APPENDIX E

Example Application: Primary Lead Smelter

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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/m^3 to 0.15 µg/m^3, 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 exceedences. 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.

Table of Contents

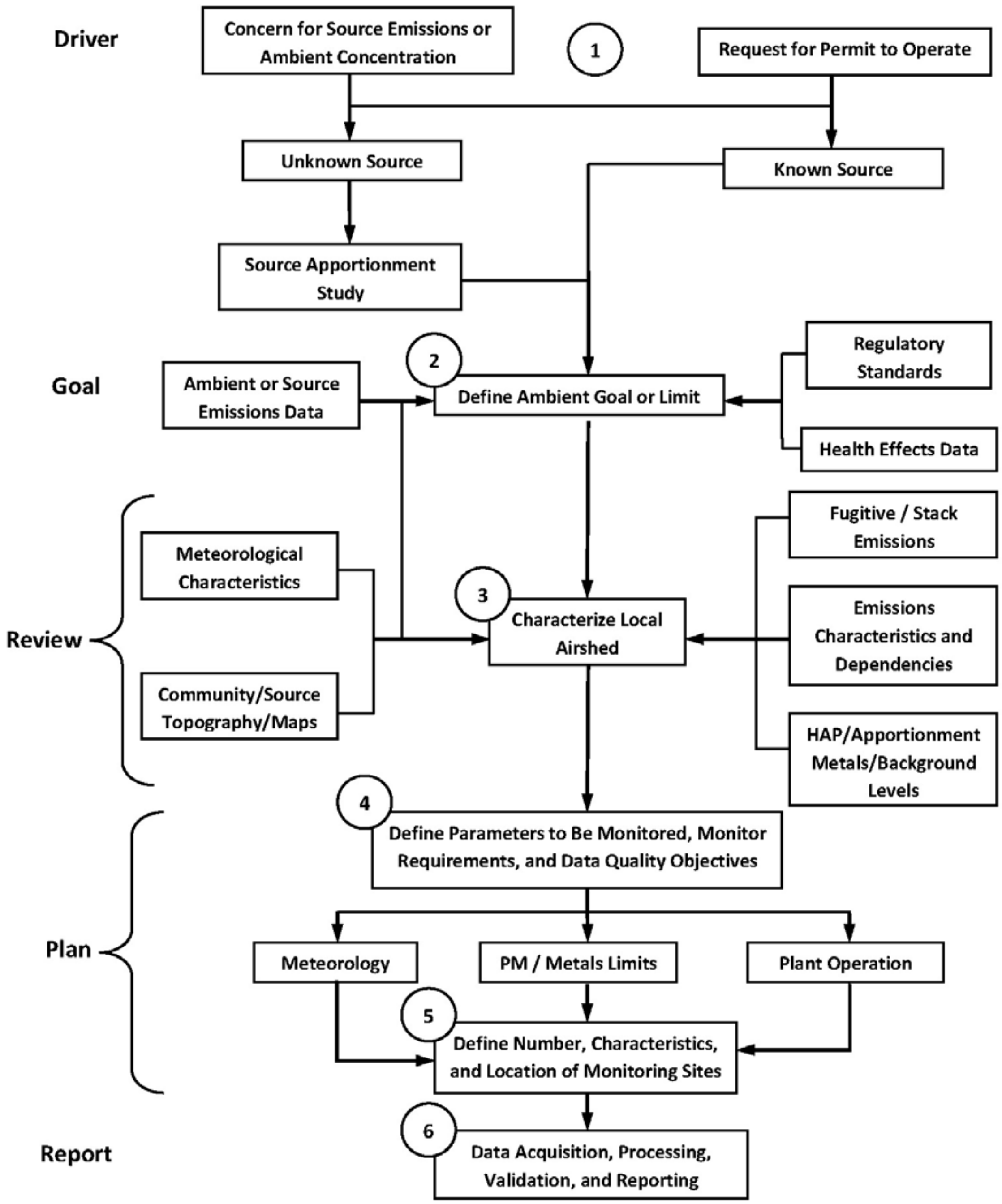

Figure 1. Procedure Flow Diagram

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.

