

# **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**

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**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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## 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.

## Table of Contents

1.0	Introduction .....	1
2.0	Background .....	2
3.0	Overview of Multi-Metals FLM Technology .....	10
4.0	Unique Aspects of Contemporary Multi-Metals Fence Line Monitors .....	15
5.0	Process Summary .....	16
6.0	Define Driver (Step 1) .....	19
7.0	Define Limits and Goals (Step 2) .....	20
8.0	Characterize Local Airshed and Emission Sources (Step 3) .....	23
9.0	Define Parameters to be Monitored (Step 4) .....	24
10.0	Develop Monitoring Plan (Step 5) .....	26
11.0	Data Processing/Quality Assurance and Control (Step 6 A) .....	35
12.0	Reporting Procedures (Step 6 B) .....	36
13.0	General Air Monitoring System Design Bibliography .....	38
14.0	References .....	41
15.0	Glossary of Definitions, Abbreviations, and Symbols.....	42

## List of Figures

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

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

Figure 3. Schematic of the Xact 620

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

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

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

Figure 7. Example of Xact 620 data report example

## List of Tables

Table 1. List of Metals of Potential Health Concern

Table 2. HAP Metals and Those of Concern - Community ( $\mu\text{g}/\text{m}^3$ )

Table 3. HAP Metals and Those of Concern Occupational/Industrial ( $\mu\text{g}/\text{m}^3$ )

Table 4. Xact 620 FLM Detection Limits

## 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.<sup>1</sup> 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**

<b><u>Name - Symbol (Atomic No.)</u></b>	<b><u>187 HAP</u></b>	<b><u>33 Urban HAP</u></b>	<b><u>CA REL</u></b>	<b><u>Ambient PM</u></b>
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.<sup>2</sup> 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<sup>3</sup>; and there is an increasing number of epidemiological and toxicological studies suggesting these PM health effects are predominantly caused by trace concentrations (ng/m<sup>3</sup>) 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.<sup>4</sup>

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<sup>5</sup>: “Transition metals have the capacity to support electron exchange and catalyze free radical production.”

- 1997, Costa and Dreher<sup>6</sup>: “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<sup>5</sup>: “...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.<sup>4</sup>: “The metals components in fine and ultrafine PM are particularly toxic and are the primary contributors to negative human health.”
- 2002, Magari et al.<sup>4</sup>: “...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.<sup>7</sup>: “...Transition metals present in ROFA (especially vanadium) participate in Fenton-like chemical reactions to produce reactive oxygen species (ROS).”
- 2002, Zelikoff et al.<sup>8</sup>: “...Both iron and nickel (inhaled) reduced pulmonary bacterial clearance in previously infected rats.”
- 2002, Molinelli et al.<sup>9</sup>: “...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.<sup>8</sup>: “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.<sup>10</sup>: “Nickel appears to be the component (of fine particulate matter) most likely to cause acute cardiac responses.”
- 2009, Konkel (Environmental Health Article)<sup>11</sup>: “(There is)...evidence linking nickel, vanadium, and elemental carbon in the air to wheeze and cough in inner city children.”
- 2009, Chen and Lippmann<sup>12</sup>: “...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<sup>12</sup>: “...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.<sup>13</sup>: “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.<sup>14</sup>: “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  $\mu\text{m}$ ), fall quickly from the air column, and do not typically reside in the respirable fraction of particulate matter.<sup>15</sup> In contrast, metals introduced to the air through anthropogenic activities tend to reside in the smallest particles (i.e. less than 10  $\mu\text{m}$ ). 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),<sup>16</sup> this size of particle can deposit deeper in the lungs eliciting a stronger inflammatory response.<sup>5</sup>

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.<sup>17</sup> However, when looking at exposure limits for Nickel, the most relevant medical and toxicological literature lists an acute (1-hour) average of 6  $\mu\text{g}/\text{m}^3$  (as reported in California EPA's reference exposure level (REL)), whereas the 8-hour permissible exposure limit (PEL) is 1,000  $\mu\text{g}/\text{m}^3$  (which equals 125  $\mu\text{g}/\text{m}^3$  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.<sup>12</sup> 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."<sup>16</sup> Further discussion on contemporary health effects of metals in ambient air is presented in Appendix C.

