume, can be difficult to identify and control. Multi-metals continuous ambient air monitors will help to identify sources and develop engineered controls to reduce problematic fugitive emissions at the facility. As stated previously, the monitors will provide early warning of excessive lead emissions to regulators and plant operators to help achieve attainment with the lead NAAQS.

Compliance at the facility will be based upon monthly averages of lead data emerging from the EPA approved TSP lead monitors on site. The data will be compared to the lead NAAQS to determine if the airshed is in attainment with federal and state ambient air standards. After the NRT multi-metals monitoring and corrective action ensue, consistent, statistically significant reductions in ambient lead concentration will indicate that the Plan is achieving the stated goals.

2.4.1 Lead NAAQS Compliance Plan

A multi-metals NRT ambient air monitor will be deployed around The Facility and data will be collected for a period of 2 years. The monitor will: 1) further characterize areas that are not in compliance with the NAAQS; 2) determine the specific times in which the majority of lead

emissions occur; 3) provide a basic source apportionment identifying problematic lead sources; 4) alert regulators and smelter operators of near-real-time lead emission spikes. During the monitoring period, a corrective action plan will be developed by regulators and The Facility designed to limit process fugitive and lead dust fugitive emissions to acceptable standards.

Figure 4 illustrates the goals of the Lead NAAQS Compliance Plan (Compliance Plan). The long term goals of the Compliance Plan will be contingent upon successful control on stack, process fugitive and fugitive dust emissions. Successful implementation of the Compliance Plan will reduce lead concentrations near Herculaneum to levels below the lead NAAQS. Long term goals will lower ambient lead concentrations to near background levels, or less than 0.05 µg/m³.

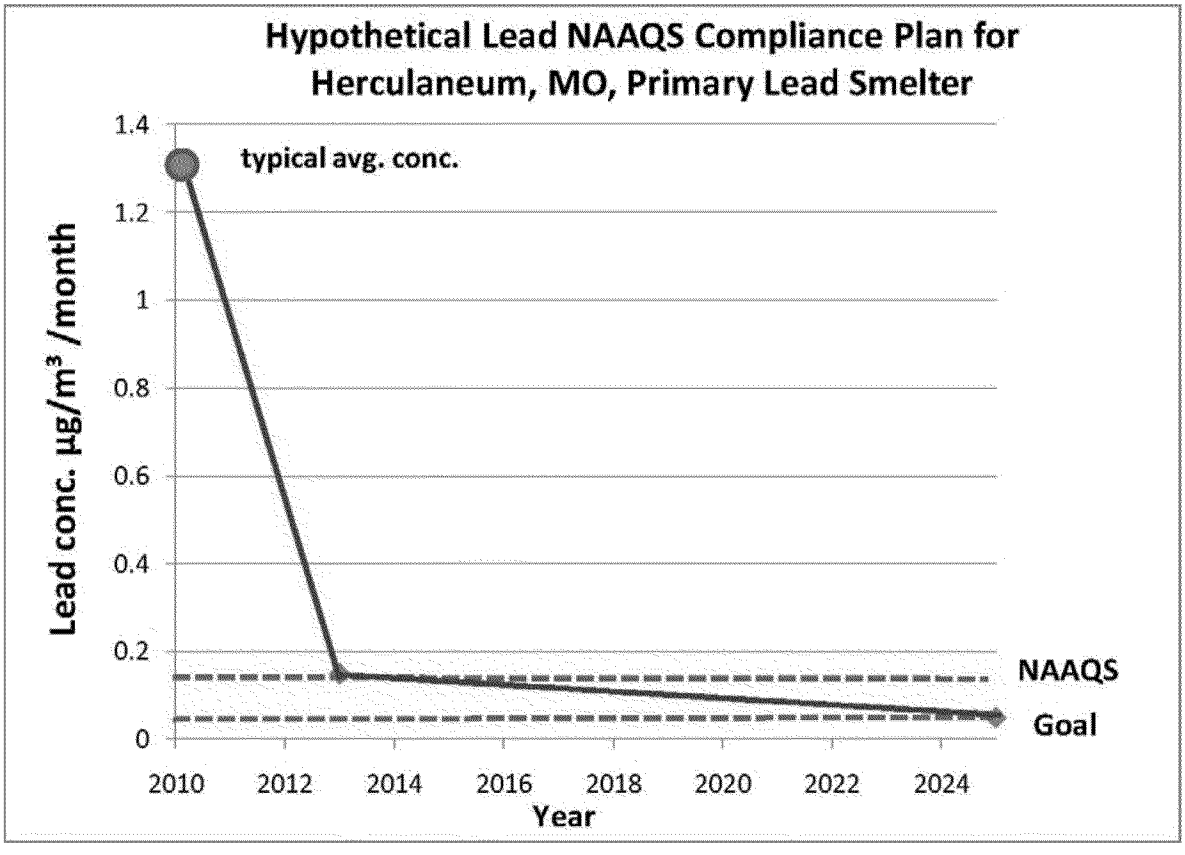

Figure 5. Hypothetical Lead NAAQS Compliance Plan for Herculaneum, MO

3.0 Local Airshed Characteristics

3.1 Meteorological Characteristics

The climate of Herculaneum, Missouri, is qualified as humid continental, with both humid, tropical air from the Gulf of Mexico as well as cold arctic air influencing weather patterns and temperatures. The zone has four distinct seasons, with an average temperature (taken in nearby St. Louis, MO) of 13.5 °C (56.3 °F). The normal high occurs in July at 90 °F, and the

normal low is in January at 21 °F. The average annual precipitation is 38.9 inches, with rainfall typically year round and the majority occurring in the spring months.

The facility is situated on the Mississippi River flood plain, in an area known as the American Bottom, just adjacent to the channel of the river. The area is generally flat, with substantial flood plain soils and limited topographic expression. (**Figure 7)**

Wind speed and direction in the Herculaneum region is variable, but is generally from northwest and south/southeast, with an average speed of approximately 10 mph. **(Figure 8, taken from St. Louis International Airport)**

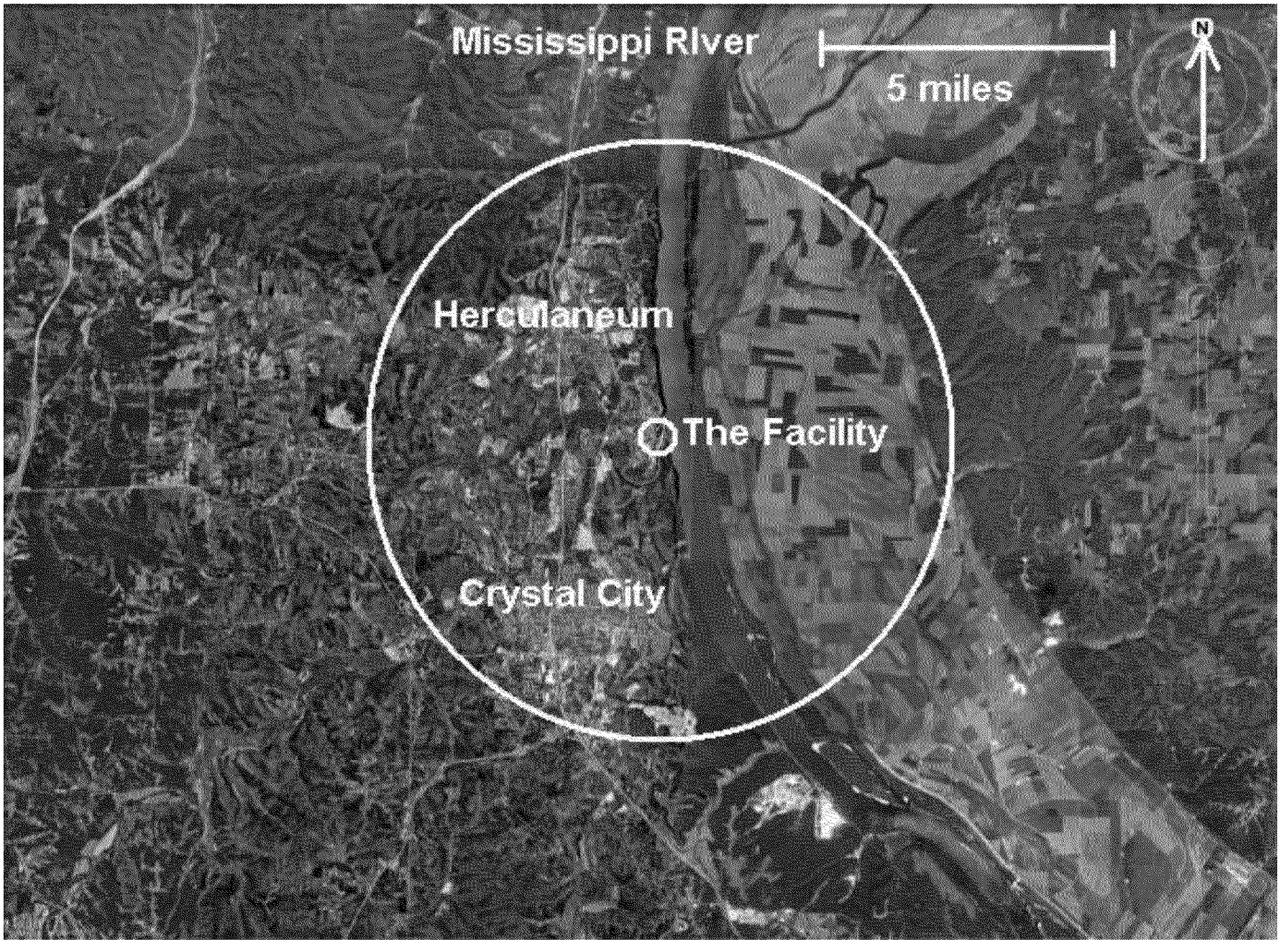

Figure 7. Map of Herculaneum Airshed

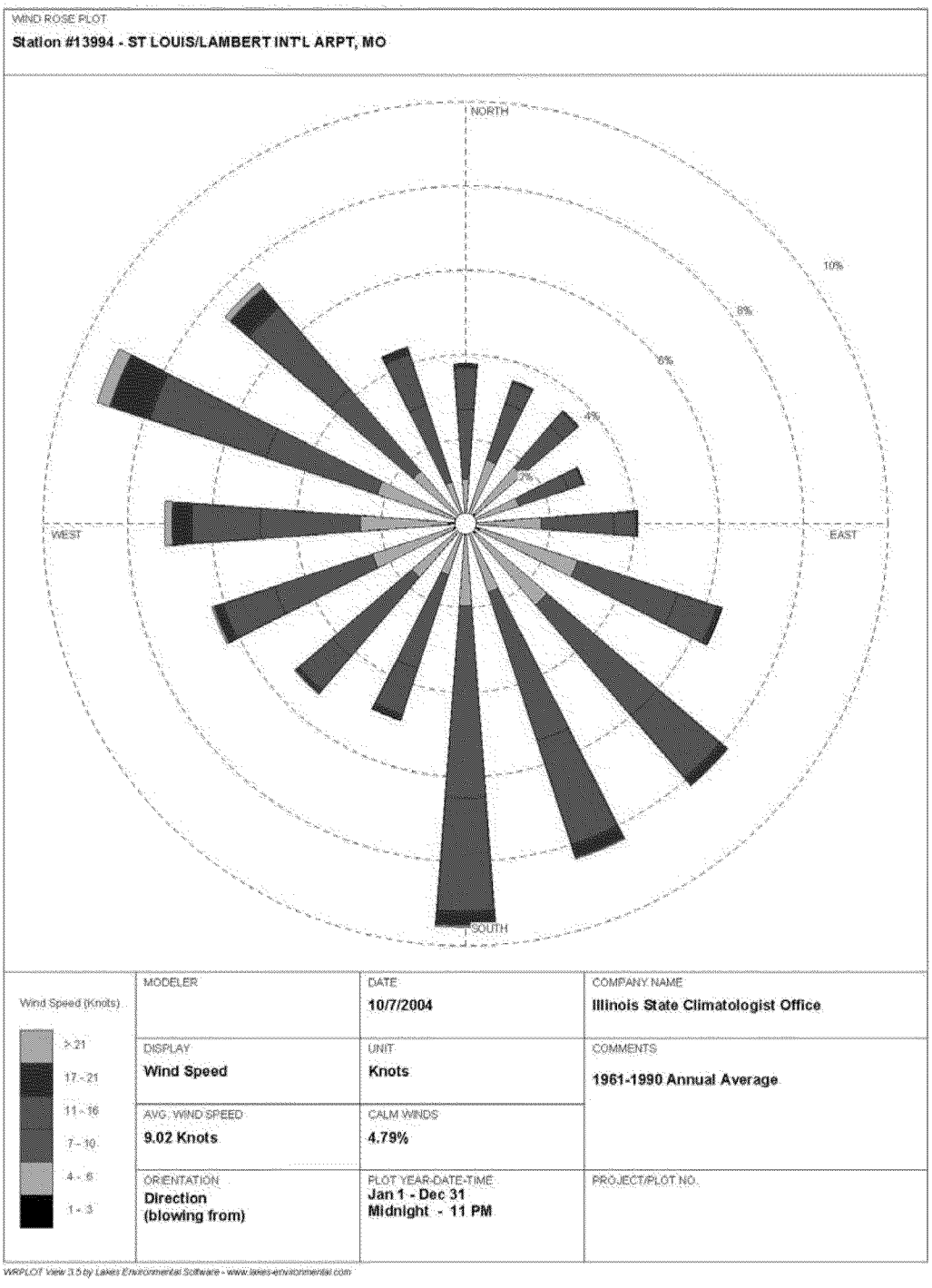

Figure 8. Wind Rose from St. Louis International Airport. 1 knot = 1.15 miles

3.2 Source Characteristics – Primary Lead Smelter Map

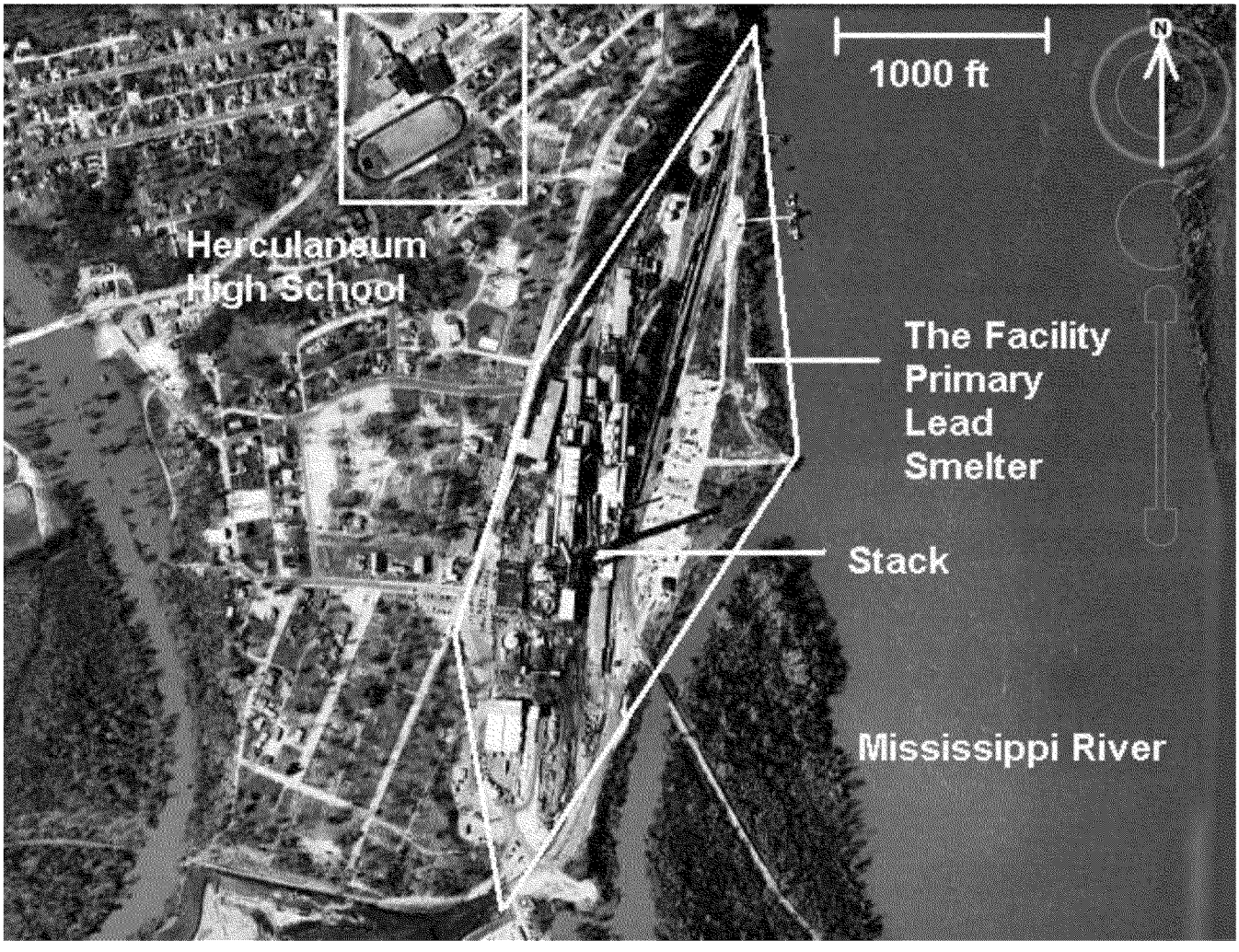

Figure 9. Primary Lead Smelter Aerial Map

3.2.1 Source Characteristics

U.S. EPA's Toxic Release Inventory (TRI) data states that in 2008 The Facility released 6,247,539 lbs of zinc, 2,534,384 lbs of lead, 1,817,224 lbs of aluminum, 315,178 lbs of arsenic, and 371,956 lbs of copper. These metals releases were calculated by the through-put of the facility and the total lead metal produced. Metals concentrations emerging from the multi-metals ambient FLM monitors should generally reflect TRI data.

Lead emissions at primary lead smelters occur from process sources, process fugitive sources, or from lead dust fugitive sources. Lead emissions can potentially occur throughout the smeltering process. Fugitive sources are of particular concern to ambient lead concentration in adjacent neighborhoods and in achieving attainment with the NAAQS.

Fugitive lead sources may include: dust from the milling, dividing and fire assaying of samples of incoming concentrates and high grade ores; dust from ore crushing, ore loading and unloading areas; hi-lead road dust; fugitive emissions from the sinter machine and the sinter building; fugitive emissions from the blast furnace area; leaks from the tapping of the kettles and settlers; fugitive emissions from various pouring and tapping activities in the drossing building; and fugitive emissions from the periodic clean out of the blast furnace and reverberatory furnace. A year 2000 source apportionment study by Cooper Environmental Services indicated that fugitive emissions from the blast furnace, lead refinery and dross plant account for 96% of lead emissions contributing to the NAAQS exceedence. Additionally, the study developed a source chemistry library to be utilized for ambient lead source identification based upon the unique mineralogy of each operational and metallurgical process (CES, 2000). For instance, the lead series generally follows a PbS - $PbSO_4$ -PbO – Pb metal trend from raw material into refined metal. Additionally, particle size of fugitive emissions released from high-heat operations like the blast furnace are more likely to have associated finer particle sizes (S.A. DHS, 2001).

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 lead concentration data in order to fully characterize potential facility sources. Local meteorological wind and precipitation data will be necessary to characterize potential contaminant transport in the area and will be used in close conjunction with the continuous ambient lead data to analyze potential emissions sources.

4.1.2 Elements, PM and Sampling Frequency

The ambient air FLM devices will monitor for the primary and secondary elements of health and regulatory concern, as well as accompanying metals.

Primary Elements of Health and Regulatory Concern: lead (Pb)

Secondary Elements of Health and Regulatory Concern: cadmium (Cd), arsenic (As)

Accompanying metals: antimony (Sb), chromium (Cr), copper (Cu), zinc (Zn), silver (Ag), manganese (Mn), selenium (Se) calcium (Ca), scandium (Sc), titanium (Ti), vanadium (V), iron (Fe), cobalt (Co), nickel (Ni), bromine (Br), tin (Sn), and mercury (Hg)

The ambient air metals FLM devices will be outfit with a TSP inlet to limit particle size of the sample matter. A TSP inlet is industry standard for ambient air lead monitoring.

4.1.3 Plant Processes and Events

Primary lead smelter operations and processes will be monitored along with ambient lead concentration and meteorology. **Figure 10** illustrates primary lead smelter processes. It is highly probable that elevated lead concentrations can be associated with specific smelter events and operations. Detailed records of primary lead smelter operations, analyzed with emerging near-real-time lead data, will provide a comprehensive set of information to identify and reduce fugitive emissions.

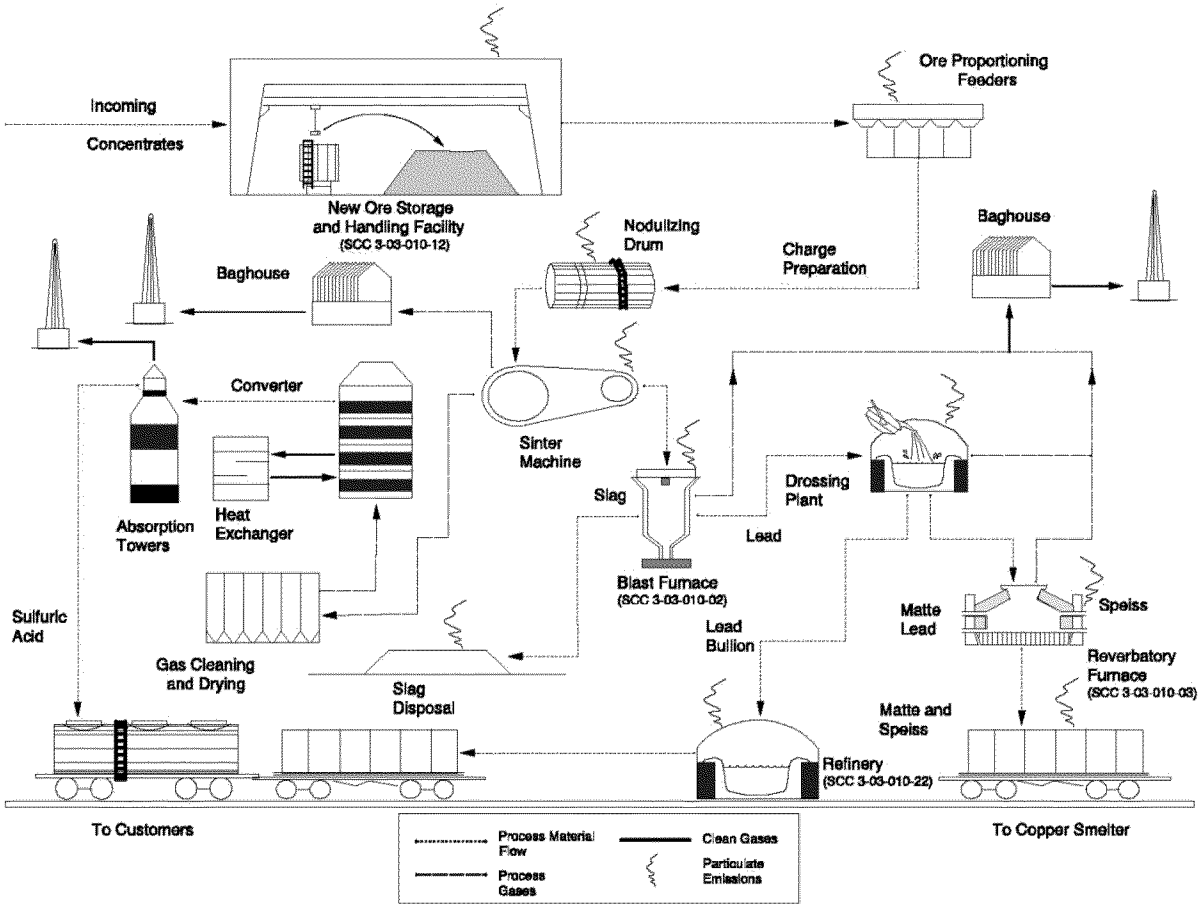

Figure 10. Conceptual Drawing of Primary Lead Smelter Processes

4.2 Monitoring Sites

Sampling locations for the multi-metals ambient air monitoring device will be determined utilizing established site guidelines for siting ambient lead monitors around stationary sources (EPA, 1997). The Hazardous Ambient Metal Compliance Plan (Plan) will use three existing lead sampling sites established by the U.S. EPA; EPA #3, EPA #6, and EPA #8. Additionally, one site will be developed specifically for the purpose of the fugitive emissions monitoring network associated with the Plan; FLM #1. The three EPA sites are located in areas at high risk from

fugitive emissions, and have the benefit of historic and corroborative data to compare to the data that will emerge from the multi-metals NRT monitors. The new site is necessary to provide data along the span of the western fence line of the property and fully characterize fugitive emissions. Therefore a total of four sampling sites will be established and a rotating monitoring plan will be discussed and developed. See **figure 11** for sampling locations.