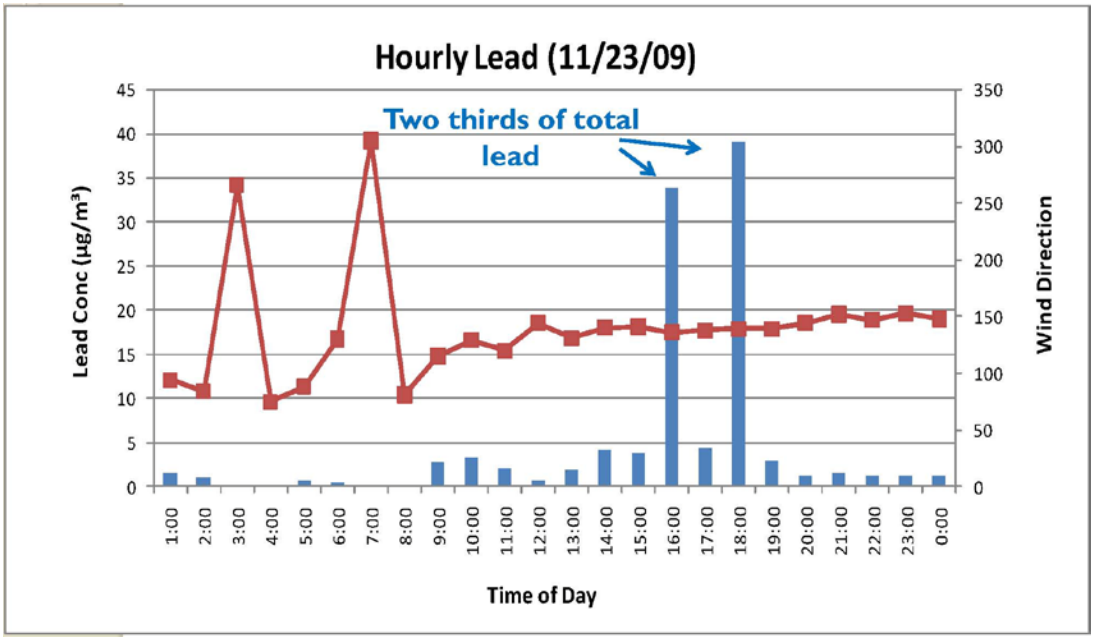

Figure 2. 24-hour Lead conc. in ambient monitor with stable wind conditions.

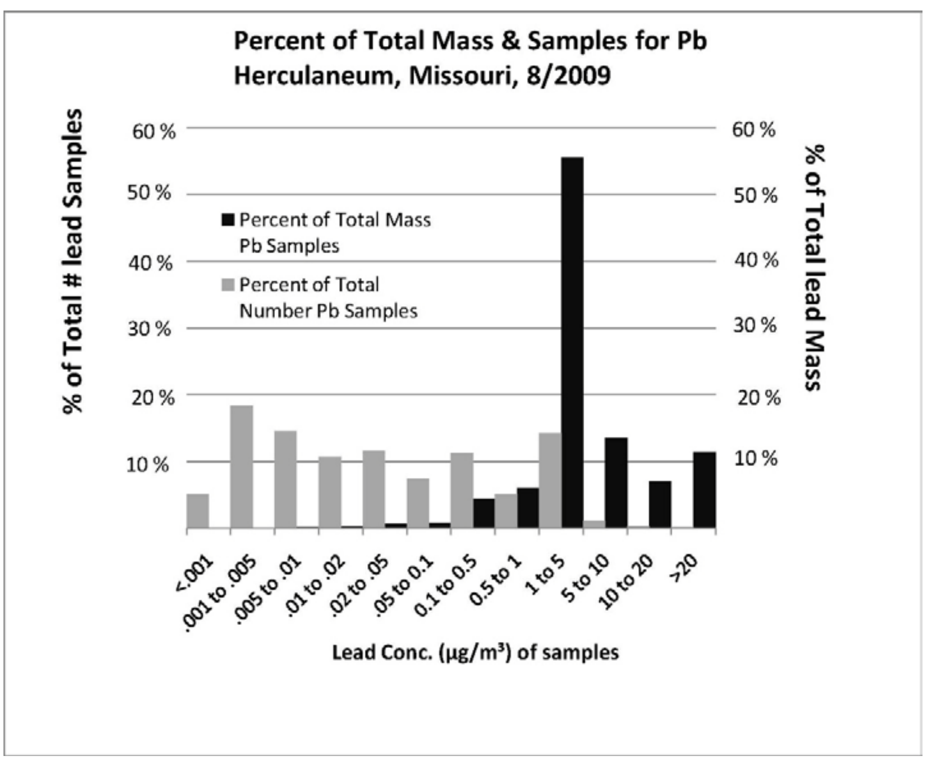

Figure 3. Percent contribution comparison of total lead

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.