**Table 2. Community Metals Concentrations of Concern ( $\mu\text{g}/\text{m}^3$ )**

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

<sup>a</sup> Metals designated as Hazardous Air Pollutants by the EPA.

<sup>b</sup> National Ambient Air Quality Standard for lead is 0.15  $\mu\text{g}/\text{m}^3$  as a rolling three month average

<sup>c</sup> 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<sub>10</sub> measurements taken in the 1980's and 1990's, but may include TSP or PM<sub>2.5</sub> measurements. These values are not absolute; they are intended to represent typical concentrations found in urban environments.

<sup>d</sup> Ambient air values exceed one or more of the regulatory health limits for that metal.

<sup>e</sup> 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.

<sup>f</sup> Typical chronic concentration for Chromium VI is for particulate matter, a typical chronic level for aerosols and mists is approximately 0.008  $\mu\text{g}/\text{m}^3$

<sup>g</sup> Typical cancer concentration is for vanadium pentoxide

**Table 3. Occupational/Industrial Limits for Metals of Concern ( $\mu\text{g}/\text{m}^3$ )**

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

<sup>a</sup> Metals designated as Hazardous Air Pollutants by the EPA.

<sup>b</sup> NIOSH REL for arsenic is a 15-minute ceiling

<sup>c</sup> OSHA PEL for beryllium has a 30-minute ceiling of  $5 \mu\text{g}/\text{m}^3$

<sup>d</sup> REL and PEL for bismuth is a respiratory limit, the total REL is  $10 \mu\text{g}/\text{m}^3$  and total PEL is  $15 \mu\text{g}/\text{m}^3$

<sup>e</sup> Additional REL of 0.1 and PEL of 0.1 for copper fume

<sup>f</sup> NIOSH REL for lead is an 8-hour TWA standard

<sup>g</sup> NIOSH short term exposure limit (STEL) for manganese is  $3,000 \mu\text{g}/\text{m}^3$  and the PEL is a ceiling limit

<sup>h</sup> NIOSH REL for mercury for skin is  $50 \mu\text{g}/\text{m}^3$  and the REL is a ceiling

<sup>i</sup> Nickel as  $\text{Ni}(\text{CO})_4$  has an IDLH of  $14,000 \mu\text{g}/\text{m}^3$  and an REL and PEL of  $7 \mu\text{g}/\text{m}^3$

<sup>j</sup> Selenium as  $\text{SeF}_6$  has an IDLH of  $2000 \mu\text{g}/\text{m}^3$  and an REL and PEL of  $400 \mu\text{g}/\text{m}^3$

<sup>k</sup> 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.