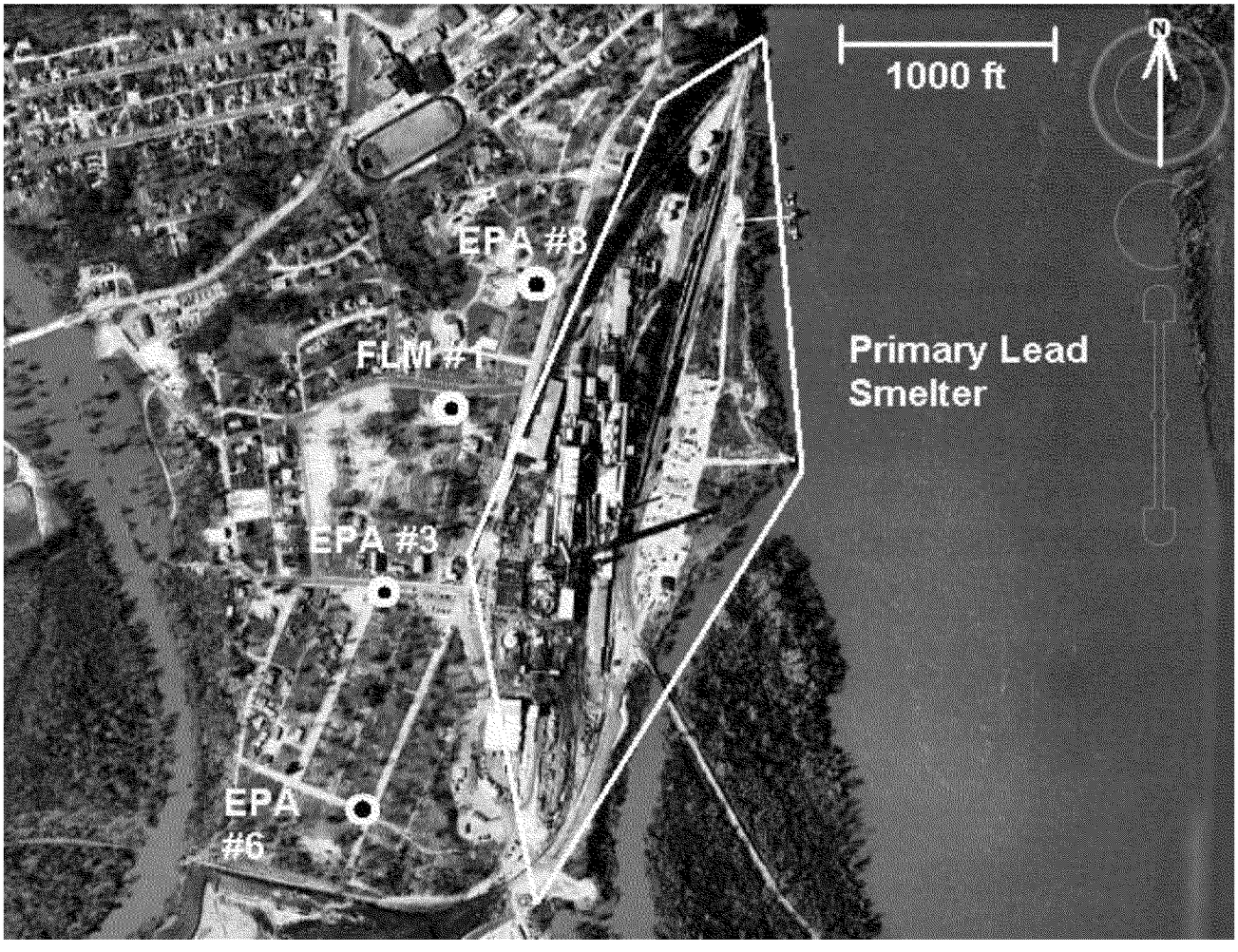

Figure 11. NRT Multi-Metals Sampling locations at Primary Lead Smelter

4.3 Monitoring Plan

In order to adequately characterize fugitive emissions, identify sources, develop corrective actions, provide near-real-time emissions alerts, and keep project costs low, one NRT multi-metals ambient air sampling device will be necessary. The NRT ambient air sampling device will rotate between the various sampling locations in order to gather data on fugitive emissions at the given locale. The device will initially be located at the site of highest ambient lead values. A fugitive emissions study will proceed, sources will be identified, and engineered controls will be developed and tested. When ambient lead concentrations show marked reduction, the sampling device will rotate to the next sampling location, which, due to the success of the fugitive emission controls at the previous site, would be the highest ambient lead concentration

site at the smelter. If a sampling point appears to be especially problematic, the air monitoring device would remain at the site for an extended period of time.

While the sample analysis technology and method of X-Ray Fluorescence utilized by the real-time multi-metals sampling devices is mainstream and EPA approved, it is not currently approved for total suspended particulate matter (TSP), which is the required parameter for the lead NAAQS. There are numerous TSP monitors on-site. The NRT multi-metals monitor will be used in conjunction with EPA 24-hour TSP lead monitors, and data emerging from the devices will be utilized for quality control, to assess compliance with the lead NAAQS, and for fugitive source apportionment.

4.3.1 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 (15) minutes, to lower resolution data like sampling once every four (4) hours. Higher data resolution provides more information to regulators and the secondary lead smelter managers to assess and protect worker and public health, and to more fully characterize smelter operations on emissions.

Air samples are collected on a tape medium that is relatively expensive. In this case, where ambient fugitive lead emissions may vary substantially throughout the day, the multi-metals ambient air sampling device will initially be programmed to sample every hour. After a year of ambient air sampling, data will be analyzed to determine how hourly lead data compares to daily averaged lead data. The sampling period may be decreased for the remaining 12 months of the Plan.

Data will be available within two hours of sampling event, streamed via wireless or cabled connection to regulators and smelter managers, 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 by regulators.

The multi-metals continuous ambient air monitors will be protected from weather conditions with a shelter and rain guard. A TSP inlet will direct the aerosol to the sampler, and electrical lines and data acquisition cables will run from the shelter to the nearest phone/internet connection.

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 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

This hypothetical example utilizes continuous multi-metals ambient air sampling devices as another tool for regulators and Facility operators to achieve compliance with the lead NAAQS. Regulators could potentially recommend the sampling device to The Facility as part of a compliance plan or State Implementation Plan, or alternately the facility may want to voluntarily initiate hourly sampling as a way to achieve compliance. Regardless, it is the mandate of the U.S. EPA and the Missouri Department of Natural Resources to protect human health and the environment and to represent the public interest, and regulators will be responsible for managing any data emerging from the ambient metals NRT sampling devices as it pertains to those priorities.

4.4.3 Plant

Near real-time data emerging from the ambient metals-air monitoring system will be available to The Facility in order to adequately characterize emissions and develop more effective emissions controls.

4.4.4 Internet and Public

Regulators will maintain a public internet location that details appropriate rules and regulations, outlines the ambient lead goals, shows the data emerging from the monitoring location(s), and provides a venue for regulators to answer any questions that the public or industry may have over the monitoring program and attainment with the lead NAAQS. Data on the site will be updated daily to ensure quality assurance of the reported values.

5.0 References

1) 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.

2) 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.

3) U.S. EPA (1982) *Basic Air Pollution Meteorology*. Report No. EPA 450/2-82-009, U.S. Environmental Protection Agency, Research Triangle Park, NC.

4) U.S. EPA (1997) *Guidance for Siting Ambient Air Monitors Around Stationary Lead Sources.* Report No. EPA 454/R-92-009. U.S. Environmental Protection Agency, Research Triangle Park, NC.

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6) California DHS, *Evaluation of Lead Levels in Children Living Near A Los Angeles County Battery Recycling Facility*, Berkeley, CA: California Department of Health Services, 1996

7) Yanca, et al. *Validation of Three New Methods for Determination of Metal Emissions Using a Modified Environmental Protection Agency Method 301,* Air and Waste Management Association,Vol. 56. December 2006.

8) South Australia Department of Human Services, *Characterization of Fugitive Material Within a Primary Lead Smelter,* Journal of Air and Waste Management Association, Vol. 51. October 2001.

10) Cooper Environmental Services, *Source Apportionment of Herculaneum Ambient Lead Concentrations By Chemical Mass Balance Receptor Modeling*, Beaverton, OR: 2000. print

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.: 20081752
MACTEC Project No.: 827008S407

Submitted To:
MACTEC Federal Programs
Research Triangle Park, NC

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Portland, Oregon 97223

December 9, 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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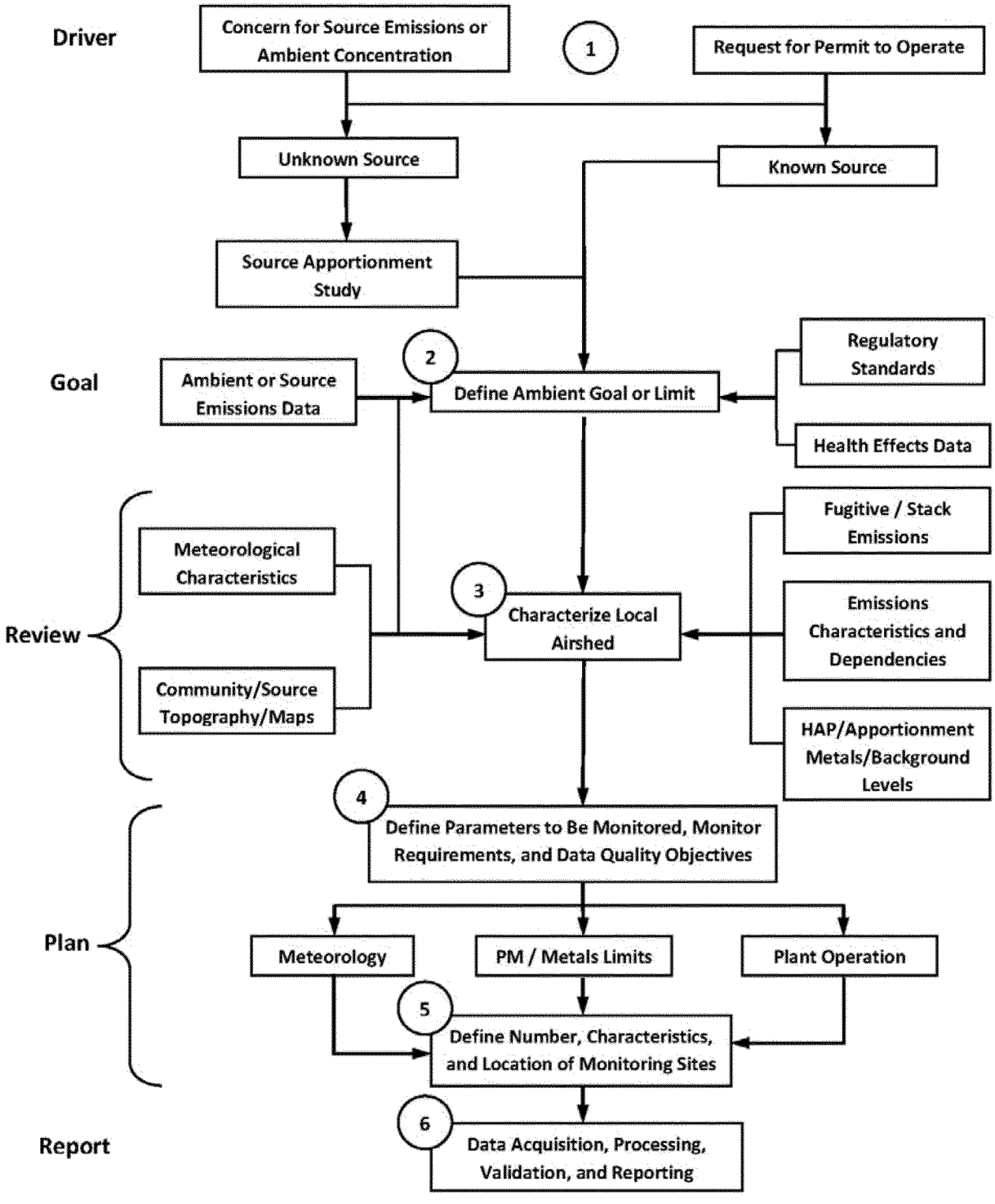

Figure 1. Procedure Flow Diagram

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 (PM_{10}) 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-born 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/m³/ 3month	0.2 µg/m³	0.085 µg/m³/24hr	0.836 µg/m³/24hr
Arsenic (As)	Region IX RSL – 0.016 µg/m³ California Acute REL 0.2 µg/m³/1 hr NIOSH 15 min. ceiling 2 µg/m³	0.100 µg/m³	0.024 µg/m³/24hr	0.189 µg/m³/24hr

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 µg/m³ at the Hayden Jail and 0.12 µg/m³ 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 µg/m³.

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 µg/m³/24hrs during inactive smelter operations and as high as 0.024 µg/m³/24hrs during active smelter operations. However, concentrations of arsenic varied widely, with the highest value recorded September 11, 2007, at 0.189 µg/m³, near the California Acute 1 hour Residential Reference Level of 0.2 µg/m³, and an order of magnitude above EPA Region IX Residential Screening Level (RSL) for cancer set at 0.016 µg/m³. 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 µg/m³/24 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 µg/m³.

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 µg/m³, 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 µg/m³/24hrs during inactive smelter operations and 0.085 µg/m³/24hrs 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 µg/m³/24hr, 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 PM□ 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 PM□ 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 PM□ lead and less than 6% of the PM□ 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 (µg/m³)	California (µg/m³)	Region IX EPA (µg/m³)	ATSDR
As	n/a	***Acute - 0.2/1 hr*** Chronic – 0.015	Non cancer Hi -0.016	n/a
Pb	***0.15 rolling 3 month avg.***	n/a	n/a	n/a
Cr	n/a	Chronic – 0.2	***Non cancer Hi - 0.01***	n/a
Cd	n/a	n/a	***Non cancer Hi – 0.01***	Acute – 0.03 Chronic – 0.01
Cu	n/a	***Acute – 100/1 hr***	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 discreet 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 µg/m³	6/6.5	2.34 µg/m³

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 µg/m³ measured at Hayden during the 1986 source apportionment study could result in 15-minute averages in the range of 7.5 µg/m³. Lead concentrations of 0.836 µg/m³/24 hour from the Remedial Investigation may have 15-minute averages as high as 20.9 µg/m³. 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 µg/m³. 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 ng/m³/1 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.

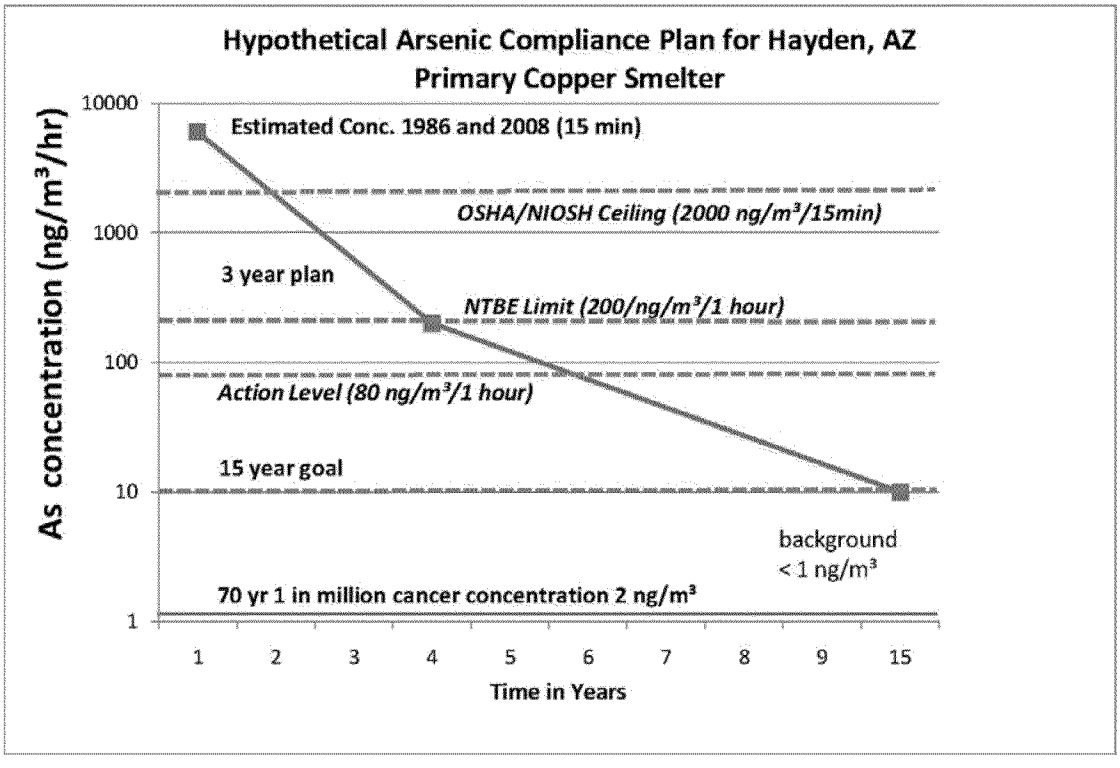

Figure 2. Potential Hazardous Ambient Metal Compliance Plan for Residential Arsenic at Hayden, AZ

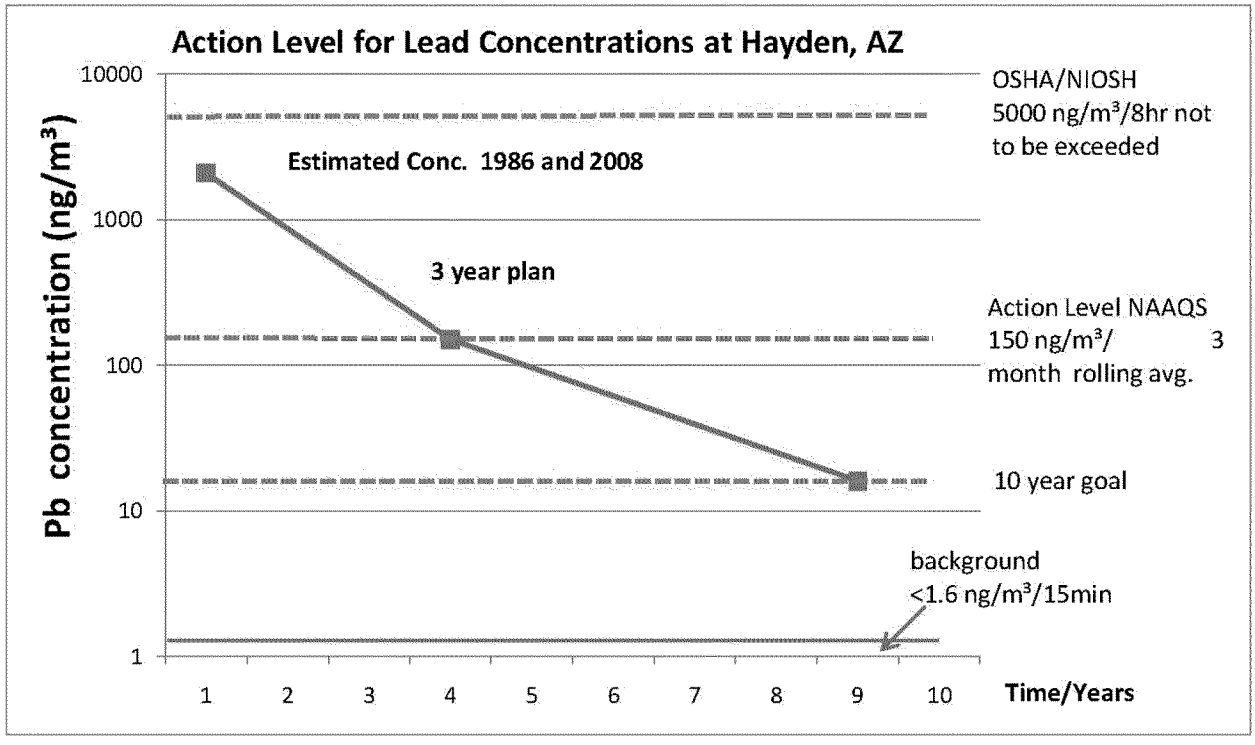

Figure 3. Potential Hazardous Ambient Metal Compliance Plan for Residential Lead at Hayden, AZ

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.

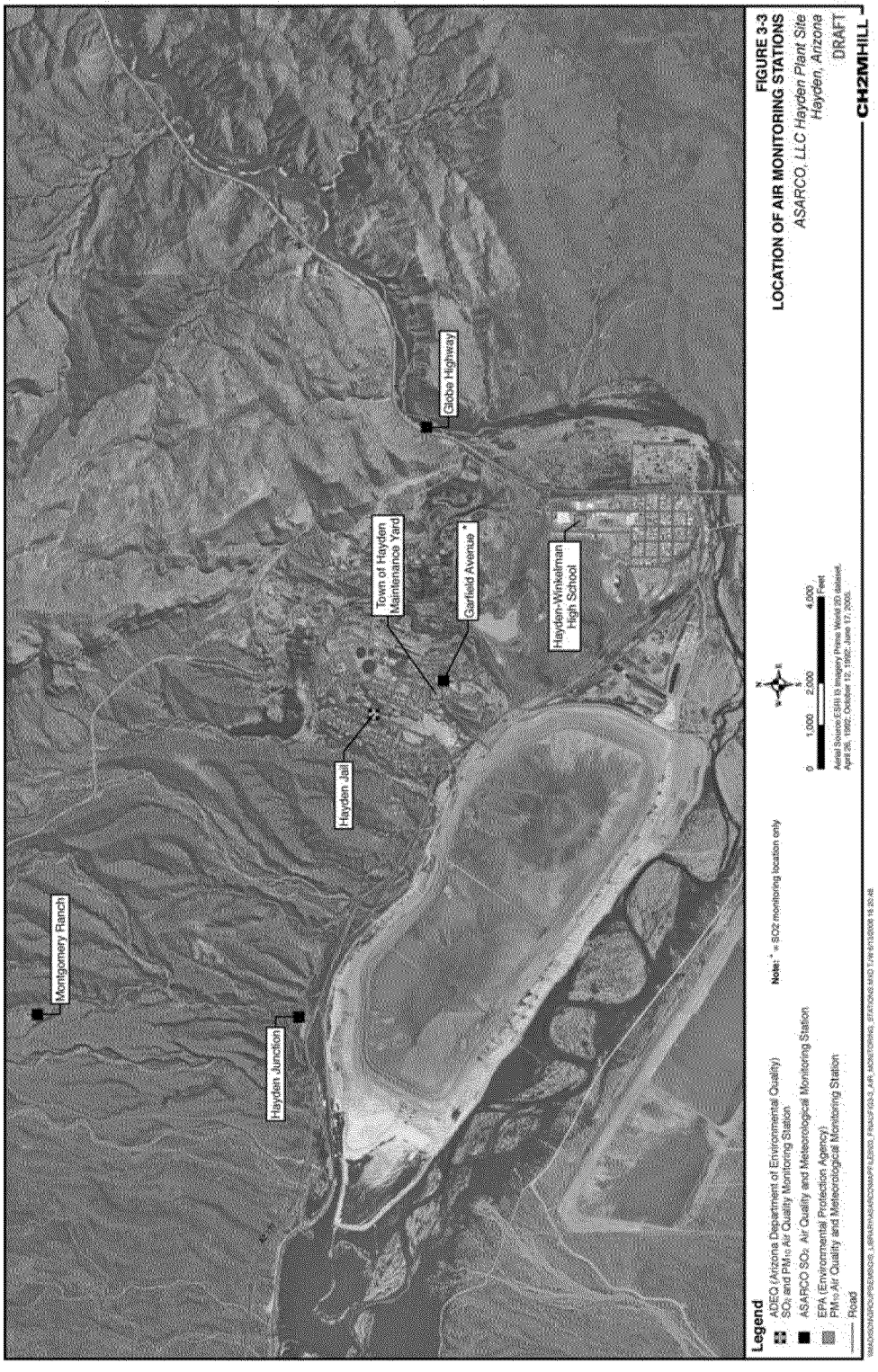

Figure 4. Local Airshed Map

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.