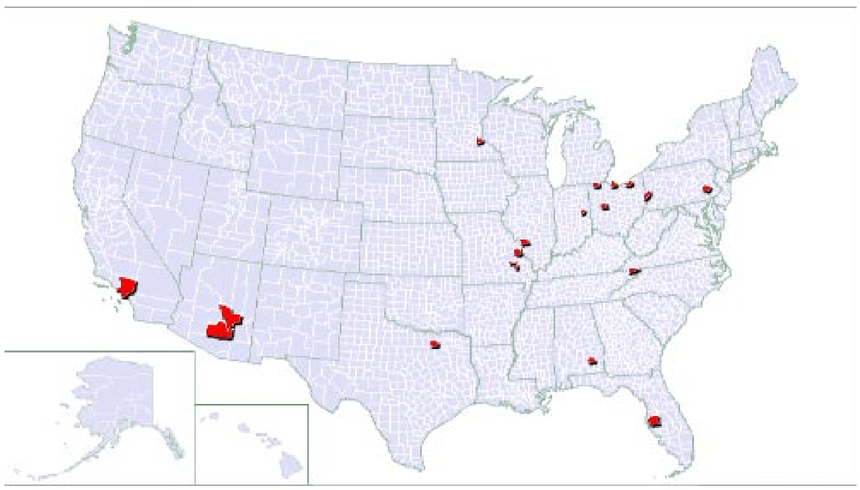

Figure 4. Nation-wide non-attainment areas for lead NAAQS

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 $\mu g/m^3$ 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.

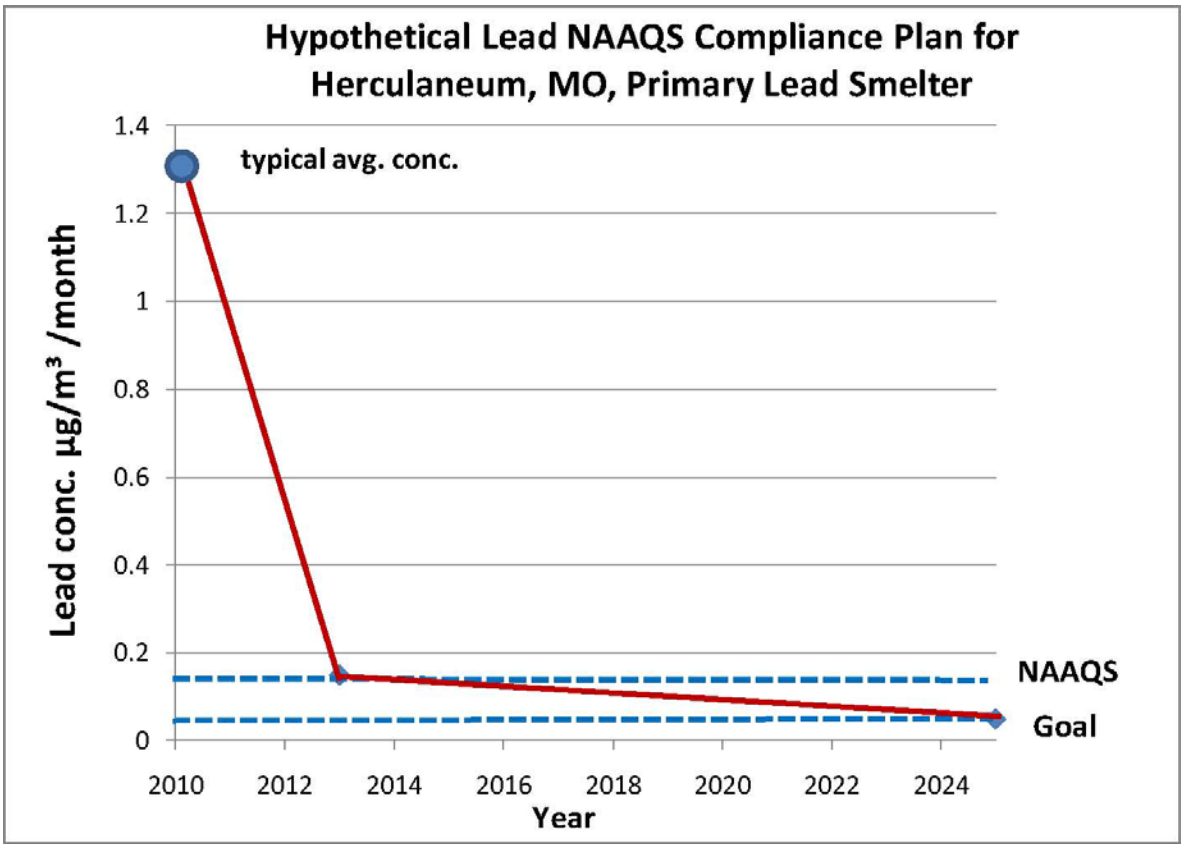

Figure 5. Hypothetical Lead NAAQS Compliance Plan for Herculaneum, MO

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)**