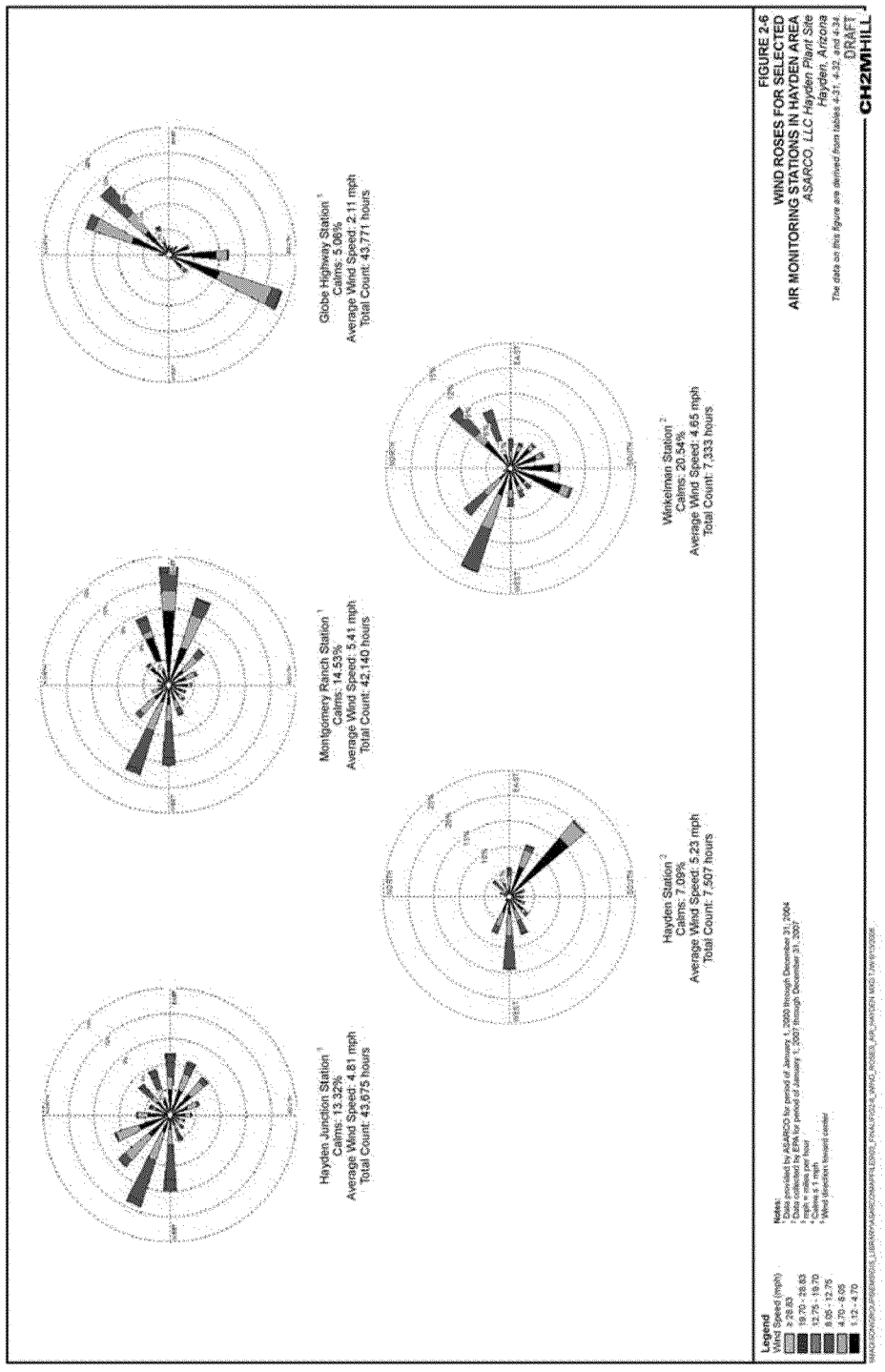

Figure 5. Wind Rose Data, Hayden/Winkelman Airshed

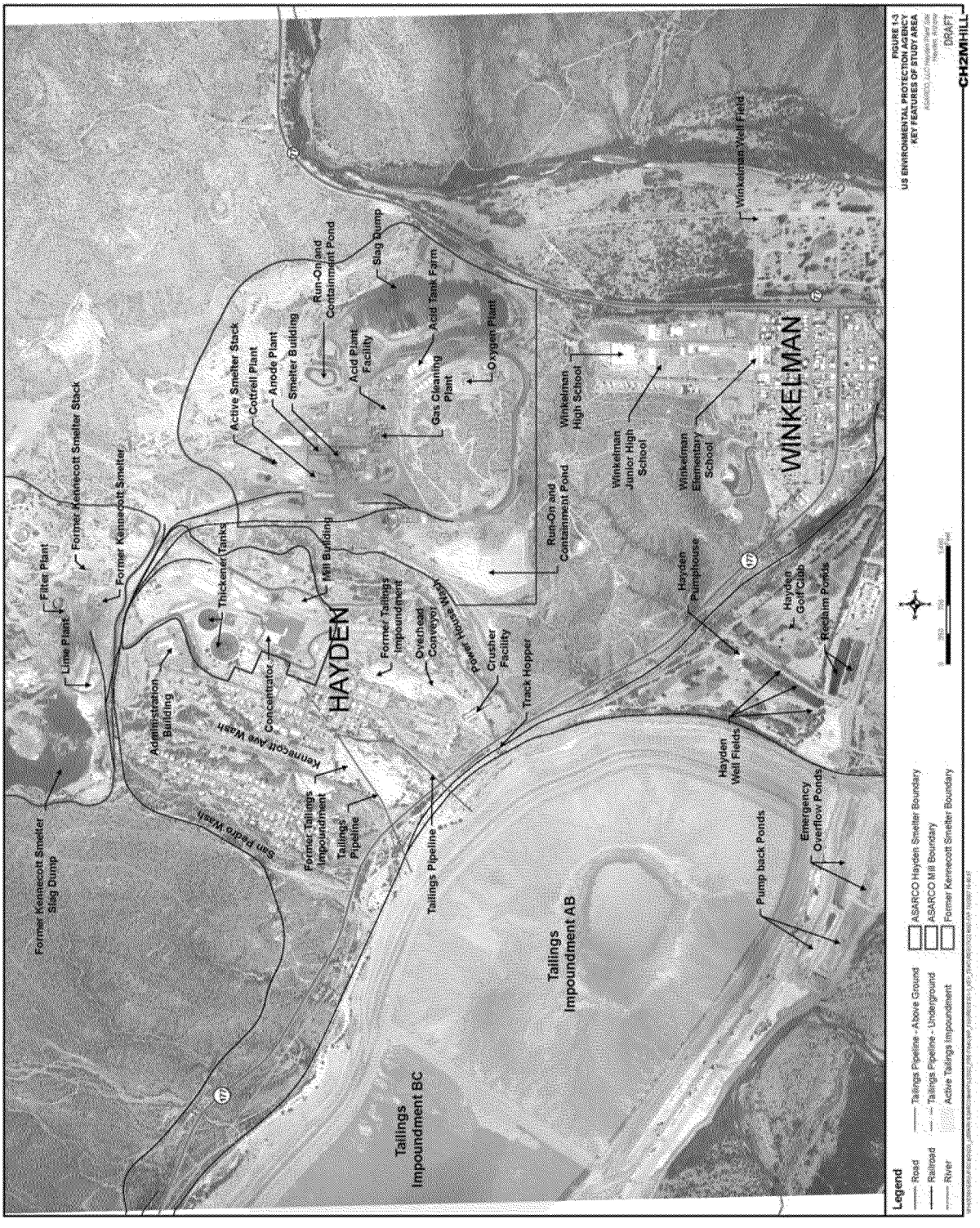

Figure 6. Hayden/Winkelman Detail

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 emit 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 course 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 SO_2 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 SO_2 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)**

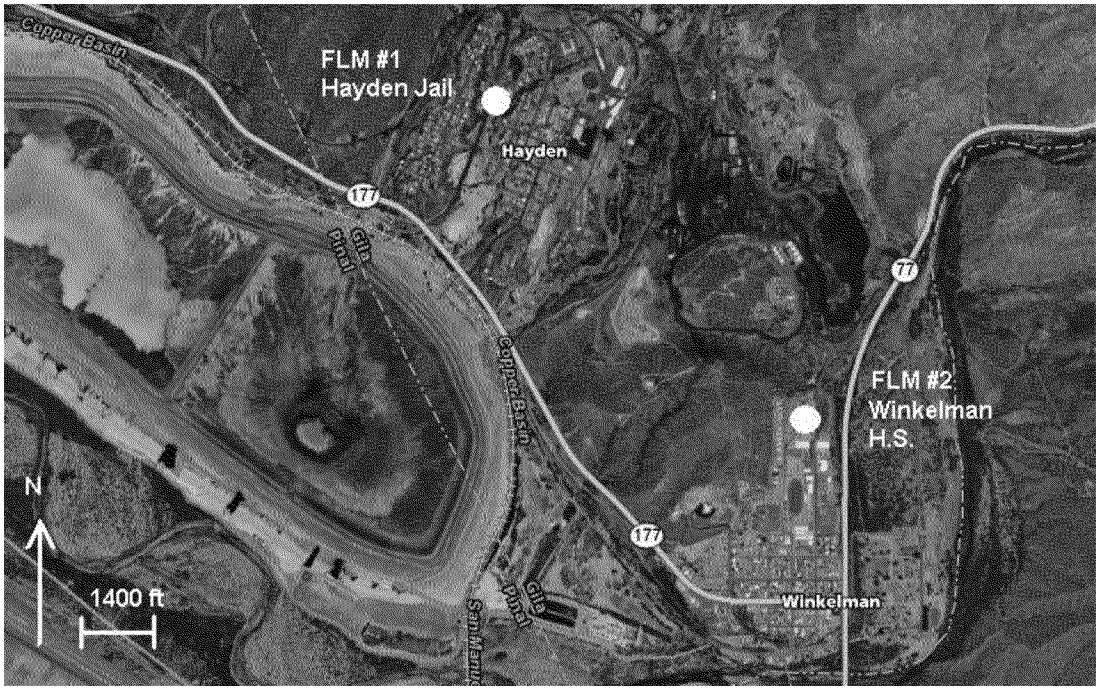

Figure 7. Multi-metals ambient air sampling locations

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.

APPENDIX G

Example Application: Ferrous Metal Foundry and Recycler

DRAFT

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

MACTEC Work Order No.: 20081752
MACTEC Project No.: 827008S407

Submitted To:
MACTEC Federal Programs
Research Triangle Park, NC

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December 9, 2010

Summary

This hypothetical example describes how the Guide for Developing a Multi-Metals, Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors (Guide) can be applied to develop a Multi-Metals Monitoring Plan for an urban residential airshed surrounding a ferrous metal recycler and foundry. Ferrous metal foundries are generally urban mid-sized industrial facilities that recycle discarded iron and scrap metal for casting and commercial resale. Primary ambient metals contaminants of concern include, in order of higher concentration, iron, manganese, chromium, nickel, zinc, copper and lead.

The U.S. Congress amended the Federal Clean Air Act (CAA) in 1990 to regulate and control specific hazardous air pollutants (HAPs) that are known to cause adverse effects to human health. Metals represent eight of the HAPs that the United States Environmental Protection Agency (U.S. EPA) specifically identified as posing the greatest potential human health threat in urban areas. These metals include arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, and nickel.

While the existing regulations of ferrous metal foundries work to limit HAP emissions, significant amounts of metals are still released from fugitive and stack emissions. Recent scientific studies on the health impact of metals in particulate matter strongly suggest that even short-term exposures to metals can be harmful to human health. Concerns from neighbors about odors and metals exposure health effects may also prompt a facility or environmental regulators to assess and reduce both fugitive and stack emissions into the surrounding airshed.

Due to erratic fugitive emissions sources and shifting wind conditions, traditional 24-hour averaged ambient metal monitors do not accurately characterize short-term ambient metals concentrations, which may vary as much as several orders of magnitude within the space of a few hours. Near-real-time (NRT) multi-metals ambient air sampling devices provide quality, high resolution data that can be used to fully characterize short-term and long-term metals exposure, assess potential risks to human health, and alert regulators, plant operators, and community leaders of problematic emissions.

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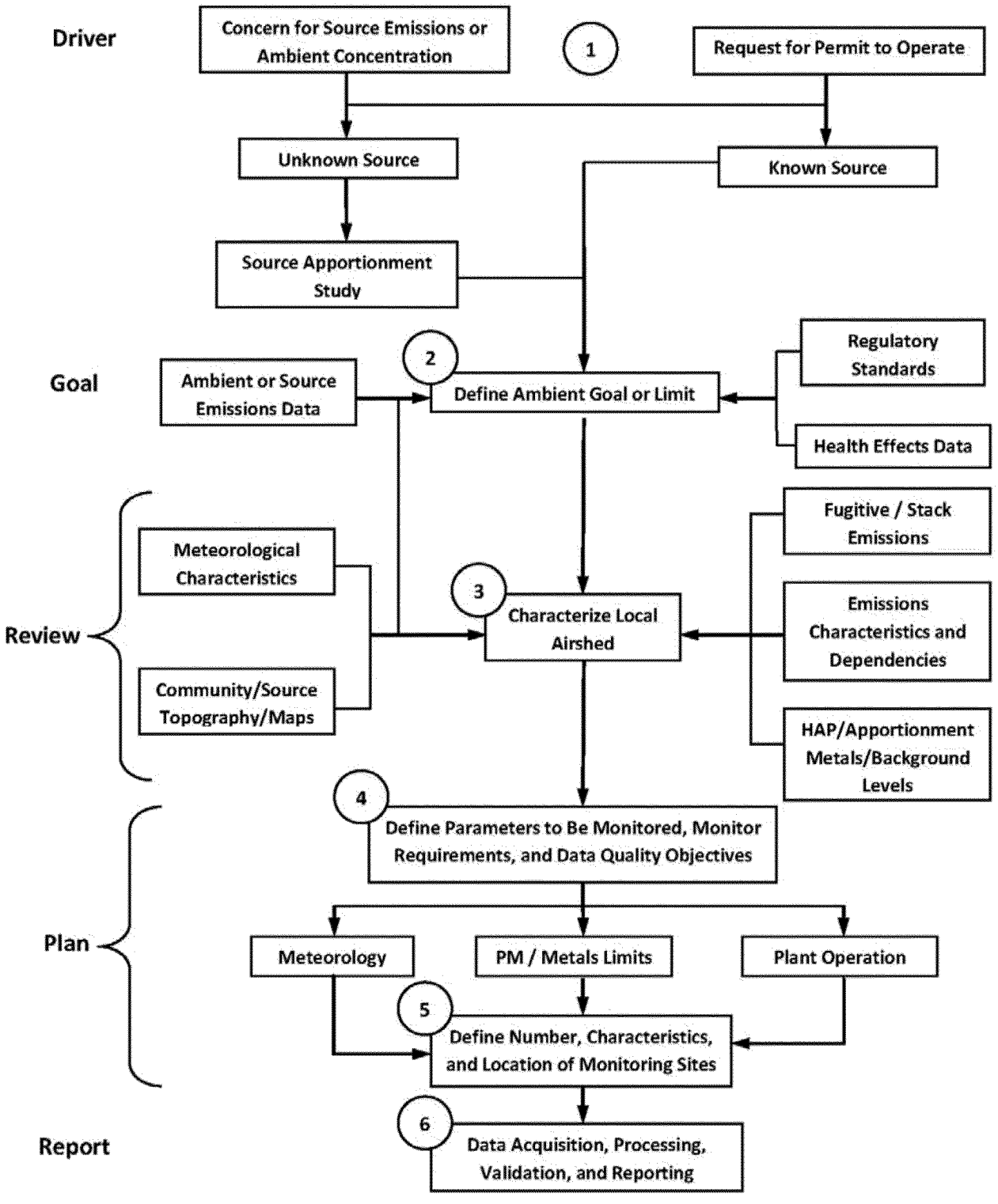

Figure 1. Procedure Flow Diagram

1.0 Driver – Ambient HAP Emissions and Neighborhood Issues

For this hypothetical example, the Guide will be applied to establish a Multi-Metals Monitoring Plan (Plan) for a hybrid residential/industrial airshed containing a ferrous metals foundry and recycler located in Portland, Oregon. The ferrous metals foundry (The Foundry) is located in an industrial area in the northwest part of the city, within a mile of the Willamette River and less than two miles northwest of downtown Portland. The area is closely bordered by residential neighborhoods and an elementary school to the south, and additional residential areas across the Willamette River to the north.

The Foundry is a global manufacturer of engineered metal components for the aerospace, mining, power generation and construction industries, and has been in operation since 1913. The facility recycles ferrous material, refines the molten iron alloy into steel and casts it into industrial components. The basic steel production process begins as raw materials such as steel scrap and foundry returns are transported to the facility by truck, along with fluxes such as carbonates and fluoride, and carbide components which are introduced to improve the strength and durability of the finished steel.

The scrap metal and the charge is then transferred to the furnaces where it is melted and tapped. The Portland facility also utilizes argon-oxygen decarburization (AOD) vessels for further refinement of the steel. Alloys such as nickel may be added to the metal to enhance strength and other desired properties. When the metal has reached tapping temperature, the molten steel is separated and transferred into overhead cranes which pour it into the AOD or a specific mold depending upon the end product. The operation continues as the metal cools to a workable temperature and the sand casts and molds are removed in a process known as the shakeout. After cooling the casting may go through additional heat treatment to strengthen the metal before final finishing and painting.

Metals emissions can potentially occur throughout The Foundry's operations; from fugitive particles associated with raw materials unloading, storage, transfer, and scrap preparation; to the furnace operations such as tapping and mold pouring; to casting, shakeout, and cooling. The Foundry's metal melting and refining processes result in the majority of metal emissions. The introduction of oxygen during refining periods produces a significant amount of particulate matter, and dust concentration in exhaust gas can be near 23,000 mg/m^3 (Davis, 2000). Iron and ferrous compounds such as Fe_2O_3 and FeO are the main components of metals foundry particulate matter emissions. However Cr_2O3, CaO, MnO, PbO and Al_2O_3 are also contributors. Manganese, chromium, nickel and lead are the primary HAPs of concern.

Metals emissions from ferrous metals recyclers are regulated by the Clean Air Act Title 40 CFR 63, National Emission Standards for Hazardous Air Pollutants, subpart EEEEE, which establishes emission rates for iron and steel foundries. The regulations have specific emissions limits for particulate matter (PM), and total metal HAPs. Compliance is based off the Maximum Achievable Control Technology (MACT) approach, which consists of periodic performance testing that establishes production through-put values based on emission factors. Stack or ambient air monitors are not required by existing regulations.

Due to the proximity of The Foundry to neighborhoods and schools in the northwest and north Portland area, the facility has been the center of significant public controversy and debate concerning toxic metals emissions for some time. In 2008, the Northwest District Association Health and Environment Committee in Portland, Oregon, responded aggressively to a U.S.A. Today article and study titled The Smokestack Effect that ranked air quality near Chapman School and other local northwest and north Portland schools in the bottom 5% of all U.S. primary and secondary schools. The study's results were based off of dispersion models related to EPA toxic release inventory (TRI) data. Numerous industrial manufacturing firms operating in the area were listed as the primary sources of elevated toxic pollutants, with The Foundry prominently identified as a main contributor. Coincidentally, recurrent odors in the neighborhood also spurred increased media attention and residential concern. The state environmental regulatory agency investigated the odors, but was not able to locate the specific source. Groups formed such as Neighbors for Clean Air, and joined the Northwest District Association to pressure The Foundry and state and local officials to address the air quality concerns in the neighborhood. While The Foundry's operations bore the most scrutiny in the media and in the public meetings, numerous other industrial facilities operate in northwest Portland, including other steel foundries, and also contribute to elevated metals concentrations in the area. Specifically, the groups petitioned state regulators to characterize the threats to the local airshed and identify sources.

2.0 Goals: Defining Ambient Goals and Compliance

For this hypothetical example, as a part of a permit renewal process and evaluation, the state environmental regulatory agency develops an ambient metals monitoring plan to characterize the human health risks within the airshed. *The goals of the Plan are to characterize the health risks to north Portland schools and neighborhoods and to gather data on the various ambient metals sources in the airshed.* In order to address the local community's concerns and ensure the protection of human health, an NRT multi-metals monitor will be used to gather comprehensive data on the airshed and assess local health risks. The Plan is based on the process illustrated in the Procedure Flow Diagram **(Figure 1)**.

An NRT multi-metals monitor will be utilized to identify the contributions of local emission sources. In February 2009 Cooper Environmental Services was able to successfully identify The Foundry's emissions chemical fingerprint and differentiate the metals concentrations from background air quality data based on well-established industry source profiles. Similar methods can be used to differentiate additional metals sources within the airshed. Further, and outside the scope of this Plan, a chemical mass balance receptor model could be developed to enforce emission standards.

Local airshed ambient air monitoring using NRT multi-metals monitoring is a viable air quality monitoring and regulatory approach due to number of issues and concerns:

1) Due to the number of industrial emission sources in the area, ambient air monitoring will provide the broadest data on the overall health of the airshed, adequately assess risks to human health and the environment, and help identify contributing sources

2) The primary receptors for air-born particulate metals contamination are the residents of north Portland and northwest Portland

3) An NRT multi-metals monitor can differentiate the metals contribution to PM and accurately assess the short-term and long-term exposure risk within an airshed.

2.1 Ambient Emissions/Primary Elements of health/regulatory concern

The primary metals of concern in northwest Portland are related to industrial emissions in the area. The HAP metals emissions associated specifically with The Foundry include manganese (Mn), lead (Pb), chromium (Cr) and Nickel (Ni).

2.1.1 Secondary Elements of Potential Health Concern

Other HAP metals include cadmium (Cd), cobalt (Co), arsenic (As), antimony (Sb), mercury (Hg), and selenium (Se). In addition, metals such as Iron (Fe) and zinc (Zn) have been identified as potential metals of concern.

2.1.2 Source Apportionment Elements

In 1979 a Portland Aerosol Characterization Study was conducted for state environmental regulators. The results found that the greatest local contributions to total suspended particulates (TSP) in northwest Portland were soil and road dust at 20.1%, followed closely by primary industrial at 7.3%. The primary industrial source chemical fingerprint used to identify ferrous metals industrial sources is similar to the ambient metals concentrations detected recently in northwest Portland, with elevated concentrations of iron, manganese, zinc, chromium, nickel and lead.

2.2 Goals: Regulatory Standards, Oregon Benchmarks and Human Health Risks

2.2.1 Regulatory Standards

Metals emissions from ferrous metals recyclers are regulated by the Clean Air Act Title 40 CFR 63, National Emission Standards for Hazardous Air Pollutants, subpart EEEEE, which establishes emission rates for iron and steel foundries that emit or have the potential to emit any single HAP greater than 10 tons per year, or a combination of HAPs at a rate of 25 tons per year. The Foundry's permit requires it to report emissions of metal HAPs including nickel, chromium, manganese, lead, cadmium, cobalt, arsenic, antimony, mercury and selenium. To model HAP emissions, the facility utilizes industry standard emission factors and actual steel production volumes. As of 2010 The Foundry is currently in the process of renewing its Title V CAA permit.

2.2.2 Goals: Oregon Benchmarks and Human Health Risks

Recent scientific studies strongly suggest that even short-term exposure to concentrations of metals associated with foundry emissions such as nickel, chromium and manganese can have adverse human health effects, and children are especially at risk. **Appendix C** provides an

overview of metals health effects as well as further discussion of recent research. The state regulatory agency's Oregon Air Toxics Program (OATP) is required to periodically review health-based ambient benchmarks and develop new ambient air quality standards based on their findings. In 1995, 2000, and 2005 the state environmental agency conducted extensive air quality sampling throughout the Portland area using 24-hour average PM samples. The studies concluded that ambient concentrations of arsenic and cadmium were above Oregon health benchmarks, while lead, manganese, mercury and chromium were all below the established levels. However, air quality in northwest and north Portland was consistently worse than the rest of the metro area. While some concerns were raised, the data did not fully characterize ambient metals concentrations, as the monitors were not located near areas of potentially high impact, and as 24-hour average samples the concentrations did not represent the full expression of short-term ambient metals spikes that can occur in an airshed.

In February 2009, Cooper Environmental Services conducted a feasibility study for a NRT multi-metals ambient air monitoring device. The monitor was located near The Foundry and sampled ambient PM metals on a one-hour time interval. During the study, the multi-metals NRT monitoring device recorded one-hour ambient chromium concentration over 25 times the national urban average; one-hour nickel was detected over 25 times the national urban ambient average; and one-hour manganese concentrations were over 125 times the national urban ambient average (**Appendix C**). Additionally, many of the OATP health benchmarks were surpassed by orders of magnitude. That being the case, the multi-metals NRT monitor data represents one-hour concentration spikes. OATP health benchmarks and national urban ambient averages are generally based on 24-hour averaged samples, which are typically lower due to dynamic airshed conditions. However, while there are no enforceable national or state ambient standards for these metals, it is clear that the local airshed is significantly impacted by the region's industrial operations, including those of The Foundry, which in turn has the potential to adversely affect the health of the local community.

While the OATP benchmarks are not enforceable, they provide a standard to assess air quality based on accepted health risk scenarios. See **Table 1** for select Oregon Air Toxics Program Ambient Benchmark metals concentrations and results from recent air quality studies in north and northwest Portland.

Table 1. Oregon Air Toxics Program Health Benchmarks in ng/m³

	Ni	Cr	Mn	Pb	Cd	Co	As	Hg
OATP Chronic Benchmarks	50	0.08 (CrVI)	90	150	0.6	100	0.2	300
OATP 24-hour average in N and NW Portland	4.24	n/a	41.9	11.7	2.57	n/a	1.74	n/a
NRT 1-hr Multi-Metals *High*	542	502 (Cr)	2560	339	n/a	n/a	1.8	3.08

2.3 Goals: Action Levels

For this hypothetical example, in order to meet Plan goals, a continuous multi-metal ambient air monitoring device will be located at critical areas of high metals impact and at sensitive nearby locations within the airshed such as local schools. Without comprehensive federal or state ambient air regulations, Oregon Benchmarks, California Acute Reference Exposure Limits (RELs), NAAQS Air Quality Standards, Agency for Toxic Substances and Disease Registry (ATSDR) standards, and Occupational Safety and Health Administration (OSHA) standards can be utilized. These standards provide a health and safety, as well as risk-based frame of reference by which regulators can determine Compliance Goals and Action Levels.

2.5 Demonstrating Compliance

The continuous Multi-Metals Ambient Air Monitoring Plan for the north and northwest Portland, Oregon, airshed is an un-mandated environmental program developed by regulators to address local air quality concerns, identify potential polluters, and protect human health and the environment. Compliance will be demonstrated by comparing data emerging from the multi-metals ambient air monitors to the stated Compliance Levels and Action Levels in the Plan. Compliance Levels and Action Levels should each have a specific form or particle size, a specific time average, and an associated concentration value. The NRT multi-metals ambient air monitoring devices can remotely communicate which allows for ongoing monitoring of the air quality within the airshed. In the event that Action Levels are triggered, the emissions source would be identified and corrective action would commence.

Compliance Levels are risk-based standards which delineate potential risk to human populations within the airshed. For this example, they are taken from Oregon Air Toxics Program benchmarks and should be considered life-time or chronic exposure values, based upon at the least 24-hour exposure data except in the case of chromium and cobalt, where EPA RSLs are used because Oregon benchmarks did not exist **(Table 2)**. Theoretically, at concentrations below Compliance Levels, no quantifiable risk due to ambient hazardous metals pollution is present in the local airshed. At concentrations above Compliance Levels, health risks, while not imminent, begin to increase within the airshed. If a Compliance Level is surpassed by a monitored parameter, the parameter would go into an assessment monitoring period. Levels would continue to be closely monitored and potential sources should be assessed. **Figure 2** illustrates the Action Level, Assessment Monitoring, and Compliance Level relationships for a general Plan parameter; nickel, in this case.

Action Levels are acute exposure levels and are taken from a variety of sources, including the ATSDR, OSHA, U.S. EPA, and California regulatory bodies. They can be used as reference points and guidelines to assess acute health risks within an airshed. In many cases, short-term residential exposure limits have not been adequately researched. In these instances, OSHA 8-hour average values were used. However, residential levels should not approach levels allowed in industrial workplace settings, therefore regulators have developed Action Levels for chromium, manganese, and cobalt at concentrations 10% of industrial standards **(Figure 5).**

Utilizing real-time meteorological and air quality data, as well as general chemical fingerprint knowledge of potential sources, regulators should be able to identify or disqualify potential sources of the emissions. Upon identification of the source, regulators will notify the probable polluter. In the event it is The Foundry or other metals fabricator in the area, regulators would meet with plant management and evaluate the emissions control technology in operation at the facility. An emissions control corrective action plan would be developed to mitigate future metals releases. Regulators would report the full incident to federal, state, and local authorities.

General assumptions on source identification will be drawn from the historic scientific literature. Real-time meteorological data will also play a significant role in identifying local sources. In the event identifying a potential source(s) proves difficult and data readings approaching or surpassing Action Levels remain persistent, a comprehensive regional chemical mass balance source apportionment study would be initiated to identify and fingerprint the local sources of air emissions, and to help evaluate the data emerging from the air monitoring devices. Regulators would sponsor the regional source apportionment study and develop a chemical fingerprint library for air pollution sources in the region.