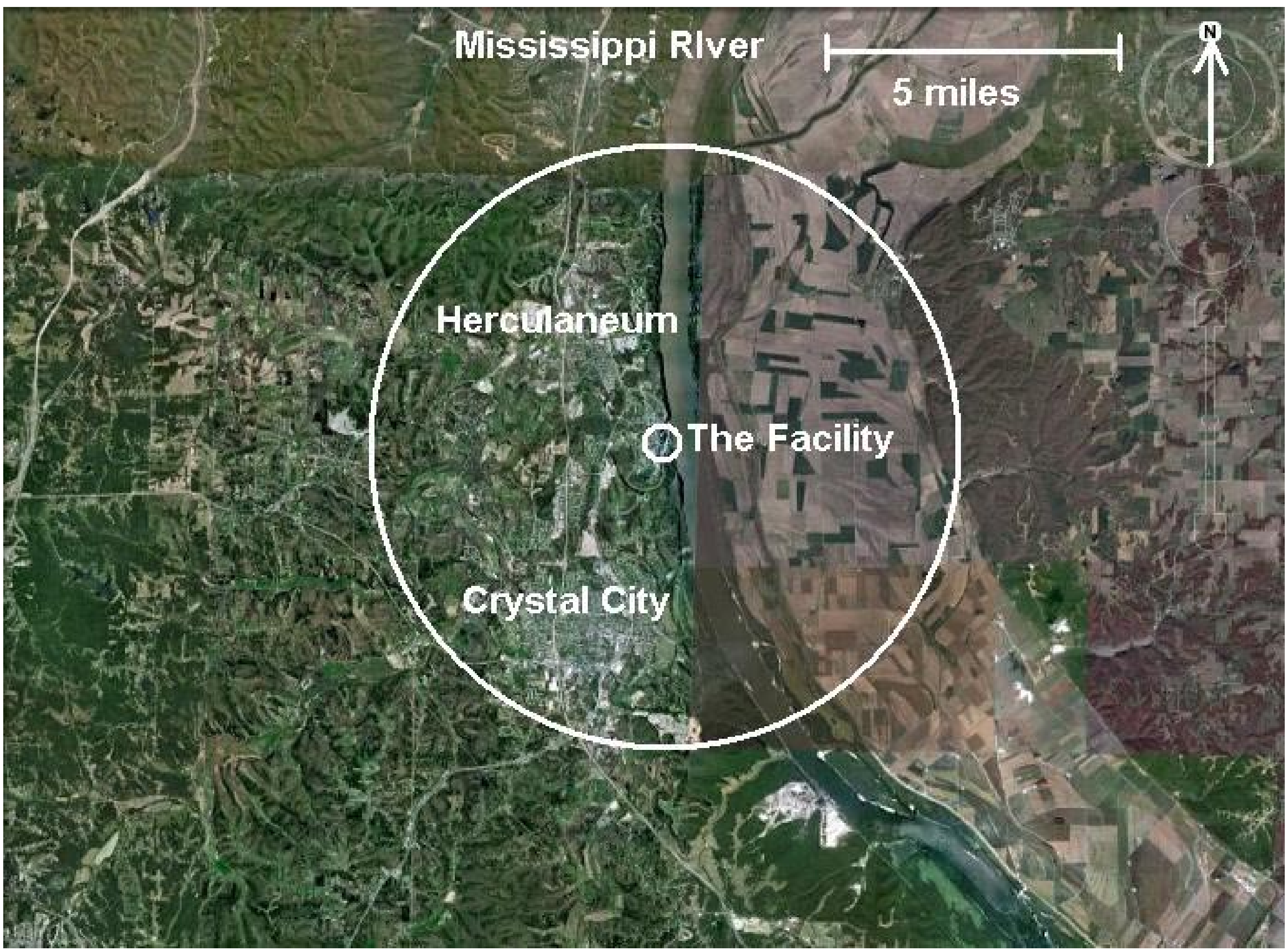

Figure 7. Map of Herculaneum Airshed

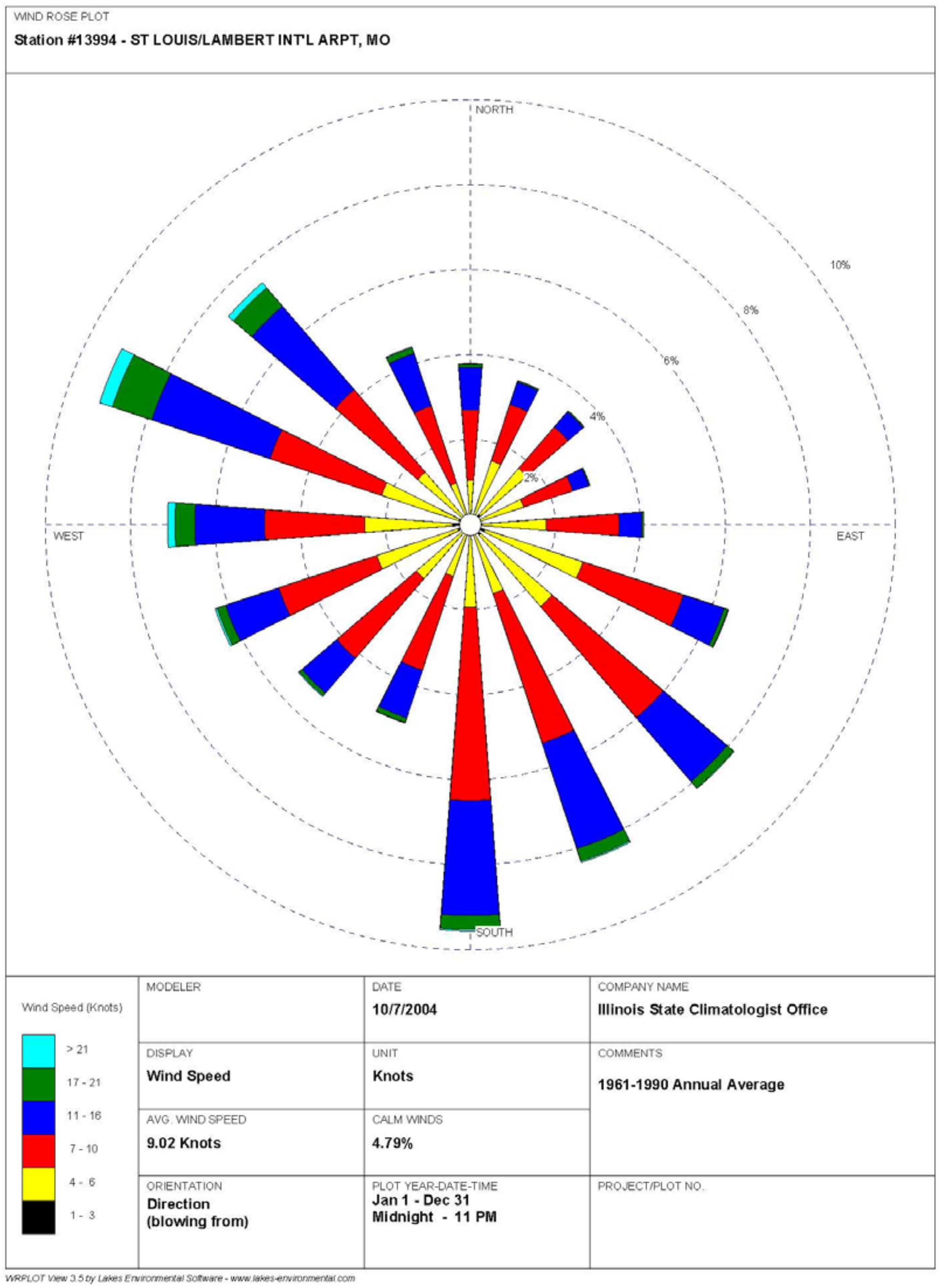

Figure 8. Wind Rose from St. Louis International Airport. 1 knot = 1.15 miles

3.2 Source Characteristics – Primary Lead Smelter Map

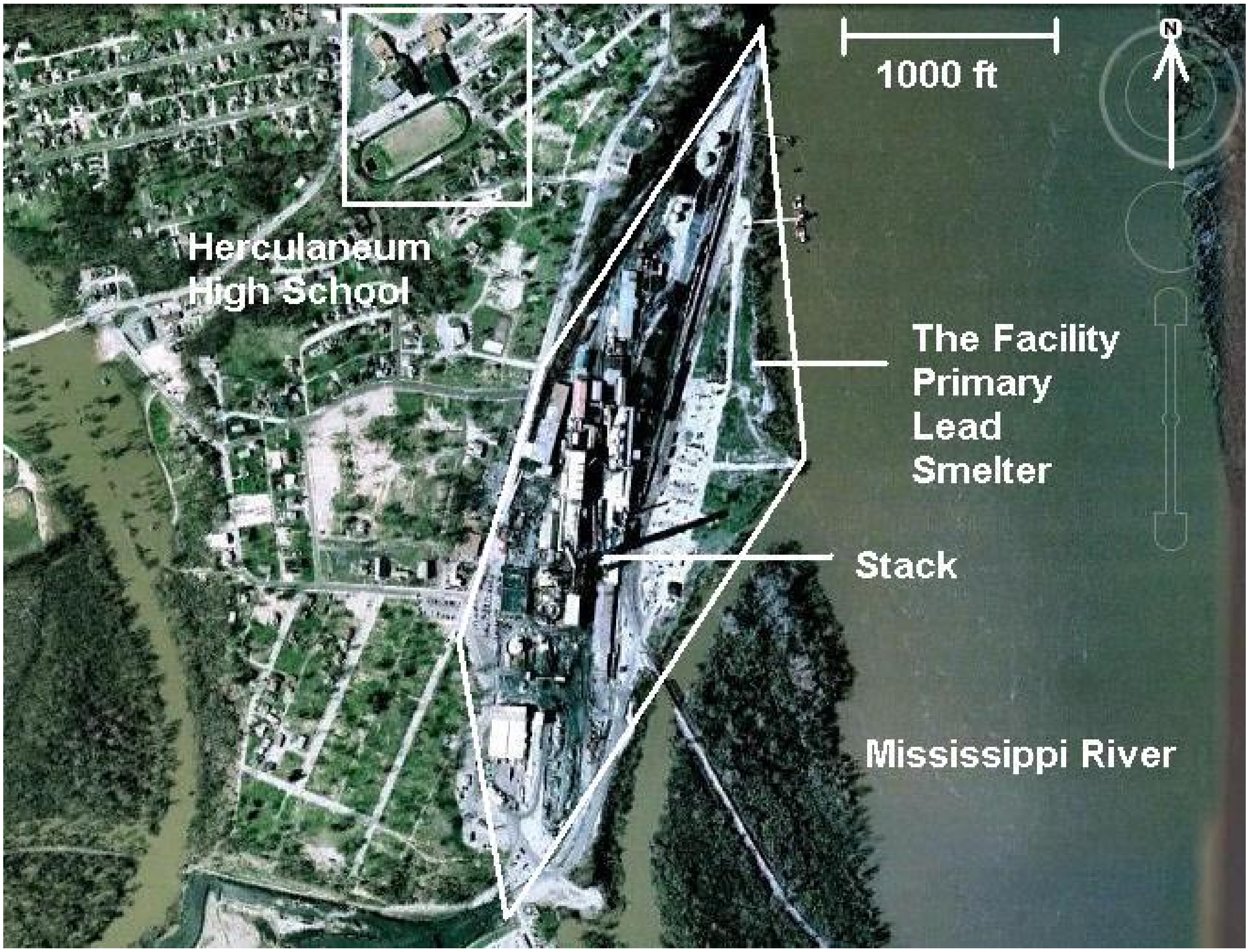

Figure 9. Primary Lead Smelter Aerial Map

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.