Table 2. Multi-Metals Monitoring Plan Compliance Levels ng/m³/24 hr

Compliance Levels	As	Cd	Co	Cr	Hg	Ni	Mn	Pb
OATP/NAAQS /RSL	**0.2**	**0.6**	**26.3** RSL	**10** RSL	**300**	**50**	**90**	**150** NAAQS

Table 3. Multi-Metals Monitoring Plan Action Levels ng/m³

Action Levels	As	Cd	Co	Cr	Hg	Ni	Mn	Pb
	200 CA Acute 1 hr	**30** ATSDR Acute 1 hr	**10** 10% OSHA 8 hr TWA	**100** 10 % OSHA 8 hr TWA	**600** CA Acute 1 hr	**6000** CA Acute 1 hr	**5.0 e5** 10 % OSHA ceiling	**150** NAAQS

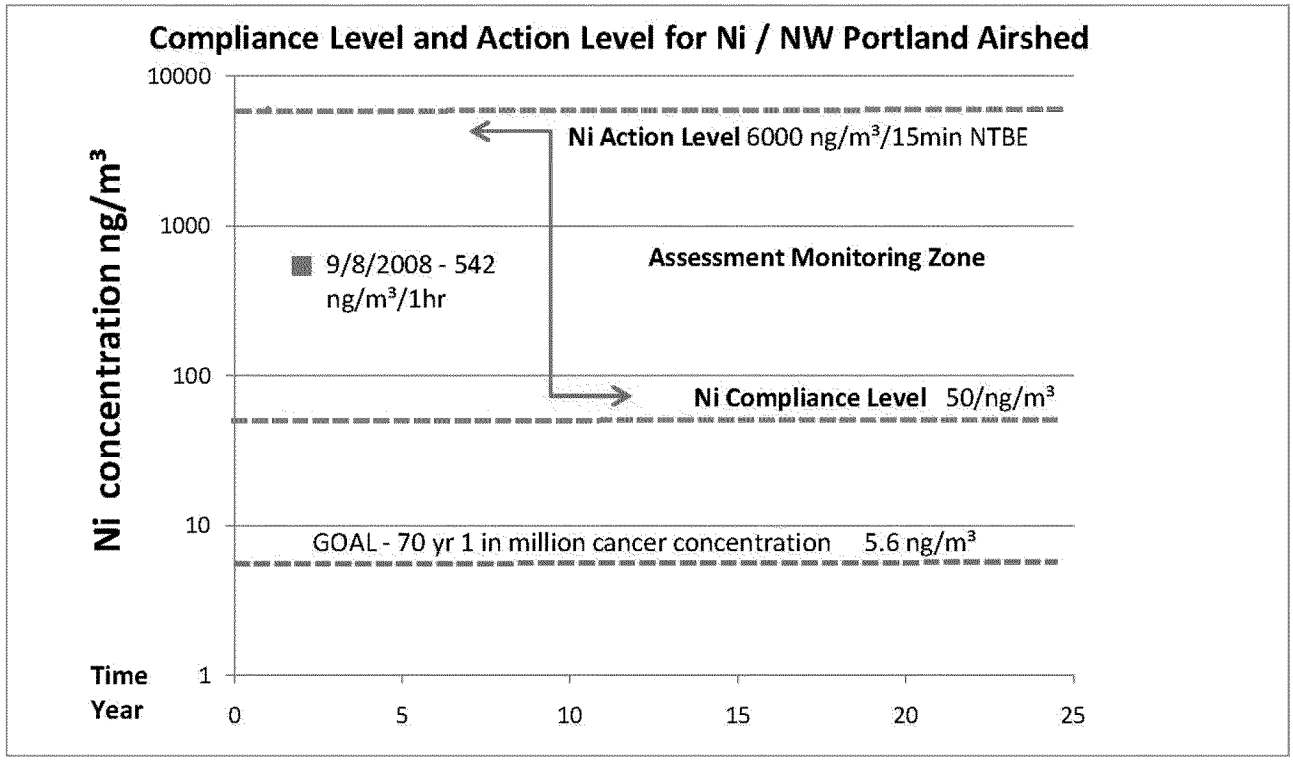

Figure 2. Hypothetical compliance Plan for The Foundry airshed using Ni as general parameter

3.0 Local Airshed Characteristics

3.1 Meteorological Characteristics

The climate of Portland, Oregon, is classified as Marine West Coast type, which is characterized by warm, dry summers and rainy, temperate winters. Summertime highs, occurring in July and August, average around 26.2 °C (80 °F). Temperature averages rarely fall beneath freezing in winter months, however the area does experience occasional major snows and ice storms due to cold winter air flowing west from the nearby Columbia Gorge. Cold snaps are short lived. The Pacific Northwest is on-average the rainiest region in the continental United States. Portland averages 941 mm (37 inches) of precipitation per year, with the majority of occurring from November thru March.

The Foundry is located near the confluence of the Willamette River and the Columbia River, in the northern reaches of the Willamette River valley and the western extent of the Columbia River Gorge. Topography increases out of the valley to the south and west. Local elevation in downtown Portland is 15.2 m (50 ft) **(Figure 3)**.

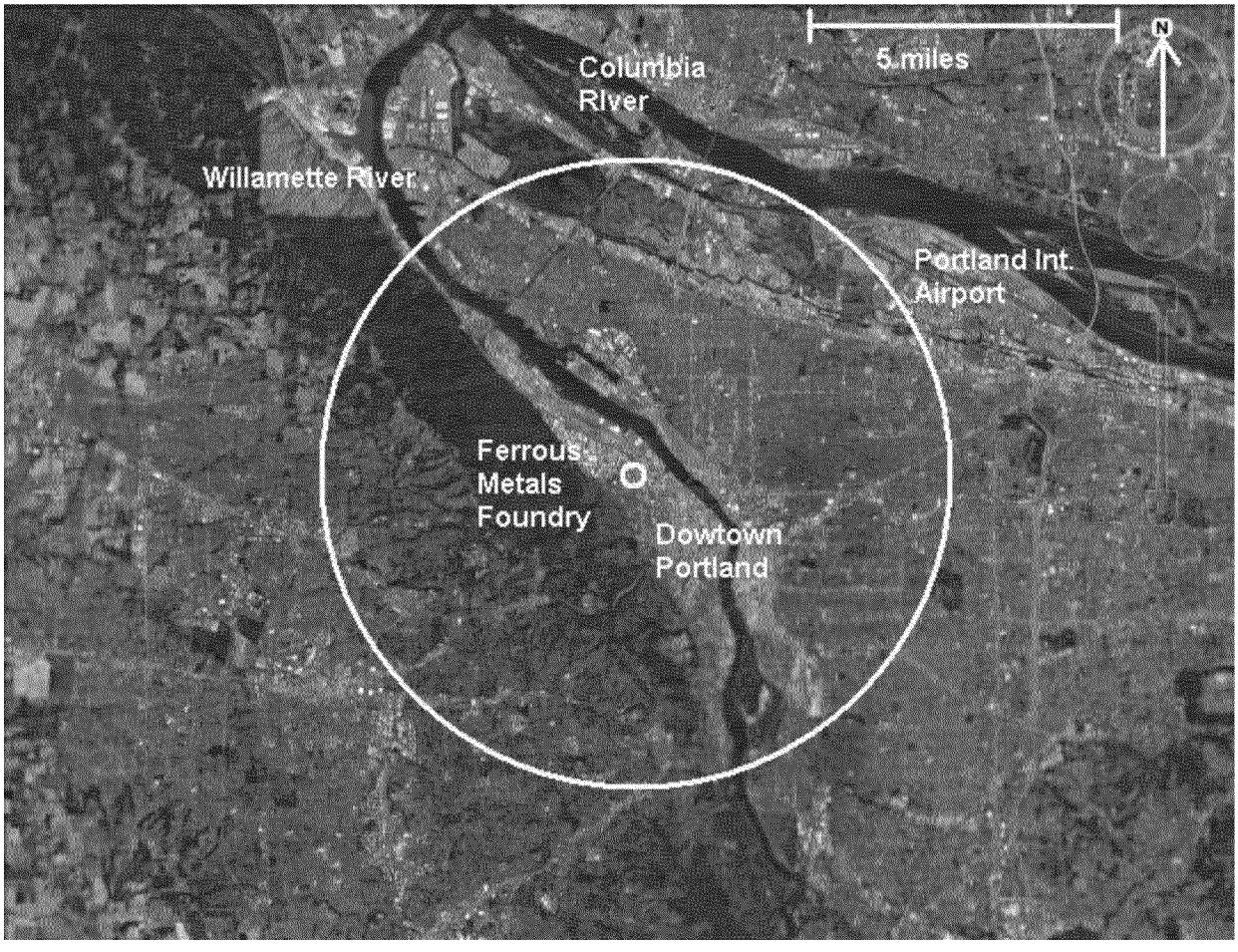

Figure 3. Map of The Foundry's Airshed in Portland, Oregon

Wind conditions near The Foundry are highly variable and seasonal, influenced by the topography of the area and the Columbia Gorge. However, winds are generally from the northwest with an average speed of 8 mph **(Figure 4).**

3.2 Source Characteristics – Ferrous Metals Foundry

U.S. EPA's Toxic Release Inventory (TRI) data states that in 2009 the facility emitted 834 lbs of manganese compounds, 124 lbs of lead, 91 lbs of chromium, 69 lbs of nickel and 62 lbs of molybdenum. These metal totals were calculated by the through-put of the facility and the total steel volumes production. Metals concentration data emerging from the ambient multi-metals sampling devices should proportionally reflect TRI data.

Metals emissions at The Foundry occur through the stacks and as fugitive emissions from foundry processes. Generally, emissions can be divided into primary emissions occurring during the melting and refining of the metal, and secondary emissions associated with charging, tapping and slagging. Emissions may also occur through handling and preparation of raw materials. The vast majority of emissions occur as primary emissions.

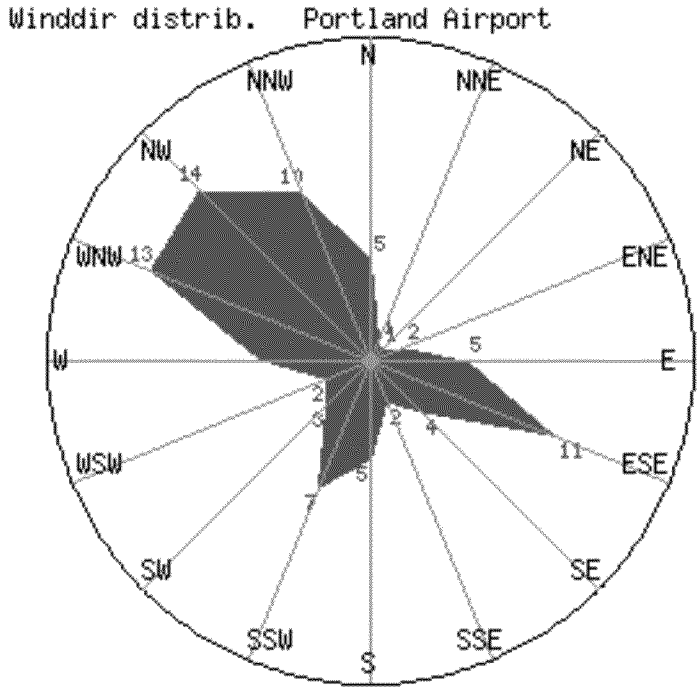

Figure 4. Annual wind direction diagram from Portland International Airport

The Foundry utilizes one 15 ton and one 9 ton electric arc furnace for the majority of the steel melting process. Upon introduction of the scrap metal and charge to the furnace, additional alloys such as nickel, molybdenum or silicon may be added depending upon the specifications of the end product. A full charge in the 15 ton furnace takes at least 2 hours to reach optimal tapping temperature at 3,200 °F.

A significant amount of metals emissions occurs during the melting process, and exhaust gas concentration may exceed 23,000 mg/m³ PM. Emissions control devices and technology like direct furnace evacuation, roof mounted hoods and canopy hoods are designed to direct airflow into baghouses and wet scrubbers before emission through the stack and into the airshed. However, the stacks at The Foundry are less than one hundred feet high, and under certain conditions may fumigate high-metal emissions into the local airshed. Additionally, a portion of the particulate matter escapes capture by the hood and is released into the local airshed untreated as fugitive emissions. See **Figure 5** for an aerial map of The Facility.

The scientific literature on metals foundry processes shows that a degree of source apportionment is possible based upon the unique particle size and chemistry of the metals air sample. For instance, a sample high in the smaller $PM_{2.5}$ range indicates high temperature fugitive or stack emissions. Samples in the coarse fraction between $PM_{2.5}$ and PM_{10} are more likely to be from mechanical or metals dust sources.

Through analysis of the TRI data, The Foundry is the largest source of metals contributing to elevated concentrations in the residential neighborhoods south of the facility. However, since there are a wide variety of industries in the north and northwest Portland airshed, including

additional foundries, an area wide source apportionment could assist in further characterizing ambient metals data in the region.

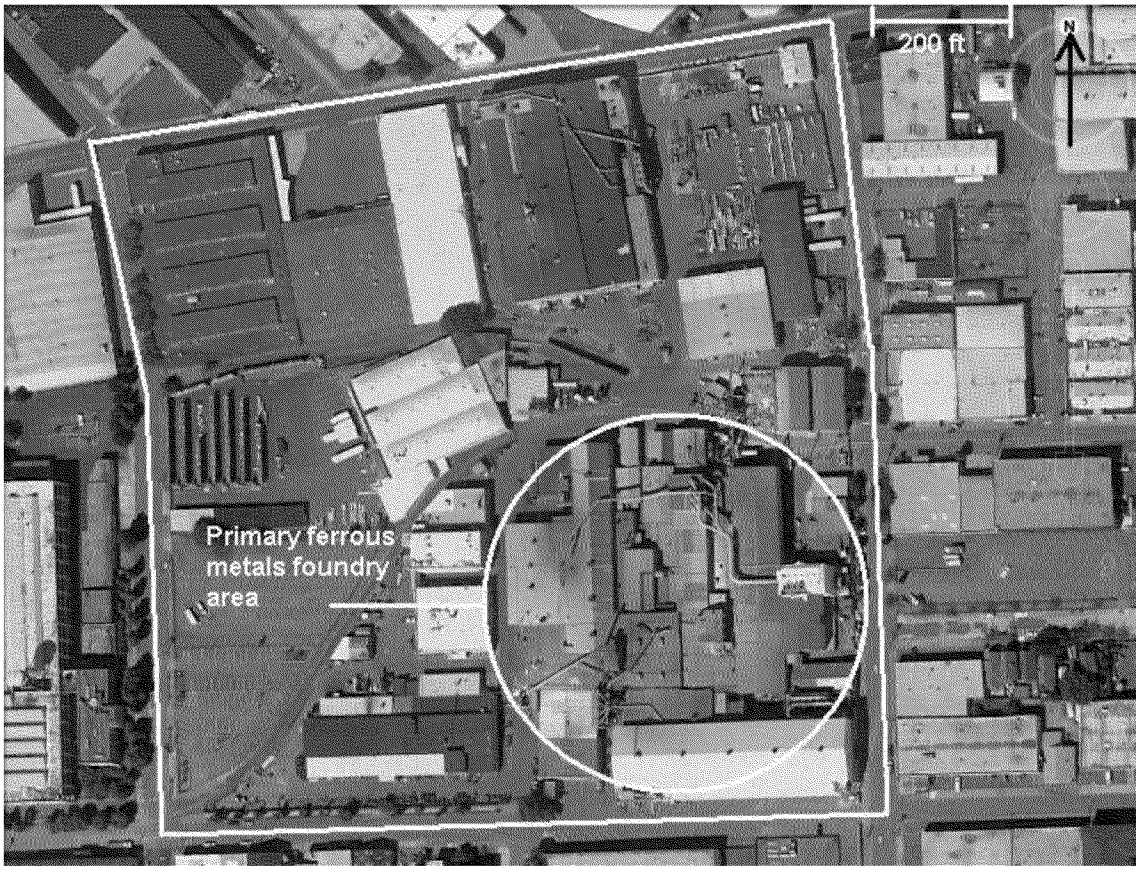

Figure 5. Ferrous Metals Foundry Aerial Map

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 in order to fully characterize sources and receptors. Variable wind speeds and direction make consistent, comprehensive air monitoring more complex. Local, real-time meteorological wind and precipitation data is be necessary to characterize any potential contaminant transport in the area and will be used in close conjunction with the continuous ambient metals data to analyze potential emissions sources.

4.1.2 Elements, PM and Sampling Frequency

The ambient air multi-metals monitoring devices will monitor for the primary and secondary elements of health and regulatory concern, as well as accompanying metals.

Primary Elements of Health and Regulatory Concern: The primary elements of concern from Foundry emissions include manganese (Mn), lead (Pb), chromium (Cr) and Nickel (Ni).

Secondary Elements of Health and Regulatory Concern: cadmium (Cd), cobalt (Co), arsenic (As), antimony (Sb), mercury (Hg), and selenium (Se).

Accompanying metals: potassium (K), calcium (Ca), barium (Ba), titanium (Ti), vanadium (V), copper (Cu), zinc (Zn), silver (Ag), gallium (Ga), iron (Fe), bromine (Br), tin (Sn), and antimony (Sb)

The ambient air metals FLM devices will be outfit with a PM_{10} inlet to limit particle size of the sample matter. A ten micrometer inlet samples both the fine and coarse particle fraction of ambient metals. In general, smaller size fraction in metals emissions indicates a high heat, melting and refining process, and therefore can be utilized for basic source apportionment of emissions. However, since the focus of the Plan is based on community health concerns, the larger size fraction is appropriate to capture the full extent of HAP emissions. As the study progresses, if finer particle size inlets are deemed necessary for source apportionment, a $PM_{2.5}$ inlet size can be employed as well.

Because of the Multi-Metals Monitoring Plan financial constraints, the specific contaminants of concern, and historic data that indicates no immediate threat to human health, multi-metals samples will initially be collected on a two-hour time interval. Two-hour sampling intervals can more accurately characterize ambient metals concentrations than 24-hour sampling, while not requiring as much financial inputs as one-hour sampling. If data emerging from the instrument indicates that more frequent sampling is necessary, the sampling interval would be adjusted.

4.1.3 Plant Processes and Events

The general processes at The Foundry include the melting, refining and casting of ferrous metals into industrial components. The majority of fugitive and stack emissions are directly related to metals melting in the electric arc furnace and refining in the argon-oxygen decarburization (AOD) vessels. Plant processes and events will be monitored closely and detailed records of Foundry operations will be kept by plant managers.

If Action Levels are exceeded and the emission is traced to The Foundry, regulators would meet with Foundry managers to discuss emission control options and a corrective action plan. If ambient metals concentrations pose an immediate threat to human health, operations would be suspended until The Foundry's emissions control technology can be repaired or replaced, or until the source of the emissions is understood and controlled.

4.2 Monitoring Sites

Multi-metals ambient air monitoring devices will be located utilizing established site guidelines for air sampling promulgated by the U.S. EPA (EPA, 1987). For this example, three sampling sites have been established to characterize ambient metals exposure in The Foundry's airshed.

The primary factors influencing multi-metals ambient air monitor locations are the variable wind regime in Portland, Oregon **(Figure 4),** sensitive receptors within the community like homes and schools, the project's financial limitations, and ease of access.

4.2.1 Ambient Metals Monitoring Site Locations

A primary driver of the Multi-Metals Monitoring Plan is the need to address community concerns over ambient metals exposure associated with The Foundry. Metals concentrations at Chapman Elementary school, located less than seven blocks from The Foundry, have especially been of concern. The goals of the plan are to characterize short-term metals emissions in the airshed near The Foundry and to assess risks to human health. That being the case, monitoring location **AMM #1** is located at Chapman Elementary School in northwest Portland.

In order to confidently apportion metals concentrations in northwest Portland to The Foundry, characterize metals concentrations, and assess impacts in the neighborhoods immediately downwind of the facility, another monitoring site location **AMM #2** is located directly south east of the facility, which is the majority downwind direction, at the corner of NW 24th Ave. and NW Vaughn St.

To assess the metals fumigation further from the facility in the center of the northwest neighborhoods, another multi-metals sampling site **AMM #3** is located at Metropolitan Learning Center, 2033 NW Glisan St. This school was also ranked in the bottom 5% for air quality in The Smokestack Effect article and study, and modeling shows impact from The Foundry and other northwest Portland industrial facilities.

These three sampling locations will sufficiently characterize the metals emissions from The Foundry as well as assess the emissions and health impacts in northwest Portland neighborhoods. **(Figure 6)**

4.3 Monitoring Plan

For this hypothetical example, a Monitoring Plan has been developed which involves a one-year study utilizing a mobile NRT multi-metals sampler, and is designed to assess ambient metals concentrations in the northwest Portland airshed without accruing large operational costs. One NRT multi-metals ambient air monitoring device will be deployed at each monitoring site, AMM #1, #2, and #3, for a period of 4 months. NRT continuous ambient metals data will be gathered and analyzed at each site to determine local health risks. After the 4 month period is over, the monitor will be relocated to the next site. In order to characterize The Foundry's metals emissions, AMM #2 will be the first monitored site, followed by AMM #1 and AMM #3. If concentrations of metals are detected above Plan Action Levels, the number of air monitors and sampling locations could be increased. The Monitoring Plan provides essential monitoring capability with a relatively small footprint and lower associated costs to assess if consistent air quality risks are present in the north Portland airshed surrounding The Foundry.

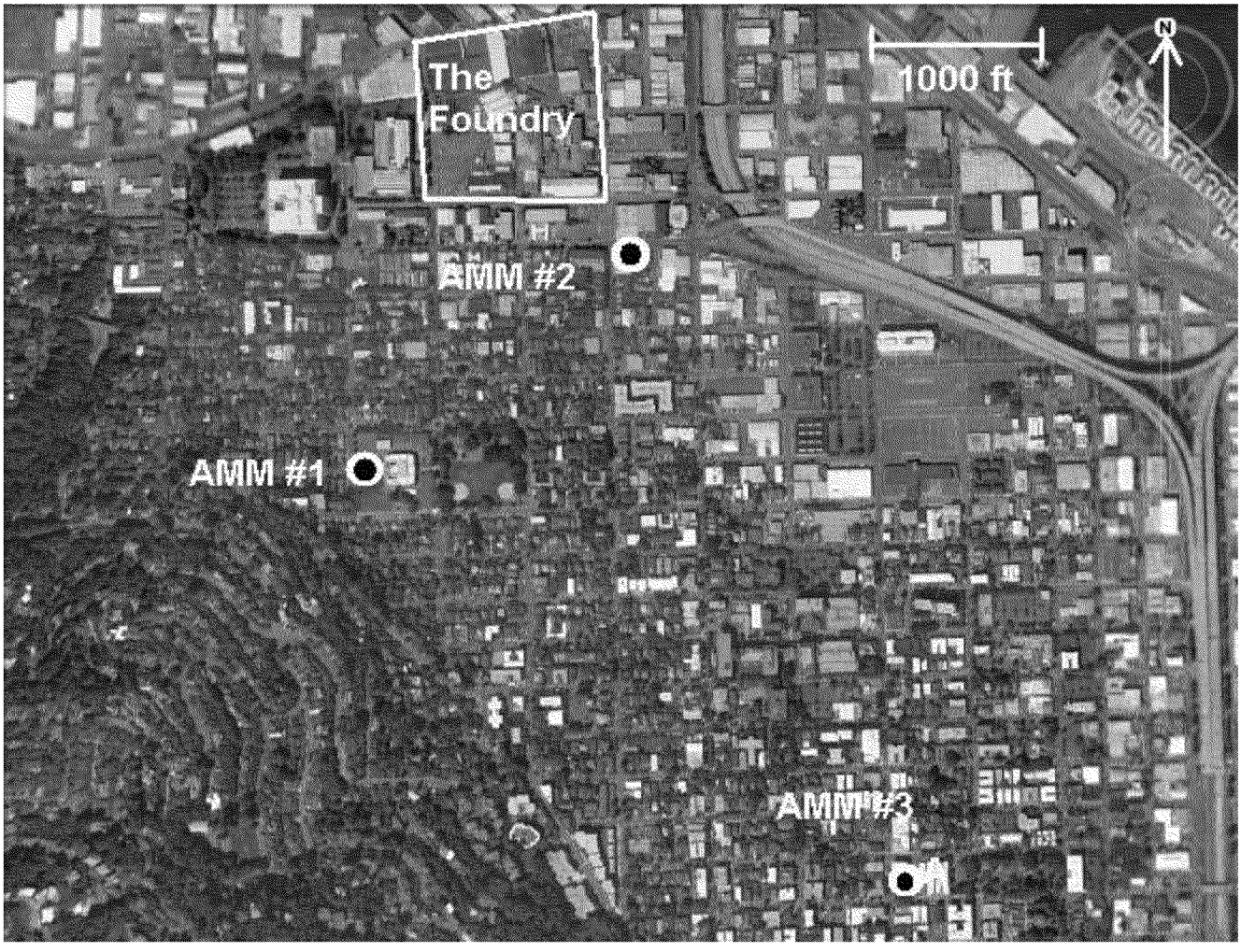

Figure 6. NRT multi-metals sampling site location s in northwest Portland

4.4 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 sampling once every four hours. Higher data resolution provides more information to regulators to assess and protect worker and public health, and to more fully characterize industrial operations on emissions. Air samples are collected on a tape medium that is relatively expensive. In this case, due to the duration of the study (1 year), the number of monitors (1), and the toxicology of the metals in question, the multi-metals ambient air sampling device will initially be programmed to sample every two hours. After three months of ambient air sampling, data will be analyzed to determine if a change in sampling frequency will maintain the data quality goals of the project while reducing associated costs.

Data will be available within two hours of the sampling event, streamed via wireless or cabled connection to regulators, 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 by regulators.

The NRT multi-metals ambient air monitors will be protected from weather conditions with a shelter and rain guard. A PM_{10} inlet will funnel particulate to the sampler, and electrical lines and data acquisition cables will run from the shelter to the nearest phone/internet connection.

If emerging data indicates that a more comprehensive ambient air monitoring approach is necessary to achieve project goals, additional multi-metals ambient air monitoring devices can be located taking into account the general wind regime in the region (see figure 4) and potential public receptors.