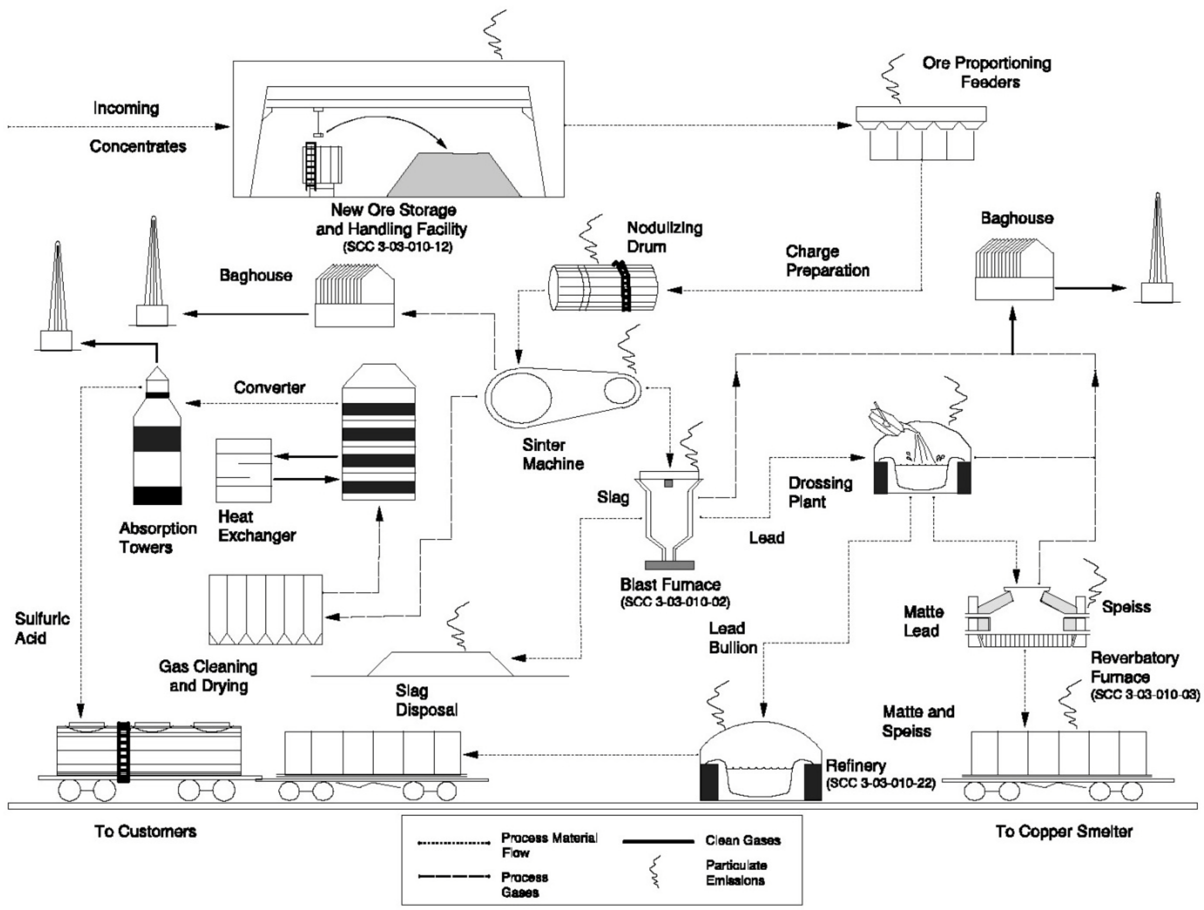

Figure 10. Conceptual Drawing of Primary Lead Smelter Processes

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.

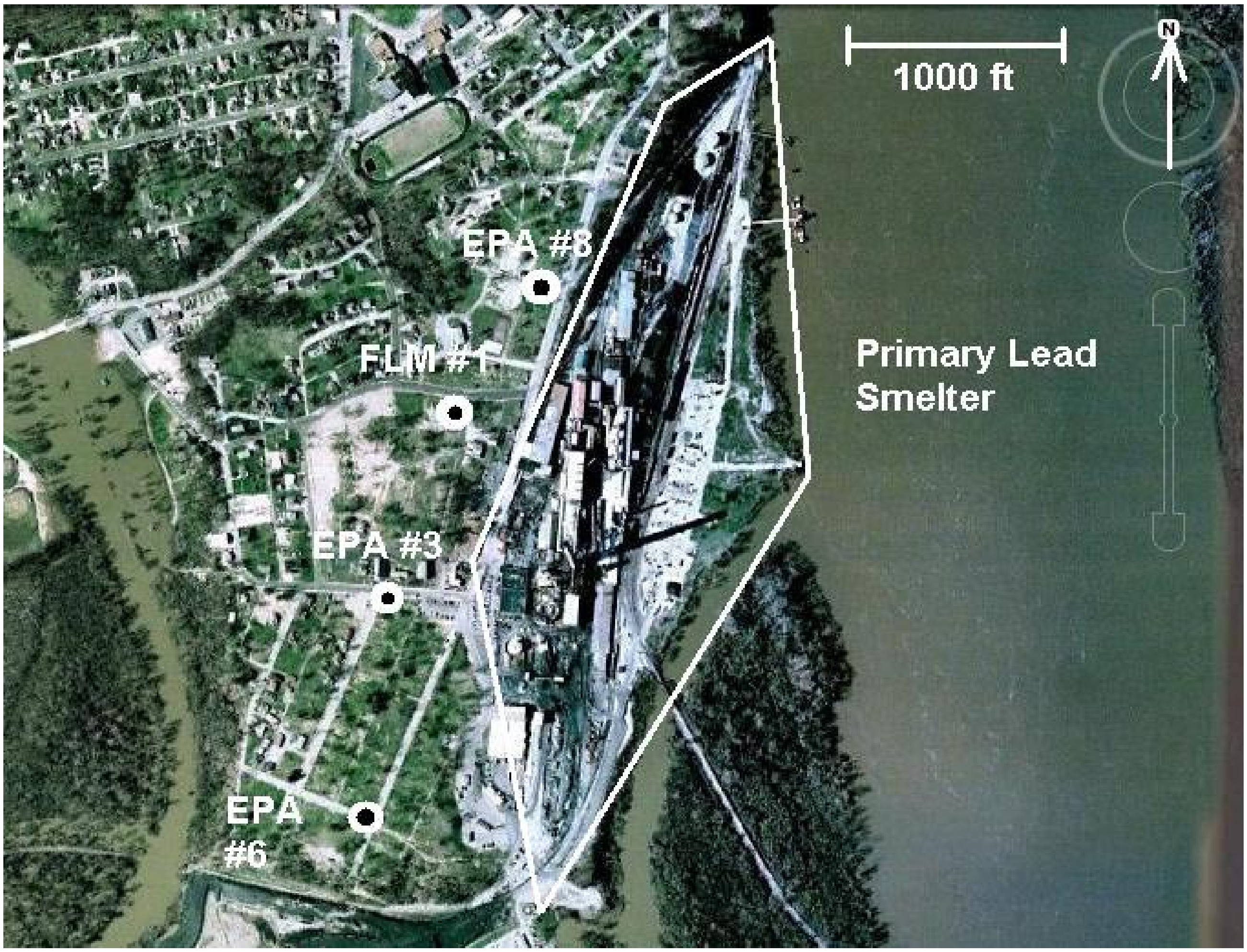

Figure 11. NRT Multi-Metals Sampling locations at Primary Lead Smelter

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

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