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 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

For this example, the Multi-Metals Monitoring Plan is a sampling program managed by environmental regulators to characterize threats to the local airshed, address the local community's request for more comprehensive air quality data, and to further regulators, engineers and scientist's understanding of hazardous metals emissions, pollutant dispersion, and industrial processes. While open to comment from local interest groups and industry, regulators at the state and federal level will have full control and responsibility for the continuous multi-metals ambient air monitoring plan.

Regulators will maintain contacts with representatives from the city governments of Portland, Oregon, local radio and television stations, representatives from relevant local industry, and potential sensitive local receptors such as hospitals and schools. Regulators will compile quarterly multi-metals ambient air sampling data and provide a report summarizing the data to the public, as well as appropriate state, federal, and local authorities.

4.4.3 Plant

Near real-time data emerging from the ambient metals-air monitoring system will be provided to The Foundry and other potential sources of metals emissions. Upon exceedence of an action level, regulators will analyze the meteorological and metals data emerging from the monitors to attempt to determine a source. If a source is identified, the probable polluter would be notified and corrective actions would ensue. In the event that multi-metals ambient air sampling data indicates that The Foundry's operations are resulting in emissions dangerous to human health and the environment, regulators would request that the facility's operations be suspended until the cause of the exceedence is determined and the issue is addressed. The Foundry would suspend operations using established safety and shut-down protocol.

4.4.4 Internet and Public

Regulators will maintain a public internet location that details the ambient air multi-metals monitoring program goals, shows the data emerging from the monitoring location(s), and provides a venue for regulators to answer any questions that the public or industry may have over the monitoring program and local industrial operations. Data on the site will be updated daily to ensure quality assurance of the reported values.

In the event a multi-metals ambient air monitoring Action Level is exceeded, regulators would notify local television and radio, as well as sensitive receptors such as schools and hospitals. Recommendations would be given for those at elevated risk like children, asthmatics 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 the state, local and federal authorities.

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APPENDIX H

Example Application: Waste Incinerator

DRAFT

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

MACTEC Work Order No.: 20081752
MACTEC Project No.: 827008S407

Submitted To:
MACTEC Federal Programs
Research Triangle Park, NC

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December 9, 2010

Summary

This hypothetical example details how the Guide for Developing a Multi-Metals, Fence-Line Monitoring Plan for Fugitive Emissions Using X-Ray Based Monitors (Guide) can be applied to a highly industrialized area of a large metropolitan airshed in which the driver is a measured transient spike in ambient arsenic concentration. In this example, the source of the arsenic emission is unknown, but it is hypothesized to be intermittent fumigations by stack emissions from a hazardous waste incinerator. The Guide therefore is used to develop an air monitoring plan to monitor and characterize local air quality issues in a highly active, industrial airshed. The primary objectives of this example are to: 1) illustrate how to develop a monitoring plan in an urban area with unknown air quality risks that is designed to qualify risks and identify emission sources, and 2) provide a guideline for a local ambient metals air monitoring plan that includes discussion of location criteria, action concentrations, airshed compliance concentrations, and a corrective action pathway.

The hazardous waste incineration facility (The Facility) is located in an industrialized area near East St. Louis, Illinois, in a town incorporated as Sauget, Illinois. The Facility has three incinerator units which combust halogenated solvents, acids, propellants, and other highly volatile and toxic chemicals. Emissions from The Facility are part of an airshed which passes over an industrial area, the Mississippi River, residential areas, and schools of Sauget, Illinois, Cahokia, Illinois, St. Louis, Missouri, and East St. Louis, Illinois. In this hypothetical example, regulators have developed a continuous multi-metals ambient air monitoring plan to monitor and characterize local air quality issues, protect human health and the environment, identify potential sources of emissions, and to alleviate the local community's concern. Continuous ambient metals air monitoring, when combined with meteorological records and facility processing records, is a tool for regulators to assess public health risks, locate polluters, and enforce compliance with applicable standards.

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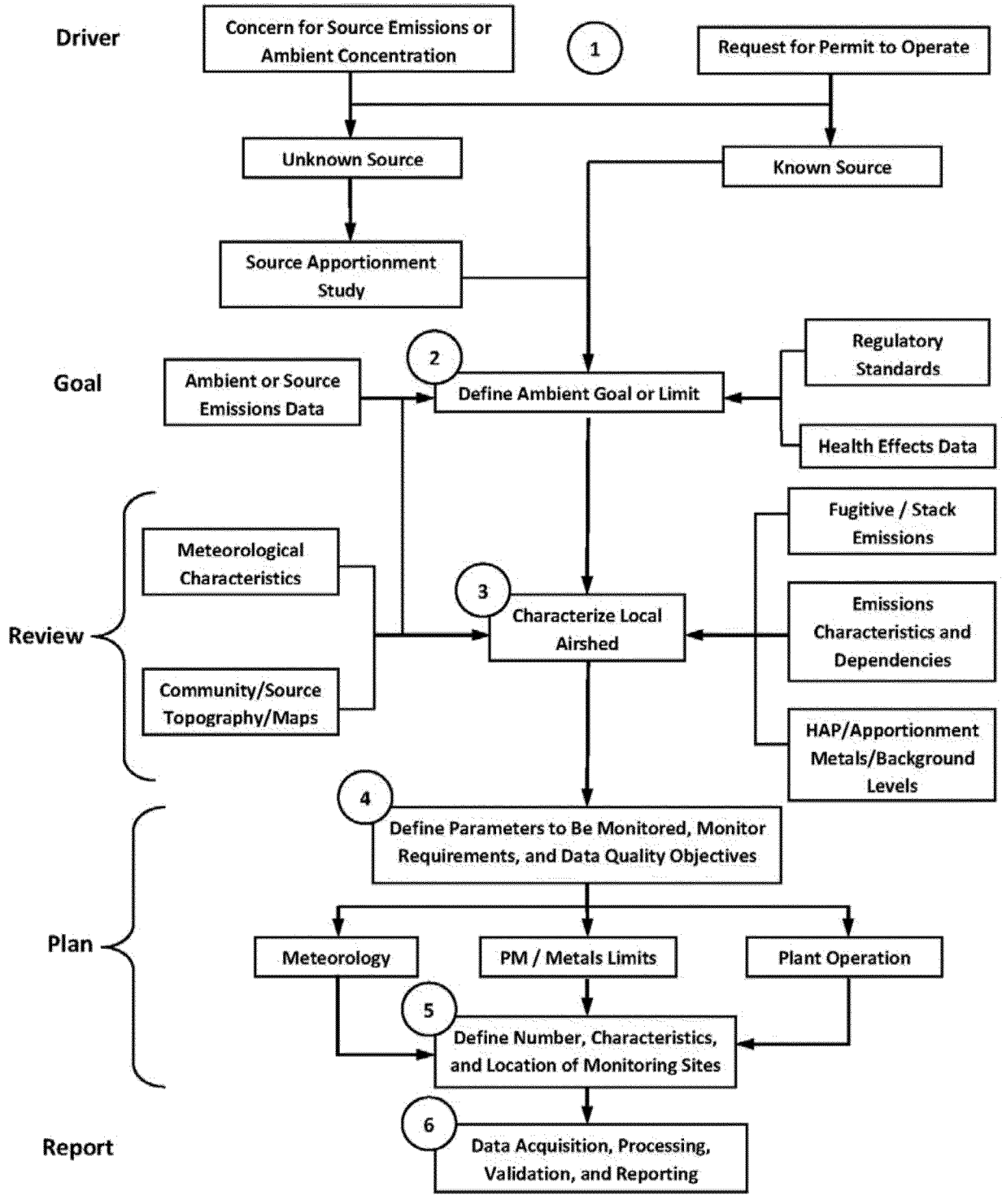


Figure 1. Procedure Flow Diagram

1.0 Driver – Arsenic (As) Episode

1.1 Arsenic Event

On April 13th, 2009, an ambient metals air quality sampler located less than two miles northeast of a hazardous waste incinerator (The Facility) in an East St. Louis, Illinois, residential area recorded an arsenic concentration of 2.34 µg/m³; a level potentially dangerous to human health and the environment. Examination of public records and meteorological data from April 13th strongly suggests that the hazardous waste incinerator is the probable source of the arsenic, however there are numerous other industrial operations in the area and The Facility does not claim responsibility for the release. Because the arsenic release appears to be an isolated occurrence, a comprehensive source apportionment study has not been conducted. However expansion of ambient air hazardous metal sampling is necessary to monitor for future releases and characterize the local airshed.

A description of the arsenic event outlines some of the issues surrounding ambient air sampling and source identification in the Sauget, Illinois, area. During the April 13th, 2009, arsenic event, early morning wind direction was from the northeast at about 7 mph. Around 10:00 am, with wind direction shifting clockwise from out of the east and south, arsenic levels were recorded at 0.76 ng/m³. However, by 12:00 pm, winds had continued to shift clockwise to where the wind was primarily from the southwest, creating a wind vector directly from The Facility to the ambient metals air sampling device, and arsenic readings quickly spiked to 2345 ng/m³. As winds continued to shift clockwise, by around 2:00 pm direction was from the west, and arsenic concentrations declined rapidly. Arsenic concentrations at the monitor decreased from 173 ng/m³ around 2:00 pm, to 11 ng/m³ around 4:00 pm, and 2.4 ng/m³ around 6:00 pm (2009, Missouri DNR). It is probable that arsenic levels remained elevated throughout the course of the day, but declined because the ambient metals air monitor was no longer directly in the air contaminant pathway. **(Figure 2 & 3)**

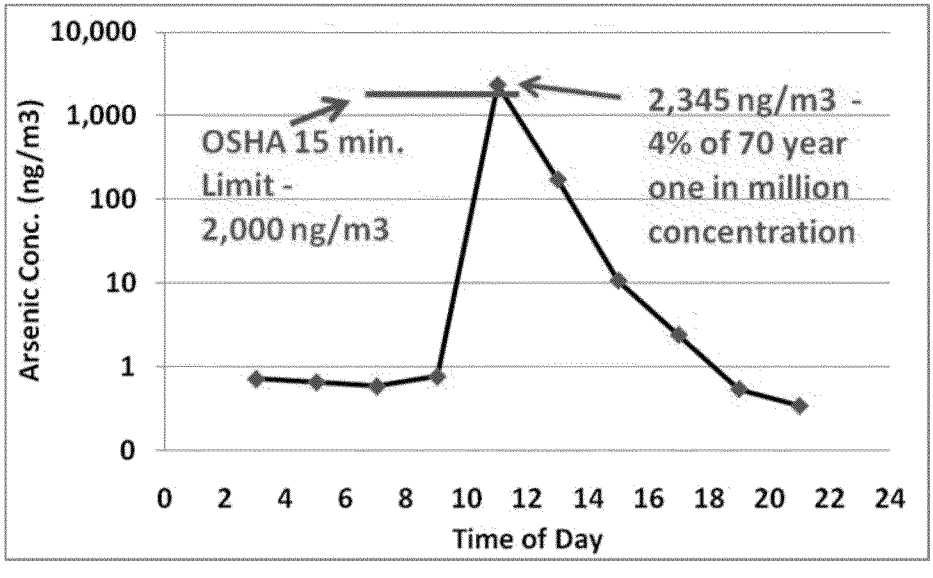


Figure 2. As conc. at metals monitor, April 13, 2009, (sample times shown as mid-points)

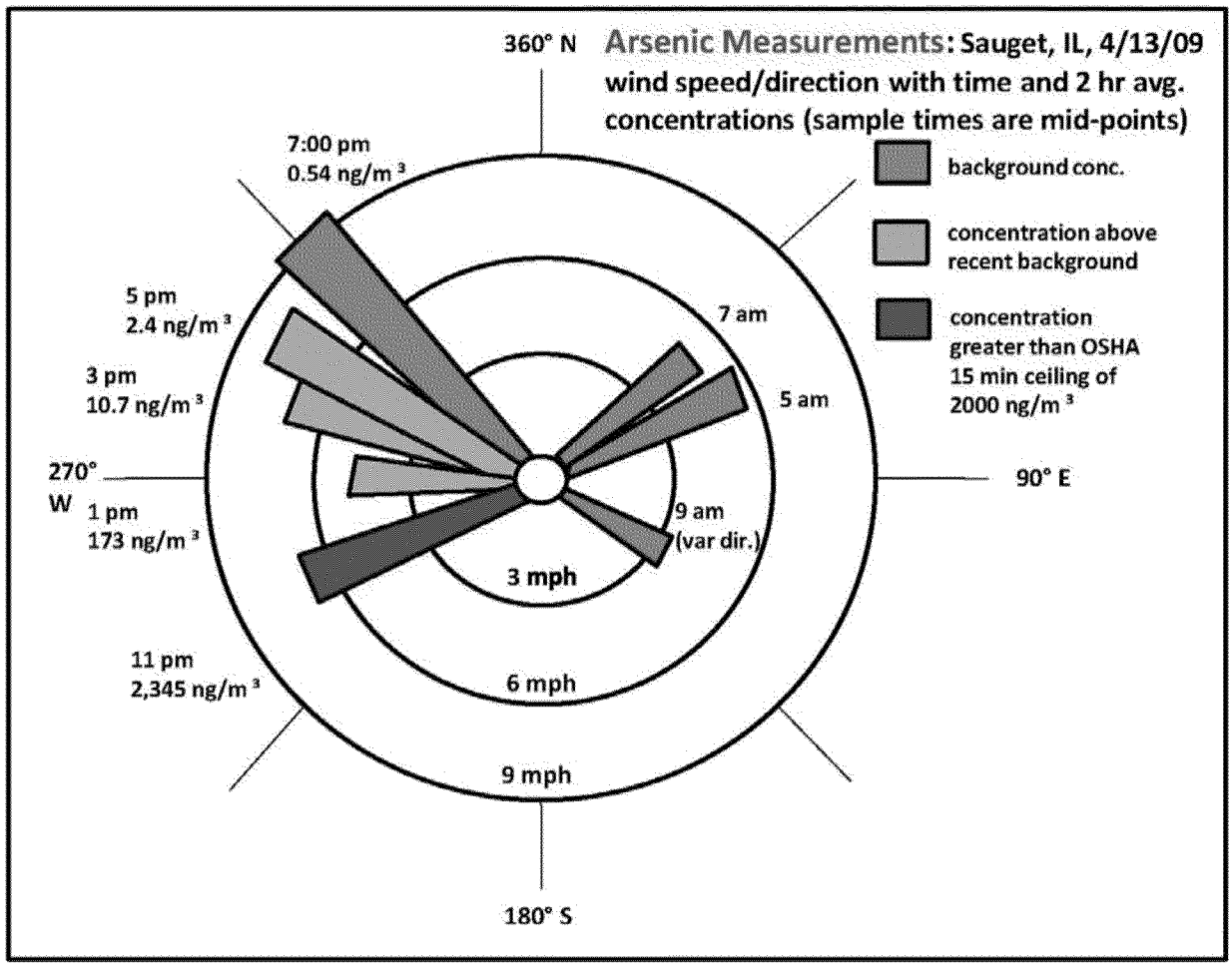


Figure 3. Arsenic Measurements with Cahokia, IL, airport wind data, 5:00 am – 7:00 pm, April 13, 2009, Sauget, Illinois

1.2 Cause/Source

The hazardous waste incineration facility is located on a 35 acre site in Sauget, Illinois, adjacent to the Mississippi River near East St. Louis, Illinois. The Facility processes hazardous waste through combustion in two fixed-hearth, dual chamber, multi-type feed incinerators with 100 feet stacks, and one rotary kiln incinerator with a 100 feet stack. The site also includes ten container storage units, three material processing areas, a waste drum decant area, and a full analytical laboratory. The Facility is permitted by the federal Environmental Protection Agency (EPA) and the Illinois Environmental Protection Agency (IEPA) under the Resource Conservation and Recovery Act (RCRA) and Title V of the Clean Air Act (CAA). The site must renew its permit every five years. The last permit was issued in 2008 and will be reviewed for renewal in 2013.

Services at The Facility include the processing and incineration of hazardous waste such as lab packs, water reactive chemicals, oxidizers/organic peroxides, halogenated solvents, organic acids, propellants, and explosives. Hazardous waste re-packaging is also conducted on-site.

The wastes are transported to The Facility by tank trucks, rail cars, or ship containers, and may be in solid, liquid, or sludge form. Due to the nature of The Facility's processes, there are numerous and diverse chemicals of concern (COCs) at the site, including organic air emissions from containers, dioxins and furans. Metals COCs include mercury, cadmium, lead, arsenic, beryllium, chromium, and antimony. Trace amounts of these metals are emitted through the stacks as part of the waste incineration process. However, faulty incineration has the potential to result in relatively large metals release to air. Fugitive release of contaminants is also of concern. Toxic Release Inventory (TRI) data from The Facility states that 37,277 pounds of arsenic compounds were shipped for off-site release or disposal in 2008. It is likely that this off-site disposal material is arsenic-contaminated incinerator ash from the waste incineration process, indicating a relatively large arsenic waste stream processed at The Facility.

The Facility is located in a highly industrialized airshed. Air emissions are from industrial activity, heavy traffic, and railway operations. Besides The Facility's hazardous waste incinerator, other industries in the Sauget, Illinois, area include a mainly inactive primary zinc smelter, a marine shipping terminal, a number of large chemical corporations, mid-sized manufacturers, and an oil company supply terminal. **(Figure 4)** The area is also the home of the Dead Creek federal Superfund site; a waterway running through the Sauget area which is in the process of dredging and remediation for elevated metals, volatile organic compounds and PCBs.

The zinc smelter, the marine terminal, and a chemical company are also located directly southwest of the multi-metals ambient air monitor site, and therefore were within the arsenic vector pathway April 13, 2009. However US EPA's 2008 Toxic Release Inventory records show that the hazardous waste incinerator handles significantly more arsenic compounds than any other nearby facility. Specifically, the zinc smelter's records state a total of 4 pounds of arsenic compounds listed as off-site disposal or release, the chemical company lists zero, and the marine terminal, though It can store over 10 million gallons of industrial chemicals including herbicides and chlorobenzenes, as a storage facility isn't required to report TRI data.

While the hazardous waste incinerator is the most likely source of the April 13th, 2009, arsenic event, there are other viable source candidates. The multi-metals ambient air monitoring plan is designed to assess the ongoing threats to the airshed, and, if a release occurs, identify the source of emissions and pursue corrective action.

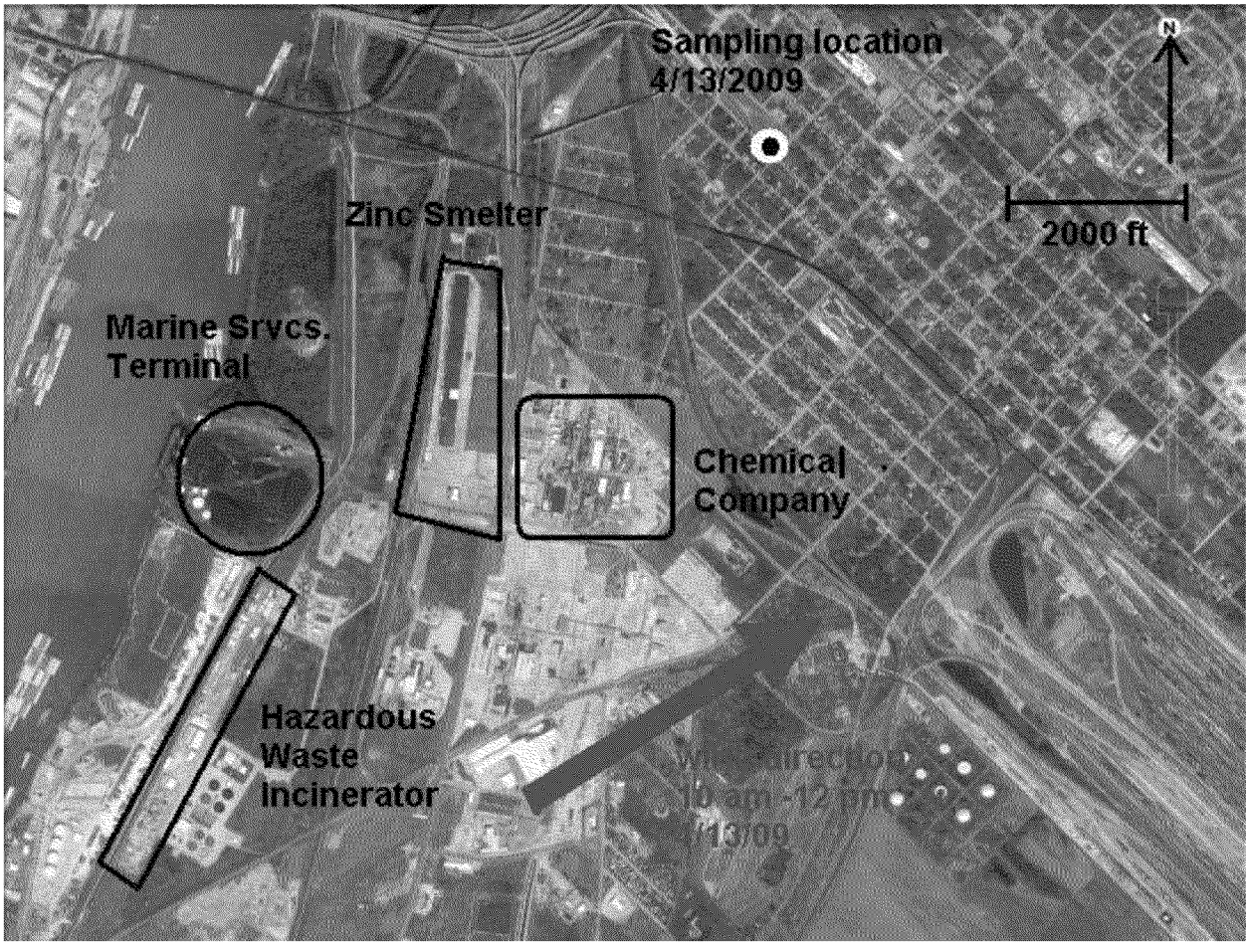


Figure 4. Map of local airshed detailing locations of potential arsenic sources, sampling location and wind direction, 4/13/2009.

2.0 Goals: Defining Ambient Goals and Compliance

In this hypothetical example, it is hypothesized that after the recent high arsenic episode, regulators decide to develop a Continuous Multi-Metals Ambient Air Monitoring Plan (Plan) to monitor local ambient air near The Facility and throughout the airshed using the Procedure Flow Diagram illustrated in **Figure 1.** The goals of the Continuous Multi-Metals Ambient Air Monitoring Plan are to provide comprehensive ambient metals air quality data within the local airshed to assess the public health threat, as well as to identify emission sources and enforce compliance with applicable standards and goals established.

Local airshed ambient air monitoring was chosen as a viable air quality monitoring and regulatory approach due to a number of issues and concerns:

1) Due to the number of potential hazardous air pollutant sources in the area, no fully confirmed source, and intermittent toxic emissions, ambient air monitoring will provide the broadest data of the overall health of the airshed and will adequately assess risks to human health and the environment.

2) The primary receptors for air-born particulate metals contamination are the residents of Sauget, Illinois, East St. Louis, Illinois, and St. Louis, Missouri.

3) The Facility has three (3) 100 feet stacks, making fence-line monitoring ineffective in characterizing a possible facility release.

4) Additional ambient data could be utilized to identify a source and proceed with corrective action including stack monitoring or a fugitive emissions study at the offending facility.

2.1 Ambient Emissions/Primary Elements of health/regulatory concern

Of the potential metals emissions in the region, arsenic concentrations in the industrial airshed are of primary concern. Numerous scientific studies indicate that short-term exposure to elevated arsenic concentrations poses significant risk to human health. During the April 13, 2009, arsenic event, concentrations exceeded acute one hour exposure limits set by the state of California at 0.2 µg/m³ by over a factor of ten, and exceeded the National Institute for Occupational Safety and Health (NIOSH) standard for acute 15 minute exposure to workers set at 2 µg/m³.

2.1.2 Secondary Elements of potential health concern

TRI Metals data from 2008 state that The Facility processed, disposed of, and/or incinerated well over 100,000 pounds of copper, zinc, silver, and manganese. Selenium is also of concern. At elevated concentrations these metals pose a significant risk to human health and the environment.

2.1.3 Source Apportionment Elements

A comprehensive source apportionment has not been conducted for The Facility or the local airshed. The Facility processes a wide range of hazardous materials and has a dynamic waste stream. Stack and fugitive emissions at The Facility generally depend upon the nature of the waste and the efficiency of the incineration process. Major source apportionment contaminants of concern at hazardous waste facilities generally include arsenic, mercury, cadmium, lead, chromium, beryllium, and antimony.

2.2 Regulatory Standards – Emission standards and Ambient Standards

United States EPA regulations 40 CFR Part 63 Subpart EEE, the National Emission Standards for Hazardous Waste Combustors, regulate emissions of hazardous air pollutants at incinerators, cement kilns, and lightweight aggregate kilns operating in the United States. The Federal Hazardous Air Pollutants (HAP) standards are based on the Maximum Achievable Control Technology (MACT) approach directed by the federal Clean Air Act which states that emission control technologies should be evaluated by their effectiveness, availability, current use, cost, and non-air environmental impacts.

The regulations limit emissions of mercury, semi-volatile metals (cadmium and lead), low-volatile metals (arsenic, beryllium, chromium, and antimony), particulate matter, acid gas

emissions (hydrochloric acid and chlorine), hydrocarbons, and carbon monoxide, as well as dioxins and furans. **(Table 1)** The USEPA has also developed feed rates for metals, hydrogen chloride and chlorine gas which are intended to curb toxic emissions and are a part of The Facility's permitted operation specifications and performance tests.

Table 1. HAP/MACT Metals Emission Limits for Hazardous Waste Incinerators for new and existing facilities

HAP MACT STNDRDS	Mercury (Hg)	Cadmium (Cd) and Lead (Pb)	Arsenic (As), Beryllium (Be), Chromium (Cr)
existing facilities	130 µg/m³	230 µg/m³	92 µg/m³ combined emissions
new facilities	8.1 µg/m³	10 µg/m³	23 µg/m³

Hazardous Waste Incinerators perform CAA-mandated Comprehensive Performance Testing every five years to gauge effectiveness of the waste incineration process and develop incineration protocol. However, successful completion of the performance test does not fully ensure that the incinerator remains in compliance between testing events. There are a number of factors that can affect incineration efficiency and stack emissions, including inadequate waste characterization, negligent monitoring of the incineration process, or issues with the incinerator's instrumentation. The relatively long period of time between performance tests also means that incremental changes in the performance of the incinerator may not be understood or characterized.

Air Quality Standards for the protection of human health and the environment that pertain to ambient air include federal Clean Air Act National Ambient Air Quality Standards (NAAQS), California Reference Exposure Limits (REL), and Regional Screening Levels (RSL). The NAAQS were developed to address nation-wide ambient air quality concerns for public health. California RELs and U.S. EPA's RSLs provide risk-based levels which, if exceeded, indicate a general increase in the health risks to a population. At levels below RELs and RSLs however no health risks are known. Occupational Safety and Health Administration standards (OSHA) and NIOSH standards were developed for worker safety and work-place industrial scenarios and give limits for 8 hour exposures, 10 hour exposures, and acute exposures to toxins and carcinogens.

Considering the metals contaminants of concern related to The Facility, lead (Pb) is regulated by the NAAQS, and mercury (Hg), arsenic (As), chromium (Cr), and cadmium (Cd) have associated air quality standards from California, Region IX of the EPA, and NIOSH that can be utilized to assess risk and compliance. **(Table 2)**

Table 2. Relevant Air Quality Standards, Reference Exposure and Screening Levels (µg/m3)

Element	Parameter	NIOSH/OSHA[a]	NAAQS[b]	Reg. IX RSL[c]	CA REL[d]
As	**Indicator**	**TSP As**	**n/a**	**TSP As**	**TSP As**
	Avg. Time	15 min.		chronic	1 hour
	Conc. Level	2		0.016	0.2
	Form	NTBE		risk based	NTBE
Cd	**Indicator**	**TSP Cd**	**n/a**	**TSP Cd**	**n/a**
	Avg. Time	8 hr.		chronic	
	Conc. Level	0.005		0.01	
	Form	NTBE		risk based	
Cr	**Indicator**	**TSP Cr**	**n/a**	**TSP Cr**	**TSP Cr**
	Avg. Time	8 hr.		chronic	chronic
	Conc. Level	1		0.01	0.2
	Form	NTBE		risk based	risk based
Pb	**Indicator**	**TSP Pb**	**TSP Pb**	**n/a**	**n/a**
	Avg. Time	8 hr.	3 mo. RA		
	Conc. Level	50	0.15		
	Form	NTBE	NTBE		
Hg	**Indicator**	**Vapor Hg**	**n/a**	**Vapor Hg**	**Vapor Hg**
	Avg. Time	8 hr.		chronic	1 hour
	Conc. Level	100		0.31	0.6
	Form	NTBE		risk based	NTBE

a. National Institute for Occupational Safety and Health or Occupational Safety and Health Administration

b. National Ambient Air Quality Standard

c. US EPA Region IX Regional Screening Level

d. California Reference Exposure Limit Not To Be Exceeded

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

Evaluation of monitoring data and meteorological conditions from the arsenic event, along with basic mathematical modeling, suggests metals concentrations averaged over 12 to 24 hours may be significantly lower than 4 hour averages, 2 hour averages or discreet 15 minute averages. Due to the nature of fugitive or erratic emissions, which are tied to specific plant processes, the majority of a metals release might occur over a relatively brief period of time. Dynamic wind conditions also result in varying concentrations recorded in an ambient metals air sampler. During the April 13, 2009, arsenic detection near the facility, arsenic levels were recorded 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 is around 362 ng/m³, which is an order of magnitude below the maximum arsenic value **(see Table 3).** The data shows that continuous, near real-time ambient metals monitoring produces high-resolution data that more accurately characterizes health risks within the local airshed.

Table 3. 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 µg/m³	6/6.5	2.34 µg/m³

2.4 Action Levels

With a limited number of COCs with National Ambient Air Quality Standards, monitoring goals of a continuous multi-metals ambient air monitoring plan are based on NAAQS, Region IX EPA Regional Screening Levels, California Reference Exposure Levels (REL), Agency for Toxic Substances and Disease Registry (ATSDR) standards, as well as NIOSH/OSHA standards for worker safety and health.

Compliance Goals for ambient toxic metals are set at levels below the NAAQS for lead and at the RSL for mercury, arsenic, chromium and cadmium **(Table 4).**

Since, high-risk receptors like children and pregnant woman should not be exposed to ambient toxic metals concentrations at or near workplace limits, Action Levels for the local airshed can be set at 10 % of OSHA workplace standards for chromium; the California REL for arsenic and mercury; the NAAQS value for lead; and the ATSDR acute value for cadmium. Action Level exceedences can be utilized to trigger corrective action, source apportionment studies, and source mitigation. (**Table 5)**

Table 4. East St. Louis/Sauget, Illinois, Ambient Air Quality *Compliance Levels* proposed for example

	Lead (Pb)	Mercury (Hg)	Arsenic (As)	Chromium (Cr)	Cadmium (Cd)
NAAQS/ Region IX RSL	150 ng/m³ Rolling 3 month avg	310 ng/m³	16 ng/m³	10 ng/m³	10 ng/m³

Table 5. East St. Louis/Sauget, Illinois, Ambient Air Quality *Action Levels* proposed for example

Lead (Pb)	Mercury (Hg)	Arsenic (As)	Chromium (Cr)	Cadmium (Cd)
150 ng/m³/3 month rolling	600 ng/m³/1hr	200 ng/m³/1hr	100 ng/m³ Per 8 hr TWA	30 ng/m³ Per 8 hr TWA

Continuous multi-metals ambient air monitoring devices will be located at critical meteorological points or at a sensitive nearby locations within the airshed such as a school or hospital. Considering the general distances of the monitoring device(s) from The Facility or other industrial fugitive emission sources, monitoring data at these residential locations near 10% the levels reflected in the OSHA work-place standards would suggest an air release of high volume and concentration. Without comprehensive federal or state ambient air regulations, ATSDR levels, EPA's RSLs, California RELs, and NAAQS Air Quality Standards provide a health and safety, as well as risk-based frame of reference by which regulators can base Compliance Goals and Action Levels.

2.5 Demonstrating Compliance

The continuous multi-metals ambient air monitoring program for the East St. Louis/Sauget, Illinois airshed is un-mandated environmental program developed by regulators to address local air quality concerns, identify potential polluters, and protect human health and the environment. Compliance will be demonstrated by comparing data emerging from the multi-metals ambient air monitors to the stated Compliance Levels and Action Levels stated in the plan. The continuous multi-metals ambient air monitoring devices can remotely communicate, which allows for ongoing monitoring of the air quality within the airshed. If Action Levels are triggered, the emissions source would be identified and corrective action would commence. **(Tables 4 & 5)**

Compliance Levels are risk based standards which delineate potential risk to human populations within the airshed. They are based on EPA Region IX Residential Screening Levels. At concentrations below Compliance Levels, no quantifiable risk due to ambient hazardous metals pollution is expected in the local airshed. At concentrations above Compliance Levels, health risks, while not imminent, begin to increase within the airshed. If a Compliance Level is surpassed by a monitored parameter, the parameter would go into an assessment monitoring period. Levels would continue to be closely monitored and a preliminary source investigation would proceed.

Action Levels are comprised of various ambient standards and are intended to provide a not-to-be-exceeded baseline for analyzing ambient metals data. If an Action Level is exceeded, a series of regulatory actions would ensue. **(Figure 5)** Utilizing real-time meteorological and air quality data, as well as general chemical fingerprint knowledge of potential sources, regulators should be able to identify or disqualify potential sources of the emissions. Upon identification of the source, regulators would notify the probable polluter. In the event it is The Facility, regulators would seek to initiate a temporary shut-down of the facility, and re-evaluate the waste

stream and incinerator processes including a subsequent additional performance test for the incinerator and installation of a stack emissions monitoring device. If an alternate local industry is identified as the source of emissions, an alternate corrective action plan would be developed. Regulators would report the full incident to federal, state, and local authorities.

General assumptions on source identification can be drawn from the historic scientific literature. Real-time meteorological data will also play a significant role in identifying local sources. In the event identifying a potential source(s) proves difficult and data readings surpassing action levels remain persistent, a comprehensive regional chemical mass balance source apportionment study would be initiated to fingerprint the local sources of air emissions, and to help evaluate the data emerging from the air monitoring devices. Regulators would sponsor the source apportionment study and develop a chemical fingerprint library for regional air pollution sources.

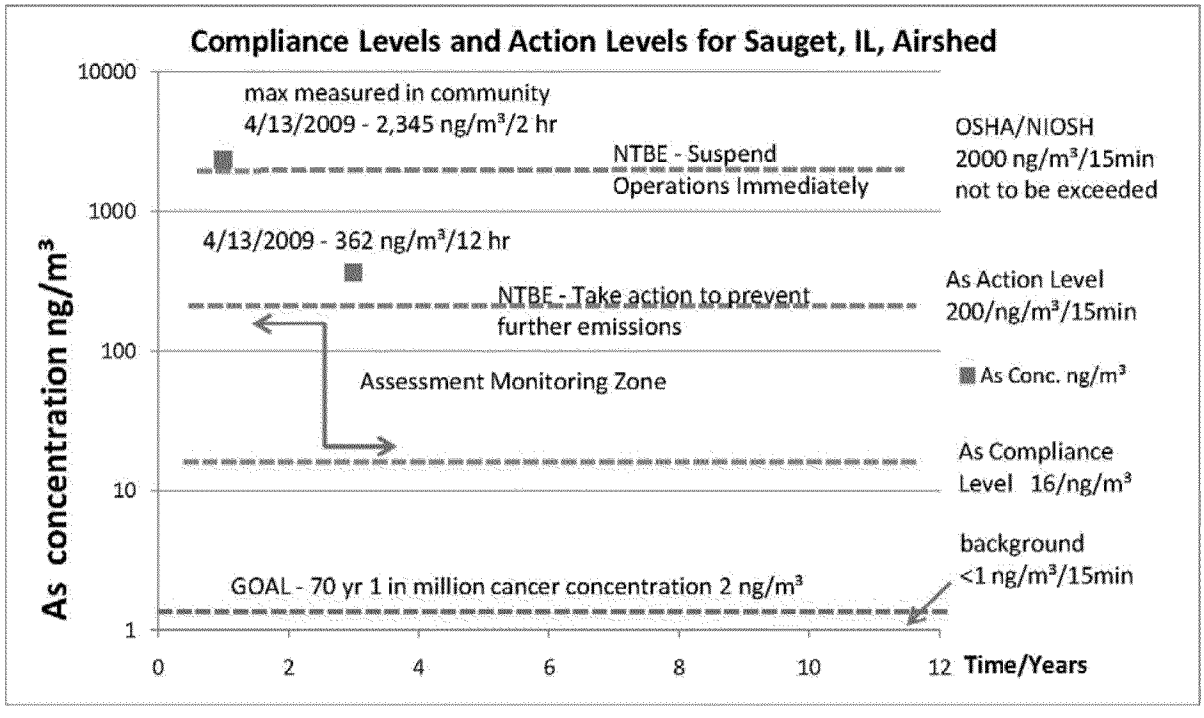


Figure 5. Compliance Plan for Arsenic in Sauget, IL, Airshed

3.0 Local Airshed Characteristics

3.1 Physical Features

The population of Sauget during the census in the year 2000 was 249 people. Nearby larger communities of Cahokia, Illinois, East St. Louis, Illinois, and St. Louis, Missouri, are located within three miles of The Facility and within the local airshed. Martin Van Lucas School, Dunbar Elementary School, and Maplewood Elementary School are all within The Facility's airshed and are potential receptors of elevated emissions from Sauget industries and the hazardous waste incinerator.

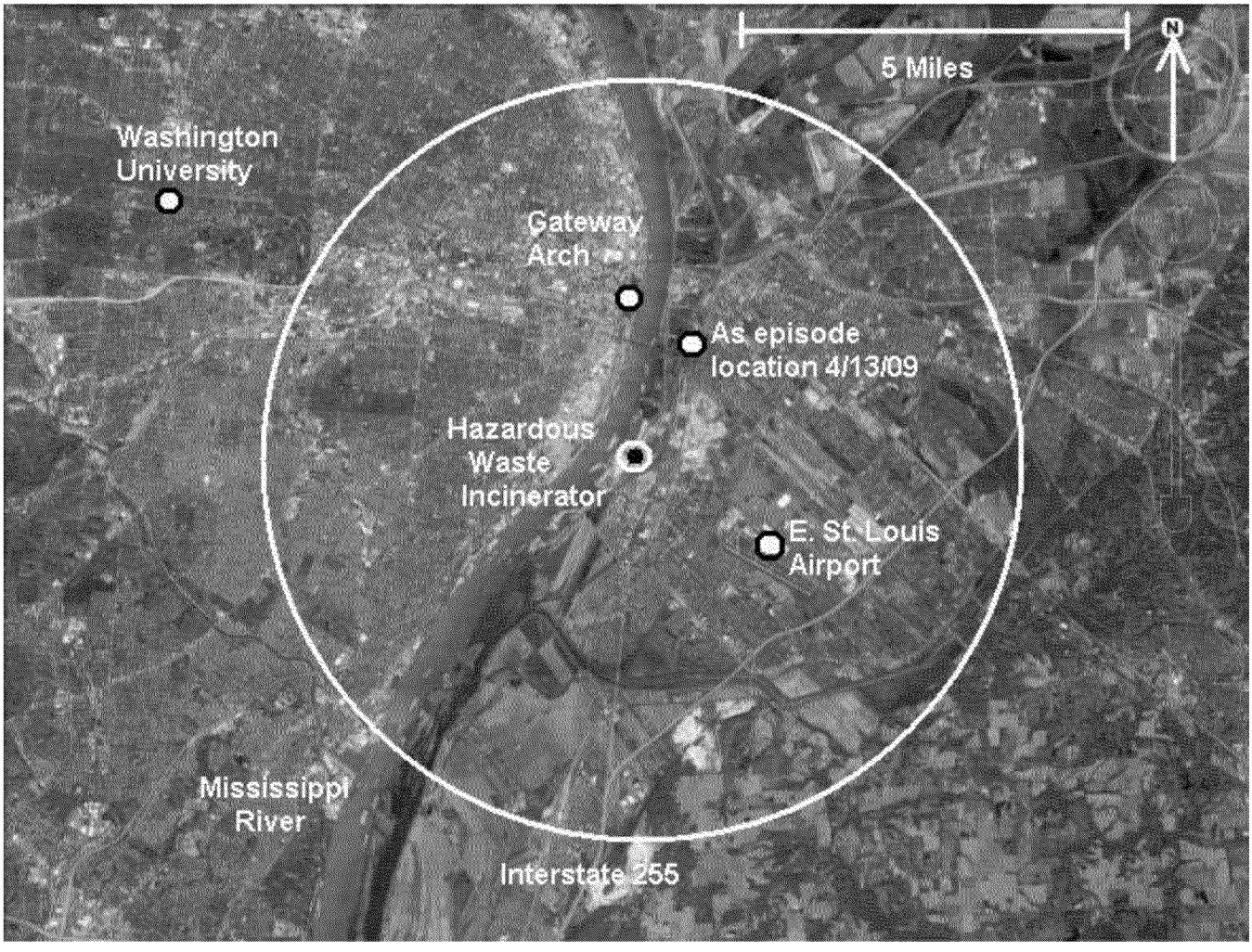


Figure 6. Hazardous Waste Incinerator Facility Map

3.2 Meteorological Characteristics

The Facility is situated on the Mississippi River flood plain, in an area known as the American Bottom, just adjacent to the channel of the river. The area is generally flat, with substantial flood plain soils and limited topographic expression. Wind speed and direction in the East St. Louis region is variable, but is generally from northwest and south/southeast, with an average speed of approximately 10 mph. **(Figure 7)**

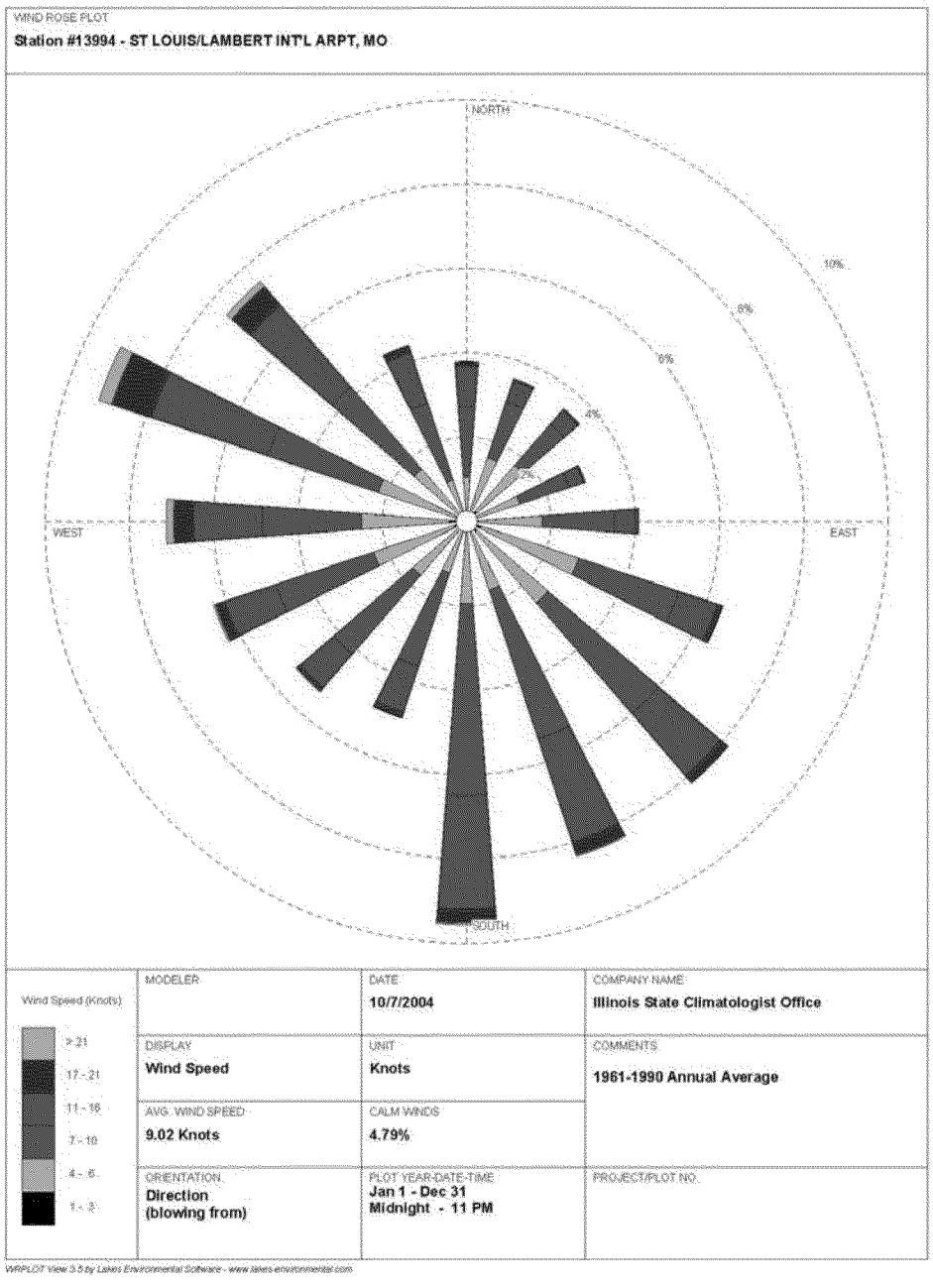


Figure 7. Average wind speed/direction, St. Louis, Missouri 1961-1990. 1 knot = 1.15 miles

The average annual temperature in the Sauget, Illinois, region is 56.3 °F, with average highs in July of 88.4 °F, and average lows in January of 22.6 °F. The area is located in the transition zone between humid subtropical and humid continental climates types, and receives on average

a total precipitation of 38.75 inches per year. A small but not insignificant majority of rainfall occurs during the spring months.

3.3 Source Characteristics –Hazardous Waste Incinerator Map

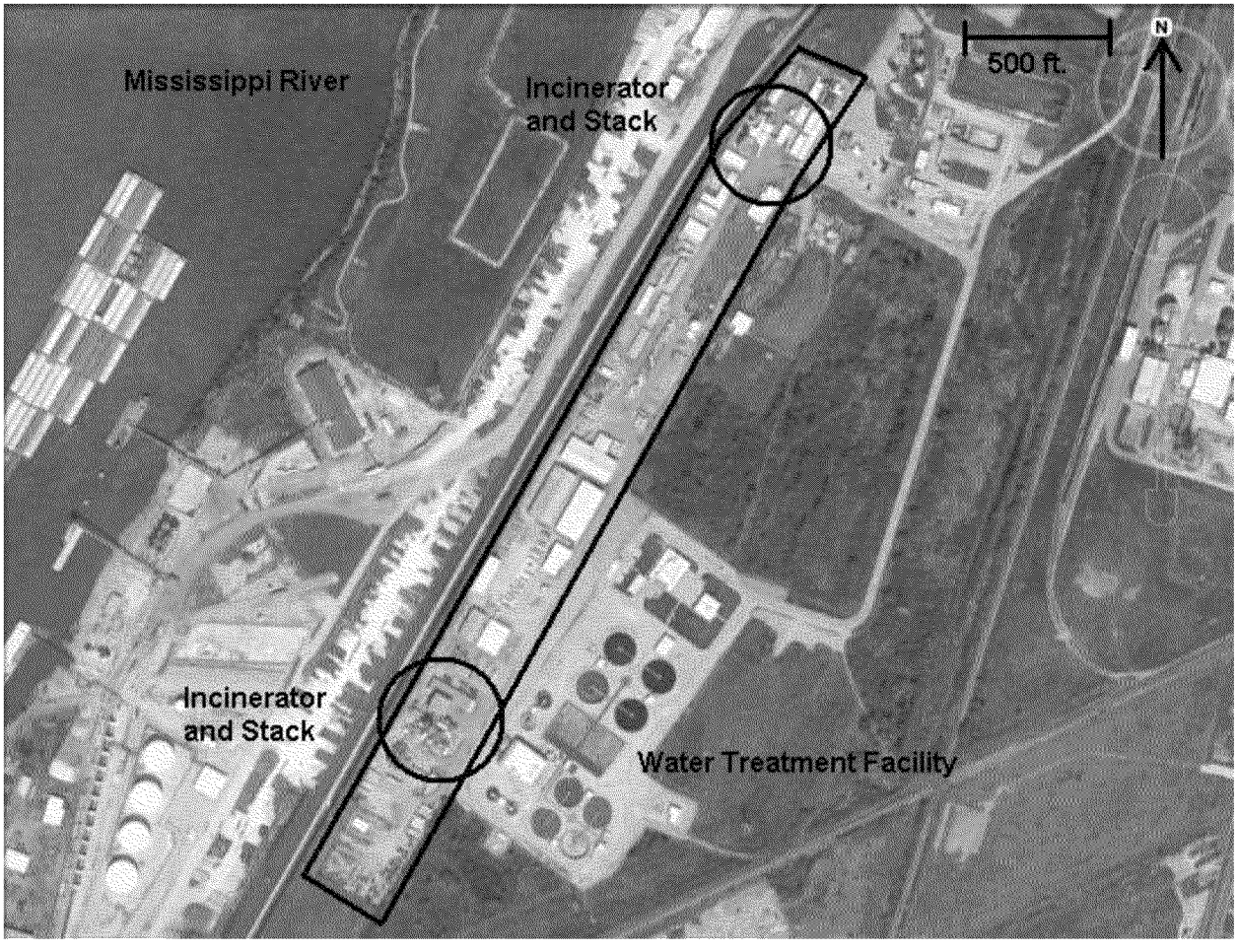


Figure 8. Hazardous waste incinerator and Mississippi River

3.3.1 Source Characteristics

Probable source locations for primary and secondary elements of concern at The Facility include the two currently operating incinerators and associated 100 feet stacks, as well as fugitive emissions from plant operations. While two incinerators are in use, there are a total of three incinerators located on site with a combined energy of 86 million BTU/hr. The incinerators process organic acids, non-halogenated and halogenated solvents, inorganic wastes, propellants and explosives, pyrophoric compounds, organic peroxides, and water reactive compounds.

Waste characterization samples are taken on average of one sample per bulk load of waste and on 10% of the drums of waste accepted. An on-site laboratory conducts analysis of the waste samples to ensure that it conforms to the associated waste characterization documents such as

Material Safety Data Sheets. Wastes are examined for characteristics such as physical state, color, layers, odor, water mix, pH, specific gravity, ignitability screen, cyanide screen, PCBs, heat value, radiation screen, and other physical and chemical attributes. Upon characterization, the waste proceeds to a storage area or a staging area to prepare for incineration. Waste feed rates into the incinerator are based on laboratory characterization and MSDS documentation. Inadequate waste characterization has a significant potential to result in toxic metals emissions.

At the rotary kiln incinerator, temperatures are maintained above 1800° F using waste feed and supplemental fuel oil. Liquid waste is injected as fine particulates. Solid waste is fed into the kiln using a conveyer or gravity feed system. Combustion parameters such as temperature, feed rate, and combustion gas velocity are closely observed to ensure efficient incineration of the waste. Incomplete or inefficient incineration during this portion of the plant process has the greatest potential to induce emissions that exceed performance standards. After incineration of the waste, residue ash is analyzed for organic constituents to ensure that it complies with land disposal standards. Non-organic constituents such as metals are chemically stabilized to reduce leaching of the material to acceptable levels. The treated waste is then disposed of in a hazardous waste landfill.

Due to the diverse hazardous waste stream, process variability is generally high at The Facility. Performance testing is designed to develop efficient incineration protocol, and involves periodic trial burns (5 years) with specific waste types which are analyzed to study the effectiveness of the incineration, and establish waste and metals feed rates. During optimal performance, a hazardous waste incinerator should remove 99.99% of the organic hazardous constituents in the waste stream. Emissions include particulate matter (PM) including metals, Hydrogen Chloride (HCl), Carbon Monoxide (CO), and remaining organic constituents. In the event that an additional elevated metals detection is potentially linked to the hazardous waste incinerator, incinerator processes and associated documentation would be requested to determine the nature of the possible emission.

3.3.2 Relevant Hazardous Air Pollutants and Apportionment Metals

Upon arriving at The Facility, waste samples are characterized to determine specific feed rates for incineration. Trace metals are present during the incineration of certain waste streams. However, metal feed rates are designed and written into the operations permit to limit metals emissions. An increase in hazardous metals emissions can potentially occur through The Facility's stacks if the incineration is operating inefficiently or a waste stream is inadequately characterized.

Metals air emissions of primary concern at The Facility include arsenic (As), cadmium, (Cd), mercury (Hg), lead (Pb), chromium (Cr), and Beryllium (Be). Secondary metals of concern are selenium (Se), copper (Cu), zinc (Zn), silver (Ag), and manganese (Mn). Typical PM size for metals is less than or equal to 10 µg.

As stated previously, the hazardous waste incineration facility is located in a highly industrialized area. The EPAs Toxic Release Inventory lists over 1,099,641 lbs of total

hazardous, on or off-site disposal or other releases in the area near the hazardous waste incinerator.

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 in order to fully characterize potential sources and receptors. Variable wind speeds and direction make consistent, comprehensive air monitoring more complex. Local, real-time meteorological wind and precipitation data is necessary to characterize any potential contaminant transport in the area and will be used in close conjunction with the continuous ambient metals data to analyze potential emissions sources.

4.1.2 Elements, PM and Sampling Frequency

The NRT ambient metals monitors (AMM) devices will monitor for the primary and secondary elements of health and regulatory concern, as well as accompanying metals.

Primary Elements of Health and Regulatory Concern: mercury (Hg), arsenic (As), chromium (Cr), lead (Pb), and cadmium (Cd)

Secondary Elements of Health and Regulatory Concern: copper (Cu), zinc (Zn), silver (Ag), manganese (Mn), and selenium (Se).

Accompanying metals: calcium (Ca), scandium (Sc), titanium (Ti), vanadium (V), iron (Fe), cobalt (Co), nickel (Ni), bromine (Br), tin (Sn), and antimony (Sb)

The ambient air metals AMM devices will be outfit with a PM_{10} inlet to limit particle size of the sample matter and to monitor for a broad range of fine to coarse particulate sizes.

4.1.3 Plant Processes and Events

The general processes at The Facility include the incineration of hazardous waste such as lab packs, water reactive chemicals, oxidizers/organic peroxides, halogenated solvents, organic acids, propellants, and explosives. Hazardous waste re-packaging is also conducted on-site. The wastes are transported to The Facility by tank trucks, rail cars, or ship containers, and are in solid, liquid, or sludge form. Facility records such as Material Safety Data Sheets, laboratory waste characterization records, incinerator operations records and stack emissions data for carbon monoxide or hydrocarbons will be available for review.

If Action Levels are exceeded and the emission is traced to The Facility, operations would be temporarily suspended using established shut-down protocol. Waste, laboratory and incineration records would be examined to identify operational issues resulting in persistent pollution of the airshed.

4.2 Monitoring Sites

Multi-metals ambient air monitoring devices will be located utilizing established site guidelines for air sampling promulgated by the U.S. EPA (U.S.EPA, 1987). For this example, four sampling sites have been established and two unique monitoring plans will be developed and discussed.

The primary factors influencing multi-metals ambient air monitor locations within The Facility's airshed are the variable wind regime in Sauget, Illinois **(Figure 6),** sensitive receptors within the community like schools and hospitals, source identification, the project's financial limitations, and ease of access.

4.2.1 Ambient Metals Monitor Locations

In this example, the probable source of arsenic emissions in the local Sauget, Illinois, airshed is the incinerator stacks of The Facility and neighboring industrial operations. The 100 feet elevation of the hazardous waste incinerator stacks promotes emissions transport to the surrounding residential and industrial areas. Ambient metals sampling locations should be placed to account for possible stack fumigation and to characterize the general airshed.

The location of the April 13, 2009, detection is in an East St. Louis neighborhood less than 2 miles to the northeast of the facility. The monitoring device that recorded the original detection is no longer present in the area. While wind patterns do not generally trend northeast, the strong data signal from the April 13, 2009, arsenic episode make the site appropriate for continued monitoring. Ambient metals monitor (AMM) location **AMM #1** is near the April 13th arsenic detection site, 1.7 miles from the hazardous waste incinerator on the roof of Martin Van Lucas Public School, 1620 Russell Avenue, East St. Louis, Illinois.

The remaining monitoring locations are at strategic locations that correlate to established wind patterns in the area. The wind rose diagram **(Figure 6)** clearly indicates that the primary wind direction in the St. Louis area is from the south. The **AMM #2** location is at the Gateway Arch Park, 2.25 miles directly north of The Facility.

Wind directions also trend strongly from the northwest. The Cahokia East St. Louis Airport is located 1.7 miles to the southeast of The Facility. There are concerns with ambient lead concentrations associated with small engine planes that still utilize leaded gasoline and may skew ambient metals data that is intended to characterize the greater airshed. However, lead concentrations associated with airport activity should be relatively low and can be accounted for in the data analysis. The airport is also currently equipped with advanced meteorological sensors that can aid in data analysis and source characterization. The **AMM #3** location is at the Cahokia East St. Louis Airport.

Schools and hospitals are areas that have dense, sensitive receptors and usually accommodate with requests for access. The third largest wind vector in the Sauget area trends from the southeast. Humboldt Middle School, located at 2516 S 9th St., St Louis, Missouri, is located 1.4

miles directly northeast of the hazardous waste incinerator. The **AMM #4** sampling location is on the rooftop of Humboldt Middle School.

See **Figure 9** for Ambient Metals Monitoring sampling locations.

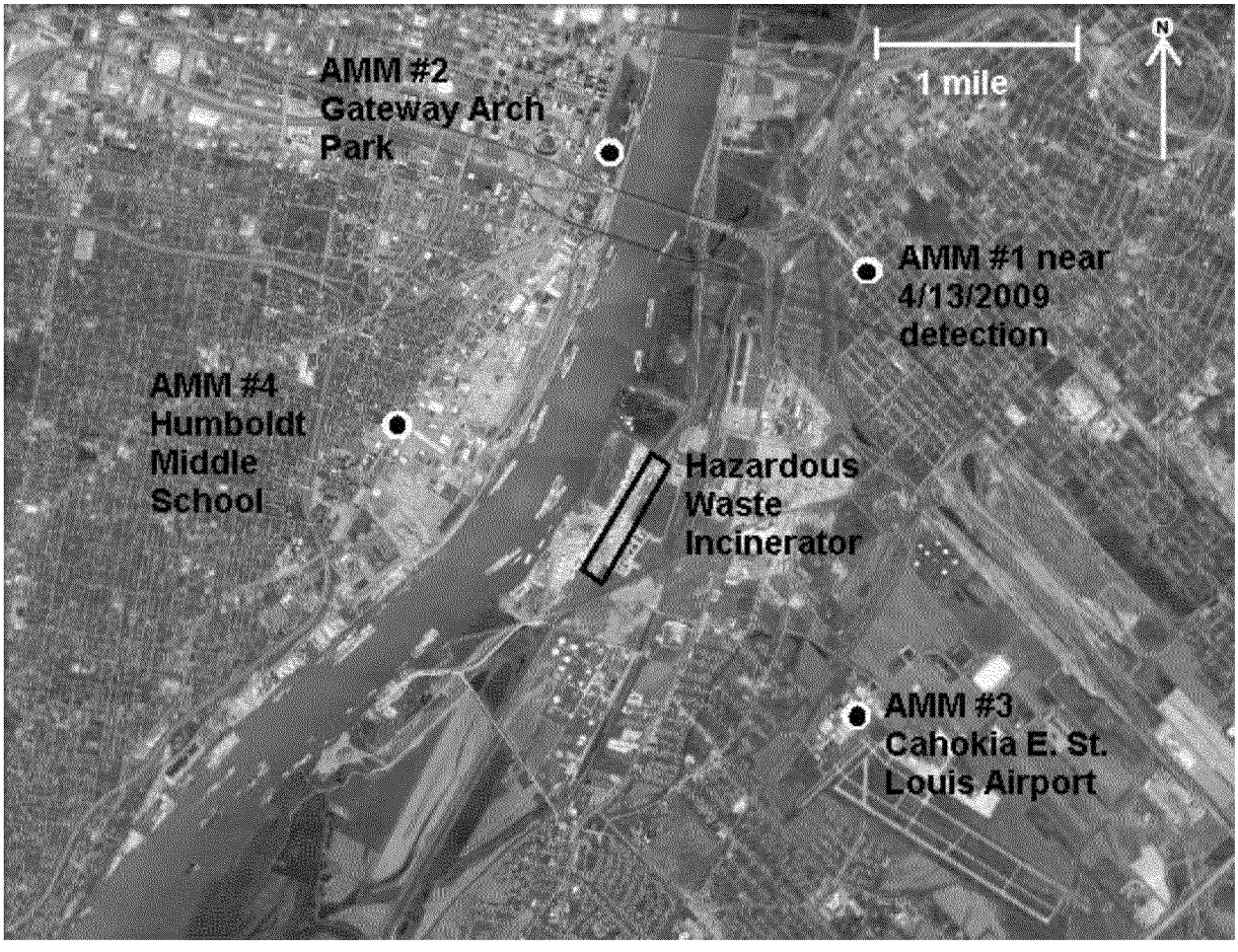


Figure 9. Continuous Multi-Metals Ambient Air Sampling Device Locations near Sauget, Illinois

4.3 Monitoring Plans

Depending upon the project's financial constraints, one to four continuous multi-metals ambient air sampling devices may be deployed. For this example, two different monitoring plans have been developed that represent relatively conservative plans. However, a hybrid of the two plans, full deployment to all sampling locations, or additional sampling locations could be added to characterize the local airshed or enlarge the study area.

4.3.1 Monitoring Plan 1

Monitoring Plan 1 (Plan 1) is designed on the assumption that the elevated arsenic concentrations recently detected in the airshed are not indicative of a chronic emissions problem at The Facility or other local industry, but that the arsenic episode still warrants

additional study and monitoring to determine the nature and extent of air quality risks. Plan 1 involves a two-year study of the Sauget area airshed to gather ambient metals data and assess risks to the local population. One continuous multi-metals ambient metals monitor (AMM) will circulate from monitoring locations AMM #1 through AMM #4 for a period of six months at each locale. Data will be gathered and analyzed in accordance with plan goals to characterize the public health risks associated with ambient metals and identify potential sources. If concentrations of metals are detected above Plan Action Levels, the number of air monitors would be increased and the corrective action outlined in Section 2, Goals: Defining Ambient Goals and Compliance would proceed.

Plan 1 provides essential monitoring capability with a smaller monitoring footprint and lower associated costs to assess if consistent air quality risks are present near the hazardous waste incinerator.

4.3.2 Monitoring Plan 2

Monitoring Plan 2 (Plan 2) is strictly designed around established wind data and the goal of developing and maintaining a thorough, comprehensive data set that characterizes ambient metals in the local airshed. For Plan 2, two multi-metals ambient air monitoring devices will be deployed at Gateway Arch Park AMM #2 and Cahokia East St. Louis Airport AMM #3. These two locations represent the most probable vector pathways for Facility emissions, as determined by area wind data. Continuous ambient metals data will be gathered at the locations for two years. If concentrations of metals are detected above Plan Action Levels but a source is not identified, the number of air monitors and sampling locations may be increased, or a source apportionment study for the area may proceed. If an emissions source is identified, the corrective actions outlined in Section 2, Goals: Defining Ambient Goals and Compliance, would commence.

Plan 2 provides a stationary, consistent approach utilizing basic contaminant transport concepts to achieve Plan goals.

4.4 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 sampling once every four hours. Higher data resolution provides more information to regulators to assess and protect worker and public health, and to fully characterize incineration and other industrial operations on ambient air quality. Air samples are collected on a tape medium that is relatively expensive. In this case, due to the duration of the study (2 years), the number of monitors (1 - 2), and the need for short-term arsenic and metals concentrations, the multi-metals ambient air sampling device will initially be programmed to sample every hour. After a full year of ambient air sampling, data will be analyzed to determine if a decrease in sampling frequency would adversely impact the goals of the project.

Data will be available within two hours of sampling event, streamed via wireless or cabled connection to regulators, 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 by regulators.

The multi-metals continuous ambient air monitors will be protected from weather conditions with a shelter and rain guard. A PM_{10} inlet will funnel particulate to the sampler, and electrical lines and data acquisition cables will run from the shelter to the nearest phone/internet connection.

If emerging data indicates that a more comprehensive ambient air monitoring approach is necessary to achieve project goals, additional multi-metals ambient air monitoring devices would be located taking into account the general wind regime in the region (see figure 3) and potential public receptors.

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 to provide a control metals concentration from which calibrations can be based. Subsequent 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

The ambient air sampling program associated with the hazardous waste processor is an un-mandated environmental sampling program to characterize threats to the local airshed and to further regulator's, engineer's and scientist's understanding of hazardous metals emissions, pollutant dispersion, and industrial processes. While open to comment from local authorities and industry, regulators at the state and federal level will have full control and responsibility for the continuous multi-metals ambient air monitoring plan.

Regulators will maintain contacts with representatives from the city governments of East St. Louis, Illinois, and St. Louis, Missouri, local radio and television stations, representatives from relevant local industry, and potential sensitive local receptors such as hospitals and schools. Regulators will compile quarterly multi-metals ambient air sampling data and provide a report summarizing the data to the public, as well as appropriate state, federal, and local authorities.

4.4.3 Plant

Near real-time data emerging from the ambient metals-air monitoring system will be provided to The Facility and other potential sources of metals emissions. Upon exceedence of an Action Level, regulators would analyze the meteorological and metals data emerging from the monitors to attempt to determine a source. If a source is identified, the probable polluter would be notified and corrective actions would ensue. In the event that multi-metals ambient air sampling data indicates that The Facility's operations are resulting in emissions dangerous to human health and the environment, regulators would request that the incinerator's operations be suspended until the cause of the exceedence is determined and the issue is addressed. The Facility would suspend incineration and hazardous waste processing using established safety and shut-down protocol.

4.4.4 Internet and Public

Regulators will maintain a public internet location that details the ambient air multi-metals monitoring program goals, shows the data emerging from the monitoring location(s), and provides a venue for regulators to answer any questions that the public or industry may have over the monitoring program and local industrial operations. Data on the site will be updated daily to ensure quality assurance of the reported values.

In the event a multi-metals ambient air monitoring Action Level is exceeded, regulators would notify local television and radio, as well as sensitive receptors such as schools and hospitals. Recommendations would be given for those at elevated risk like children, asthmatics 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 the state, local and federal authorities.

5.0 References

1) 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.

2) 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.

3) U.S. EPA (1982) *Basic Air Pollution Meteorology*. Report No. EPA 450/2-82-009, U.S. Environmental Protection Agency, Research Triangle Park, NC.

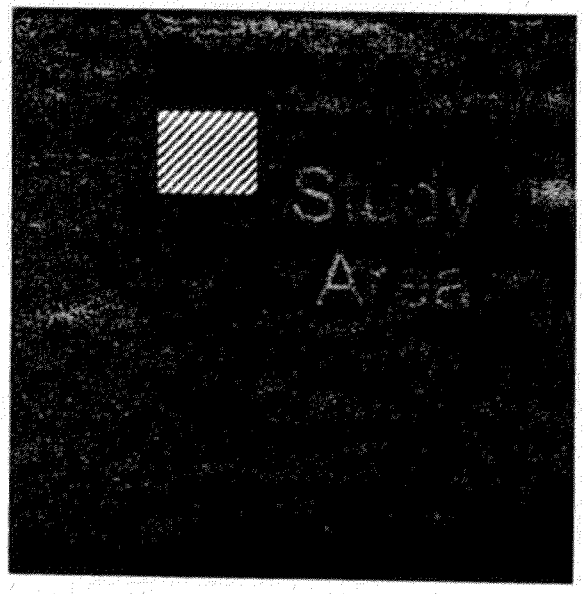
4) Yanca, et al. *Validation of Three New Methods for Determination of Metal Emissions Using a Modified Environmental Protection Agency Method 301,* Air and Waste Management Association, Vol. 56. December 2006.

5) Missouri Department of Natural Resources (2009) Data from Ambient Air Quality Study

FIGURES

Figure 1
East St. Louis Location Map

Study Location



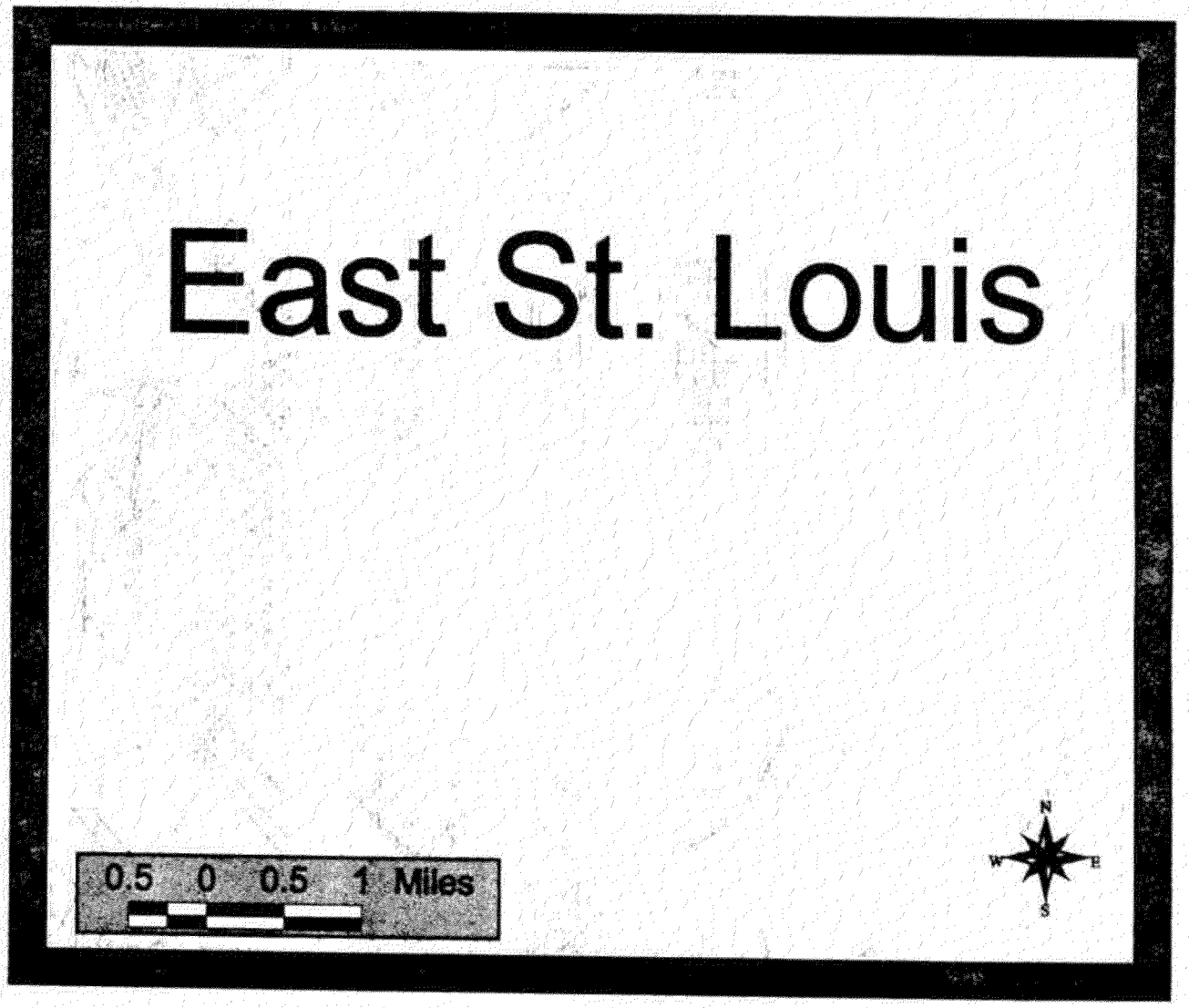


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Figure 2
East St. Louis Neighborhood Map

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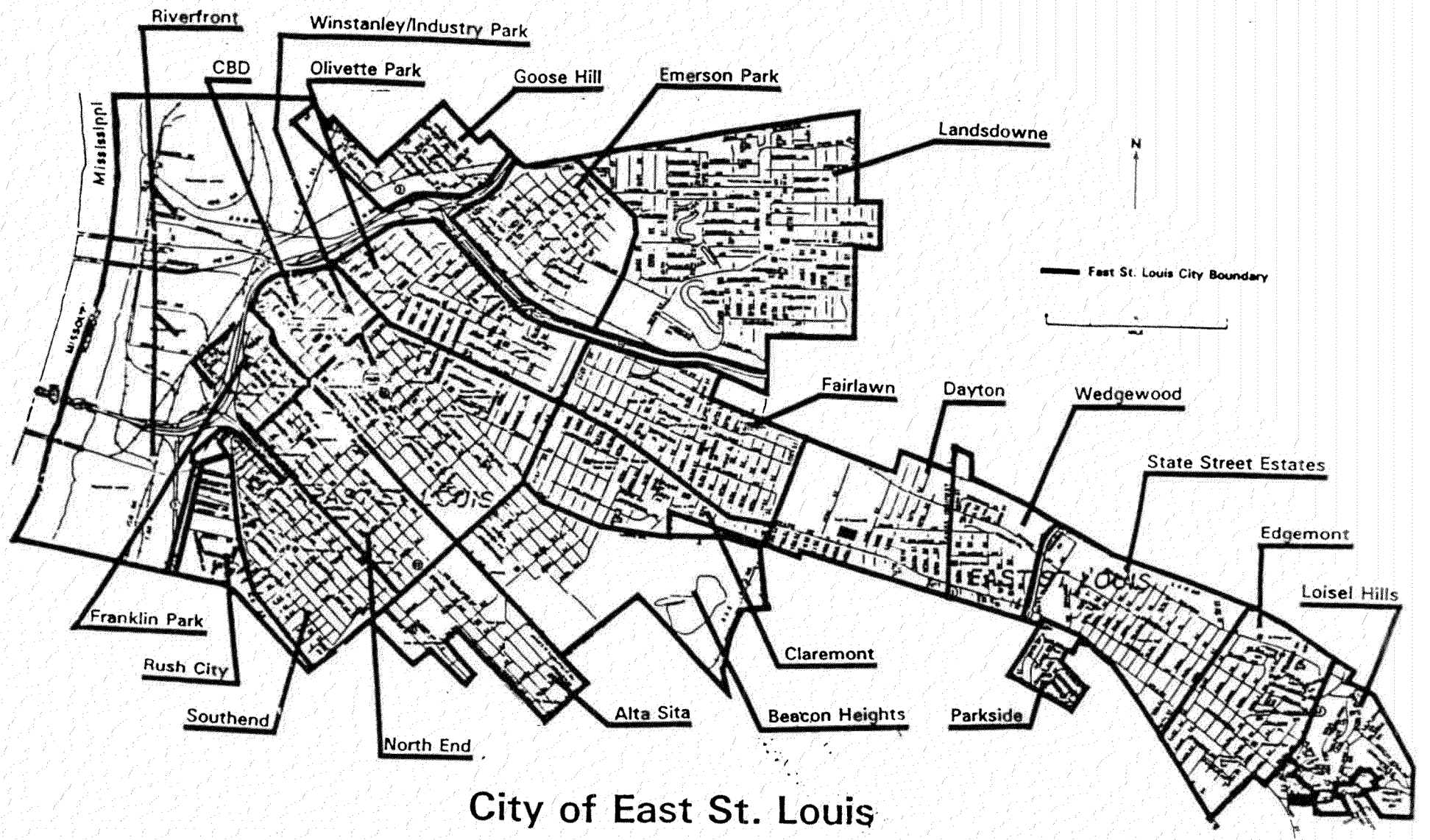
Figure 2 - East St. Louis Neighborhood Map



City of East St. Louis

Figure 3
Participant Blood Lead Levels

Participant Blood Lead Levels

- ✖ PbB > 10 ug/dl
- • PbB < 10 ug/dl
  Study Area

Blood lead levels (PbB) at or above 10 ug/dl are considered elevated by the Illinois Department of Public Health. Study participants with elevated blood lead levels are denoted in this and subsequent maps by ✖.

0.5 0 0.5 1 Miles

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Figure 4
Lead Levels in Dripline Soil and Elevated Blood Lead

Lead Levels in Dripline Soil and Elevated PbB

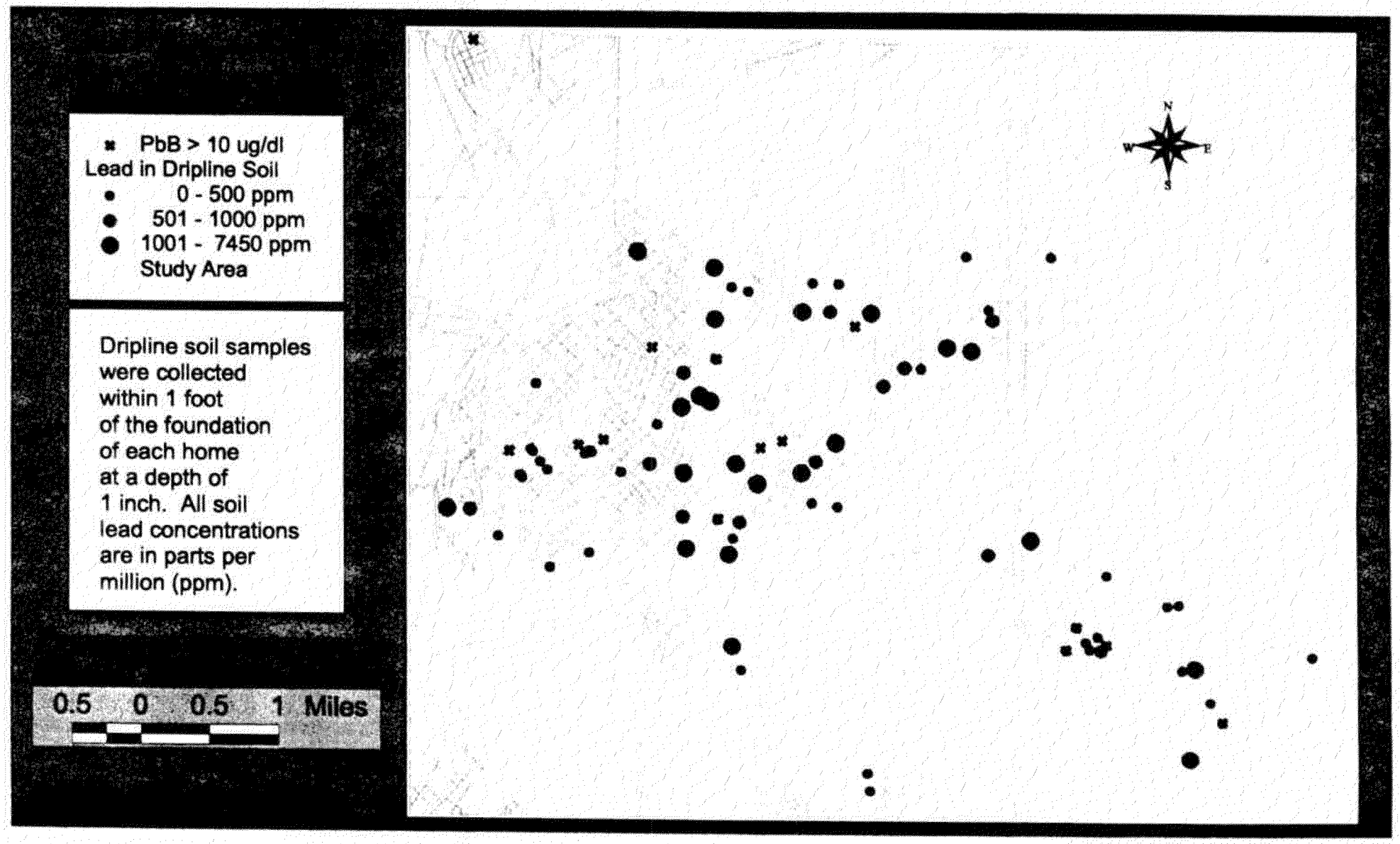

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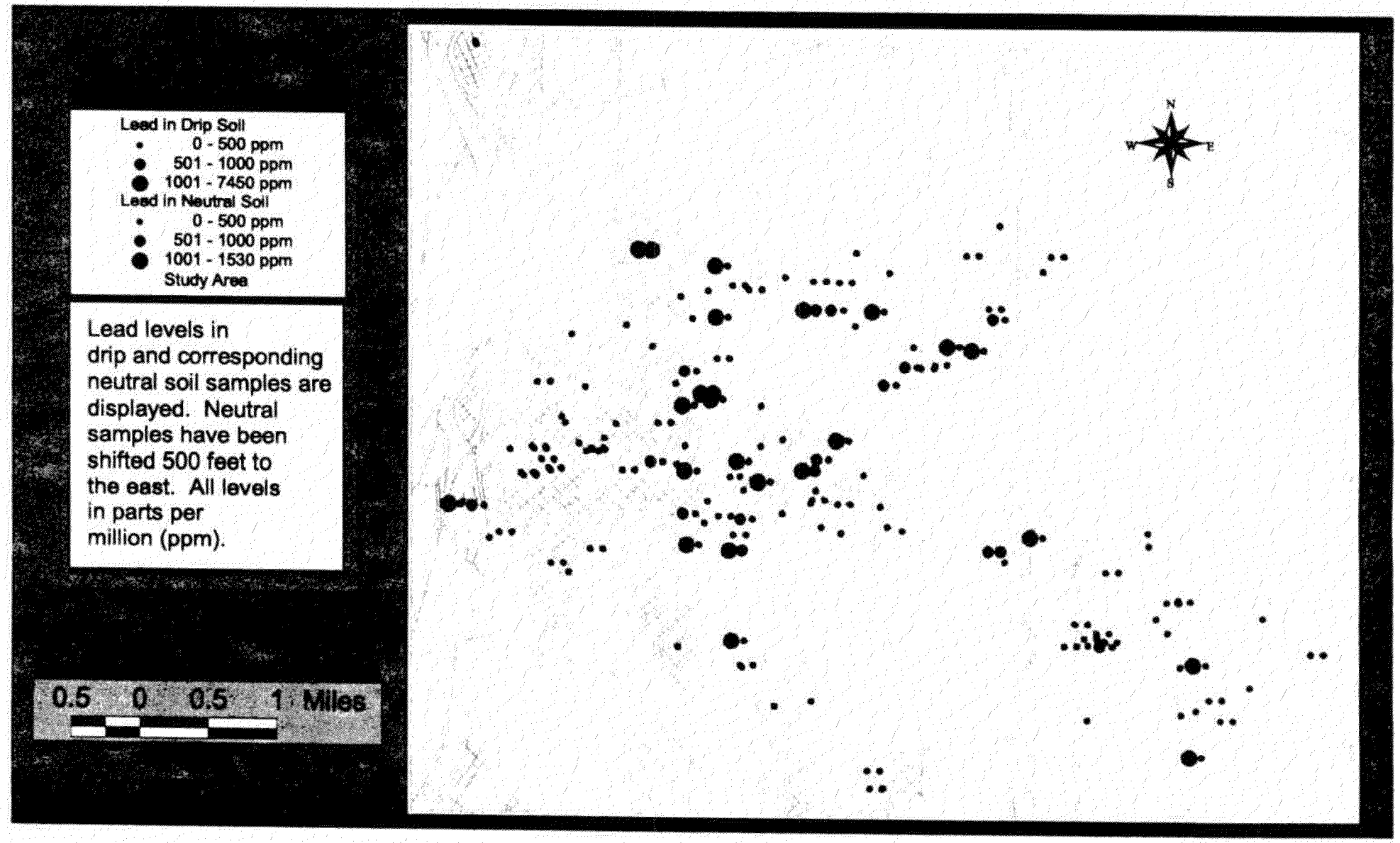
Figure 5
Lead Levels in Drip and Neutral Soil Samples

Lead Levels in Drip and Neutral Soil Samples



Lead levels in drip and corresponding neutral soil samples are displayed. Neutral samples have been shifted 500 feet to the east. All levels in parts per million (ppm).

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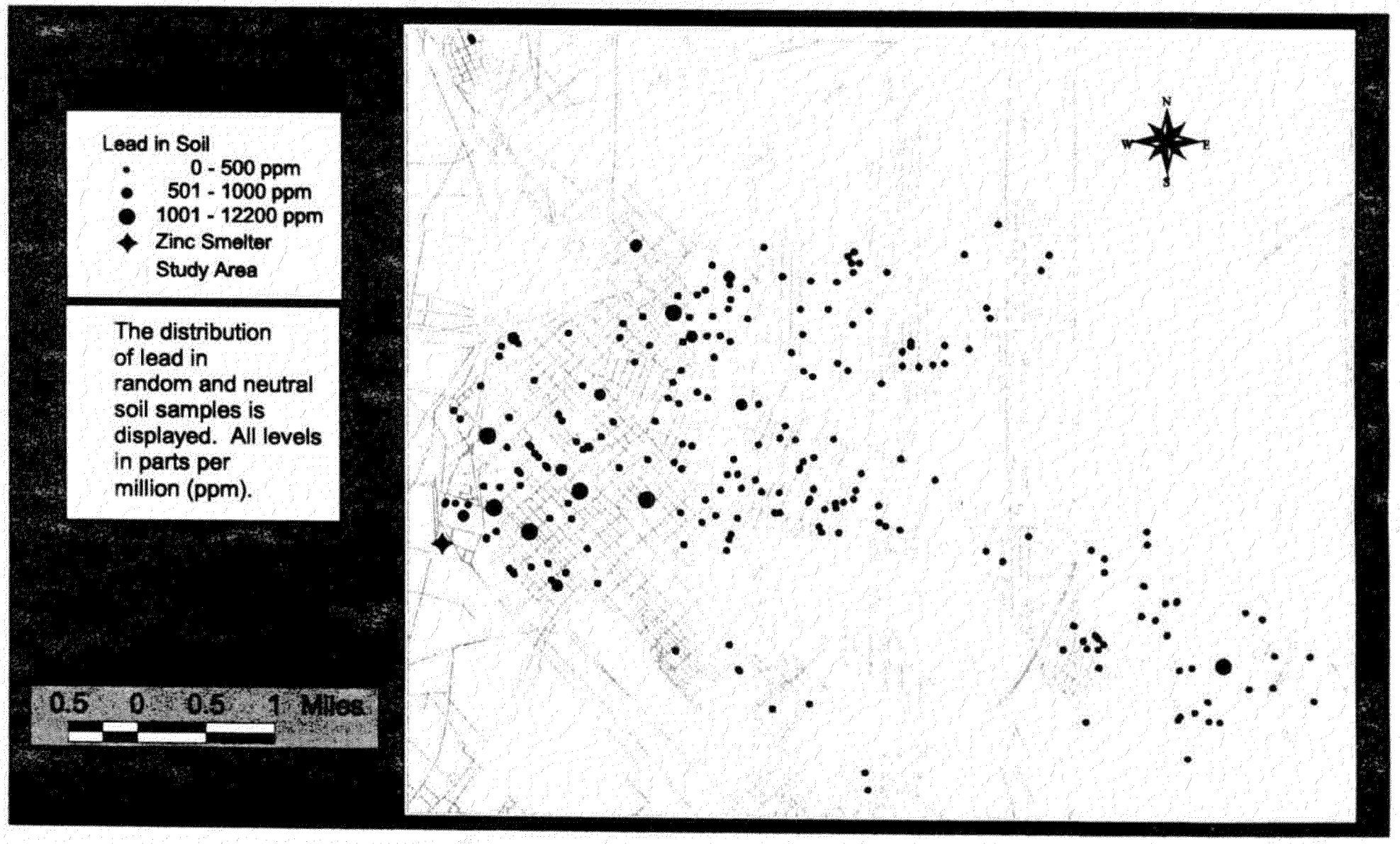
Figure 6
Lead Levels in Neutral and Random Soil Samples

Lead Levels in Neutral and Random Soil Samples



The distribution of lead in random and neutral soil samples is displayed. All levels in parts per million (ppm).

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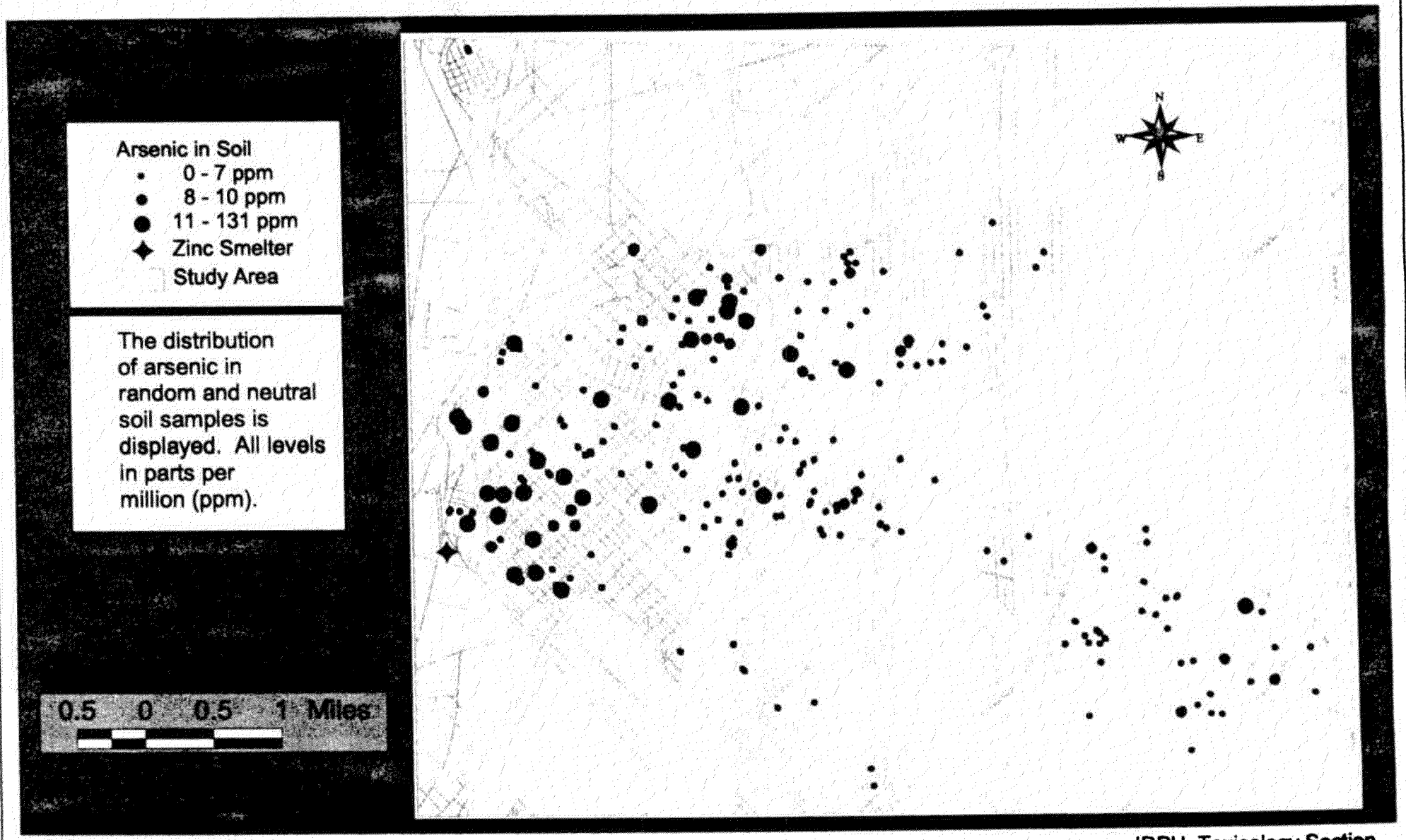
Figure 7
Arsenic Levels in Neutral and Random Soil Samples

Arsenic Levels in Neutral and Random Soil Samples



The distribution of arsenic in random and neutral soil samples is displayed. All levels in parts per million (ppm).

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Figure 8
Cadmium Levels in Neutral and Random Soil Samples

Cadmium Levels in Neutral and Random Soil Samples

Cadmium in Soil
- 0 - 2 ppm
- 3 - 9 ppm
- 10 - 51 ppm
- Zinc Smelter Study Area

The distribution of cadmium in random and neutral soil samples is displayed. All levels in parts per million (ppm).

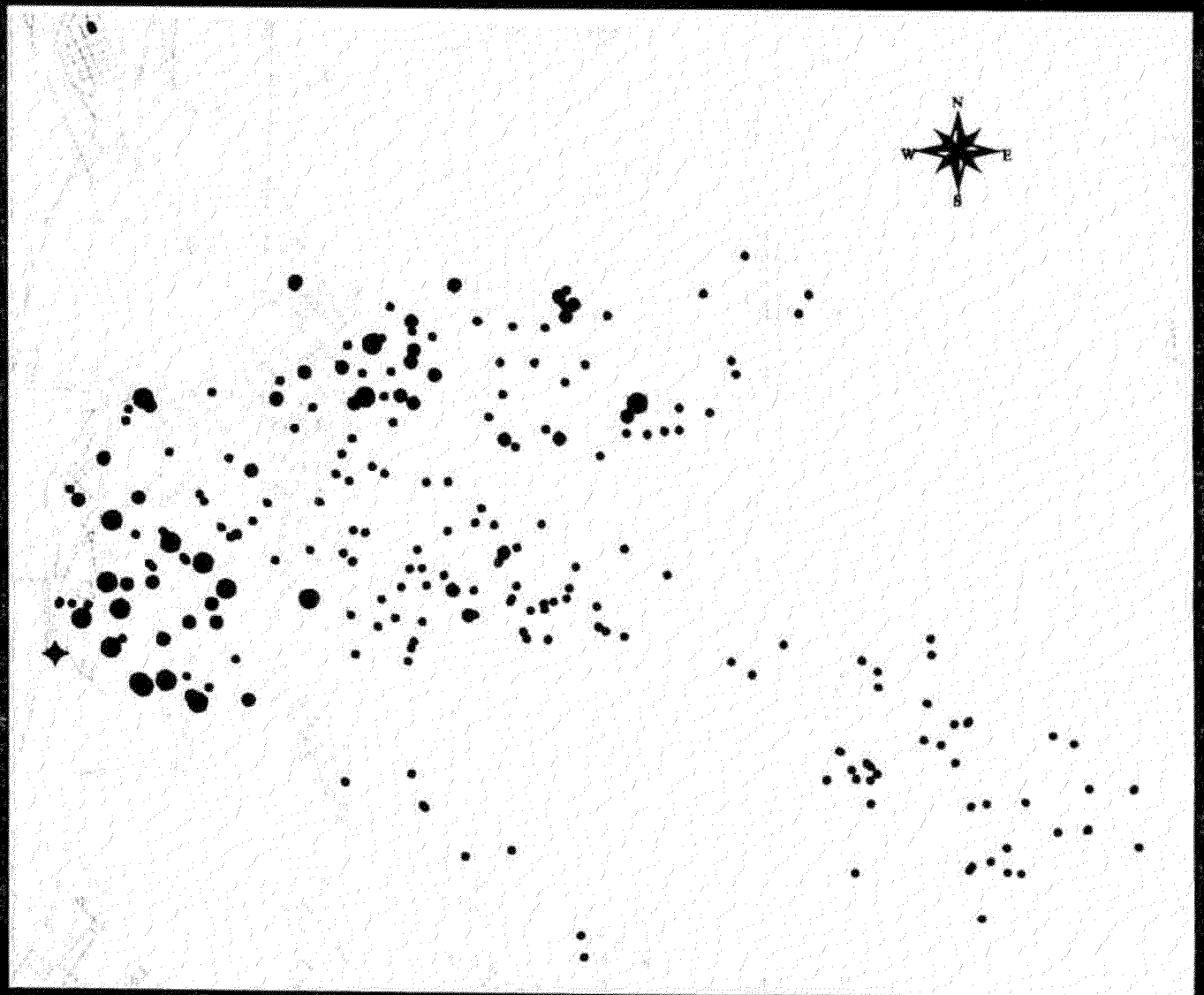

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Figure 10
Outdoor XRF Values and Elevated Blood Lead

Outdoor XRF Values and Elevated PbB

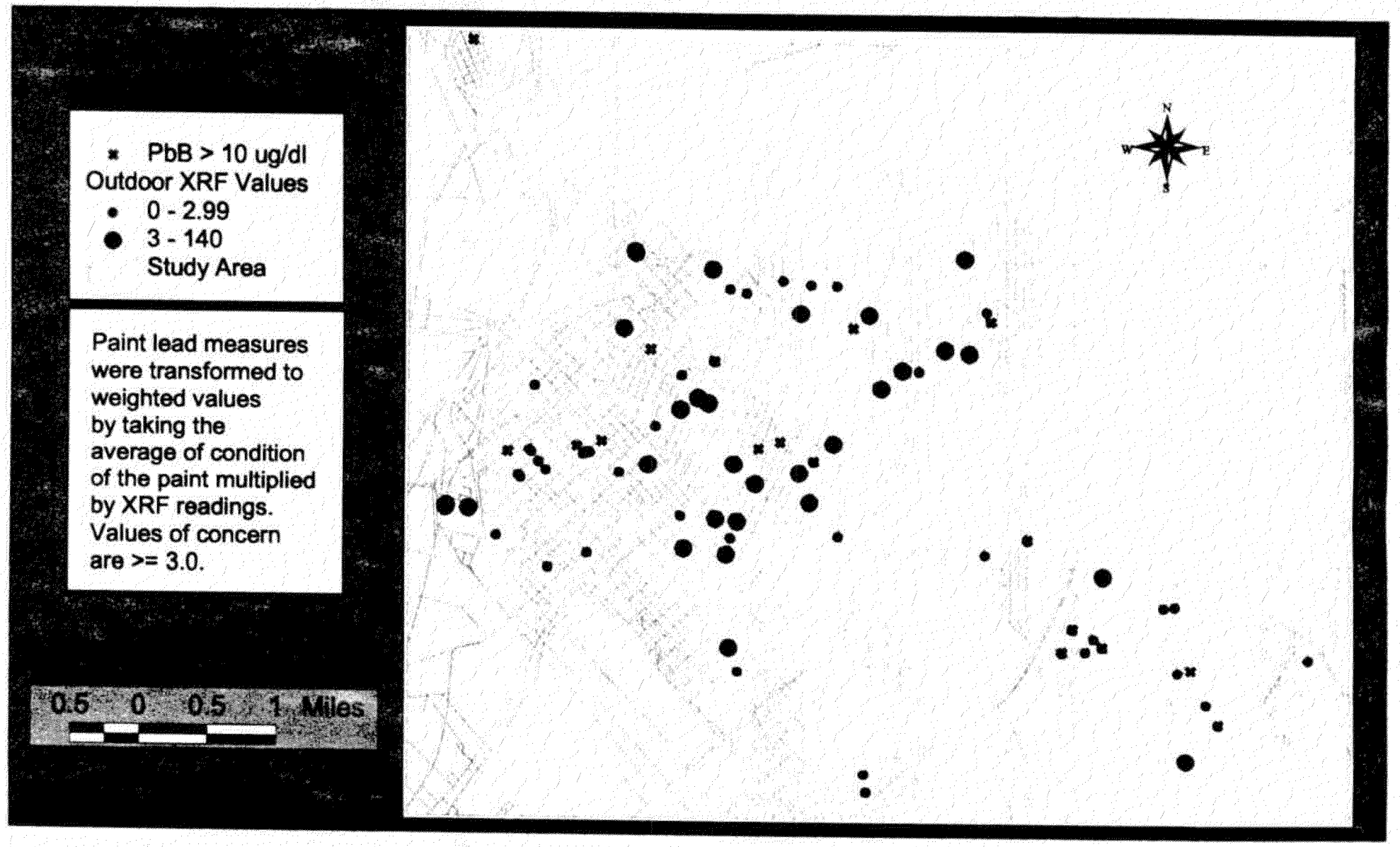

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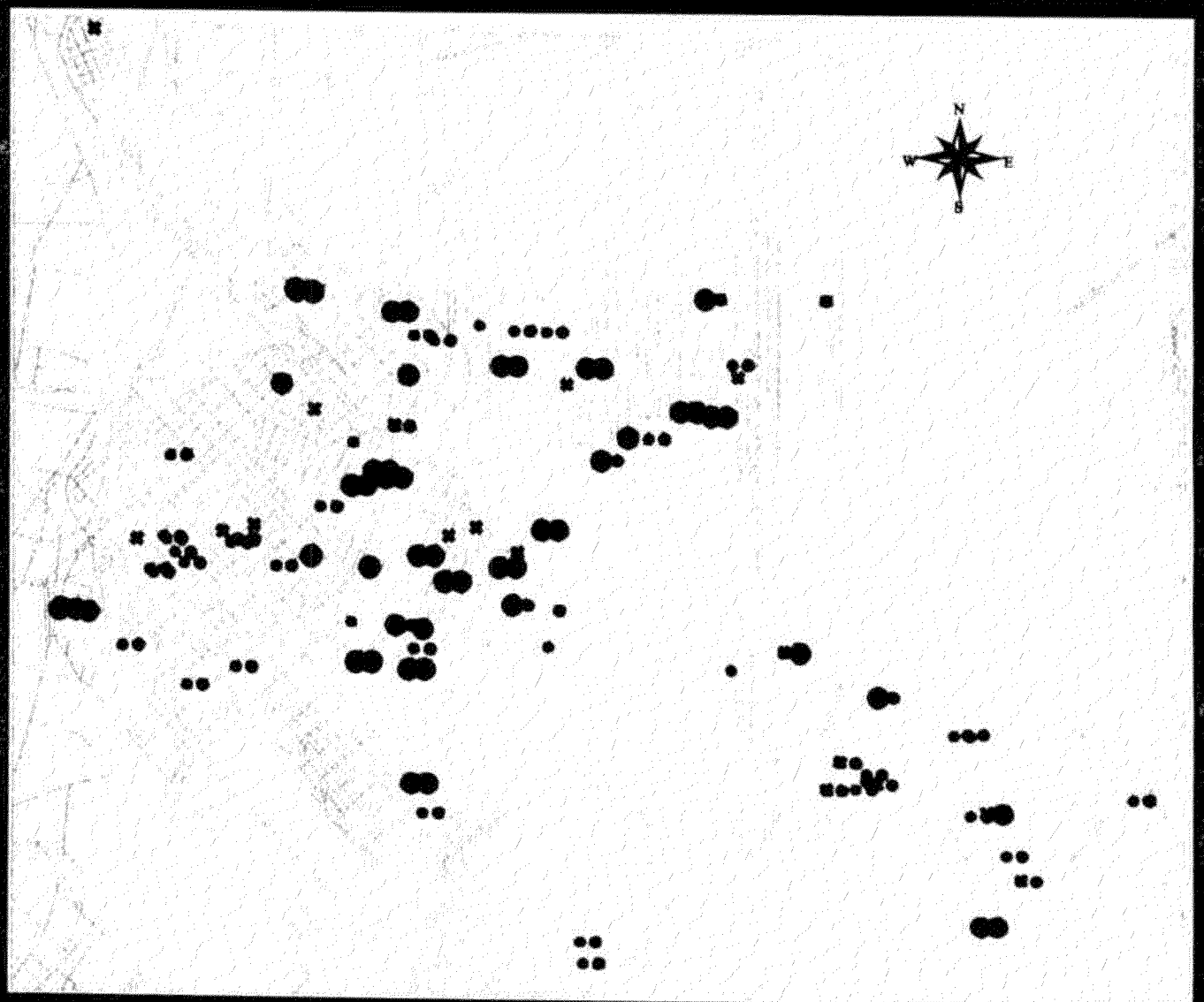
Figure 11
Dripline Soil, Outdoor XRF Values, and Elevated Blood Lead

Dripline Soil, Outdoor XRF, and Elevated PbB

LEGEND

- PbB > 10 ug/dl
- Lead in Dripline Soil
  - 0 - 500 ppm
  - 501 - 1000 ppm
  - 1000 - 7450 ppm
- Outdoor XRF Values
  - 0 - 2.99
  - 3 - 140
  - Study Area

A statistically significant correlation was demonstrated between outdoor XRF values and lead concentrations in dripline soil samples ($r=0.44$, $p<0.0001$). Dripline soil samples were shifted 500 feet to the east for display purposes.



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