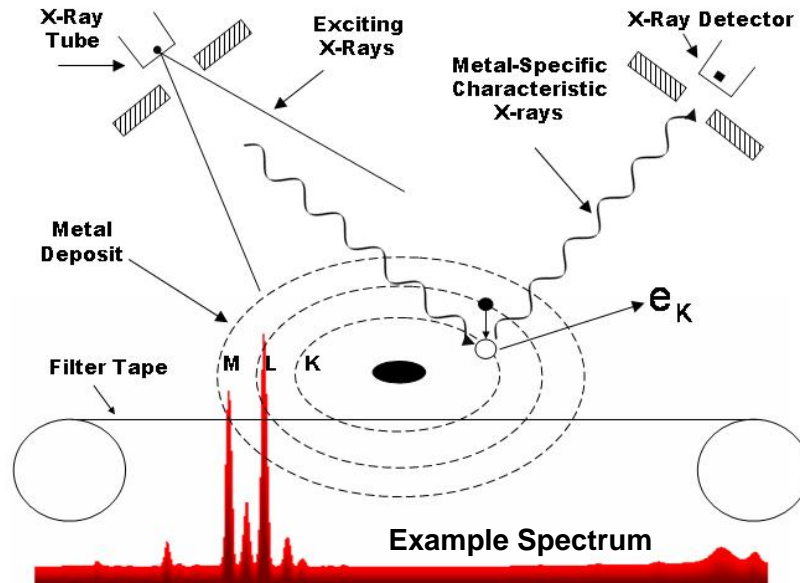
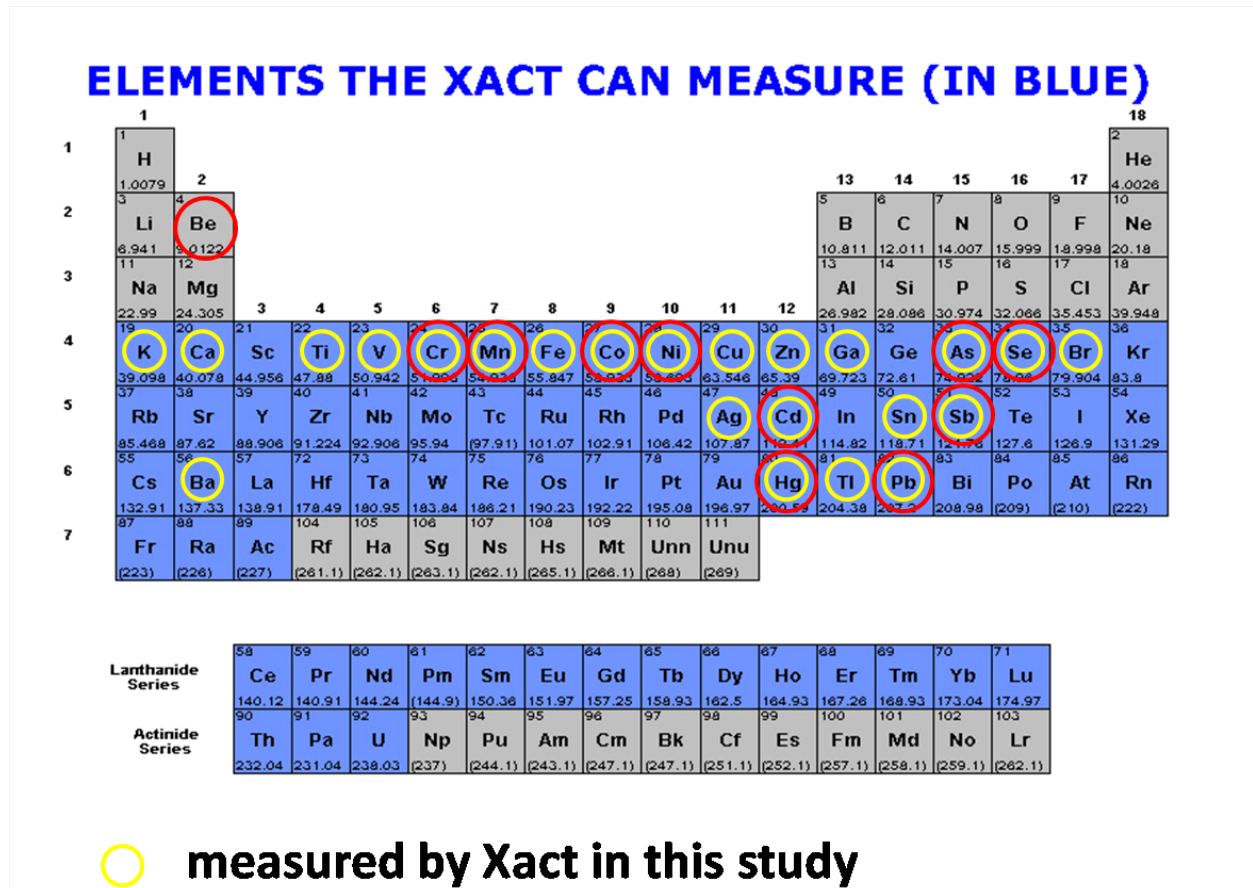
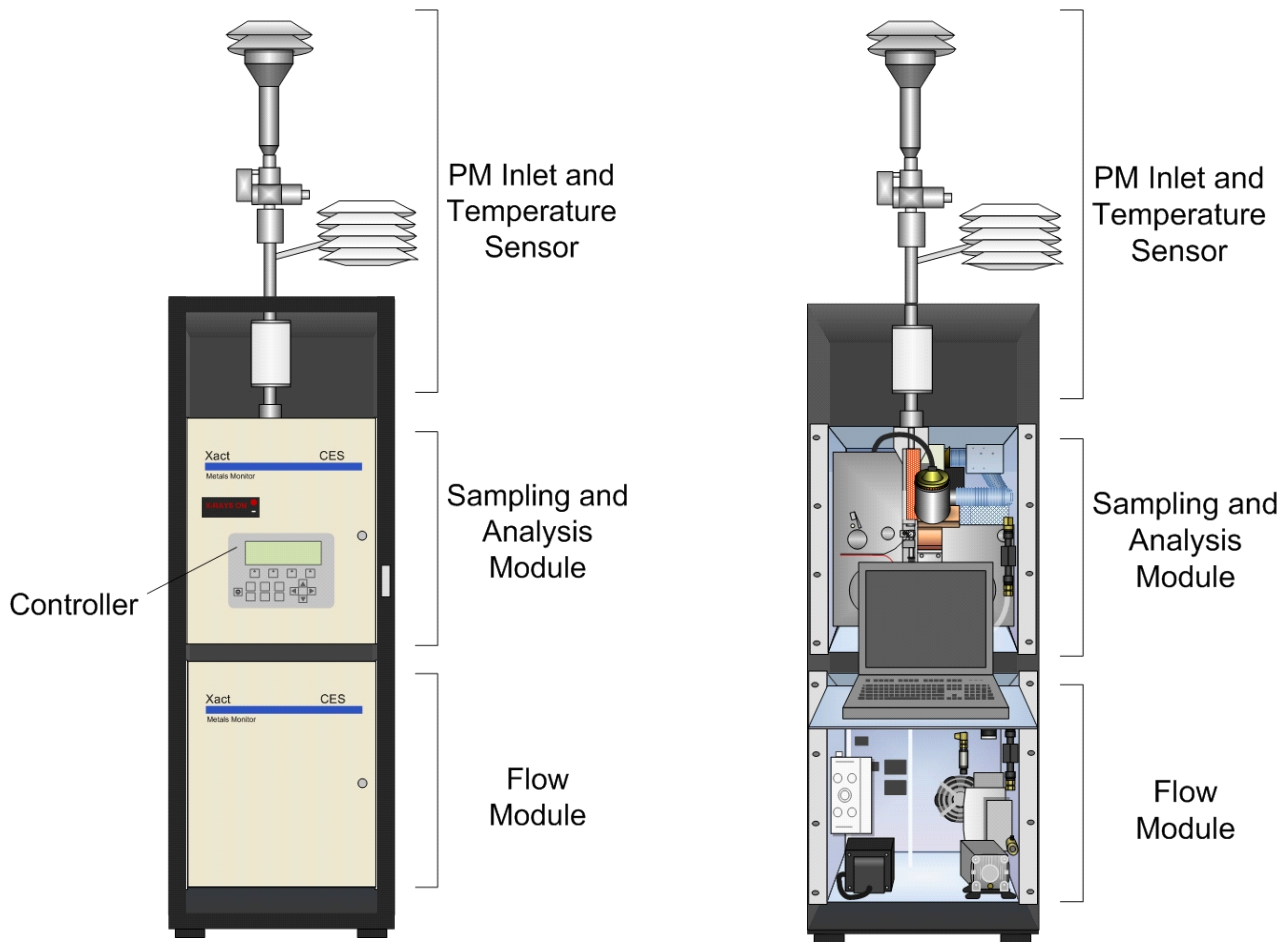


Figure 1: Diagram showing the main features of the multi-metals FLM technology



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

A schematic of an ambient multi-metals monitor is illustrated in Figure 3<sup>18</sup>. 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<sub>10</sub> 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<sub>10</sub> 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<sup>3</sup>) 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 IO3.3; 1 Sigma; Interference Free; ng/m<sup>3</sup>)**

Element	Atomic Number	4-hour	3-hour	2-hour	1-hour	30 min.	15 min.	FRM/IO 3.3 24-hour <sup>a</sup>
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

<sup>a</sup> 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<sub>2</sub>, 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.



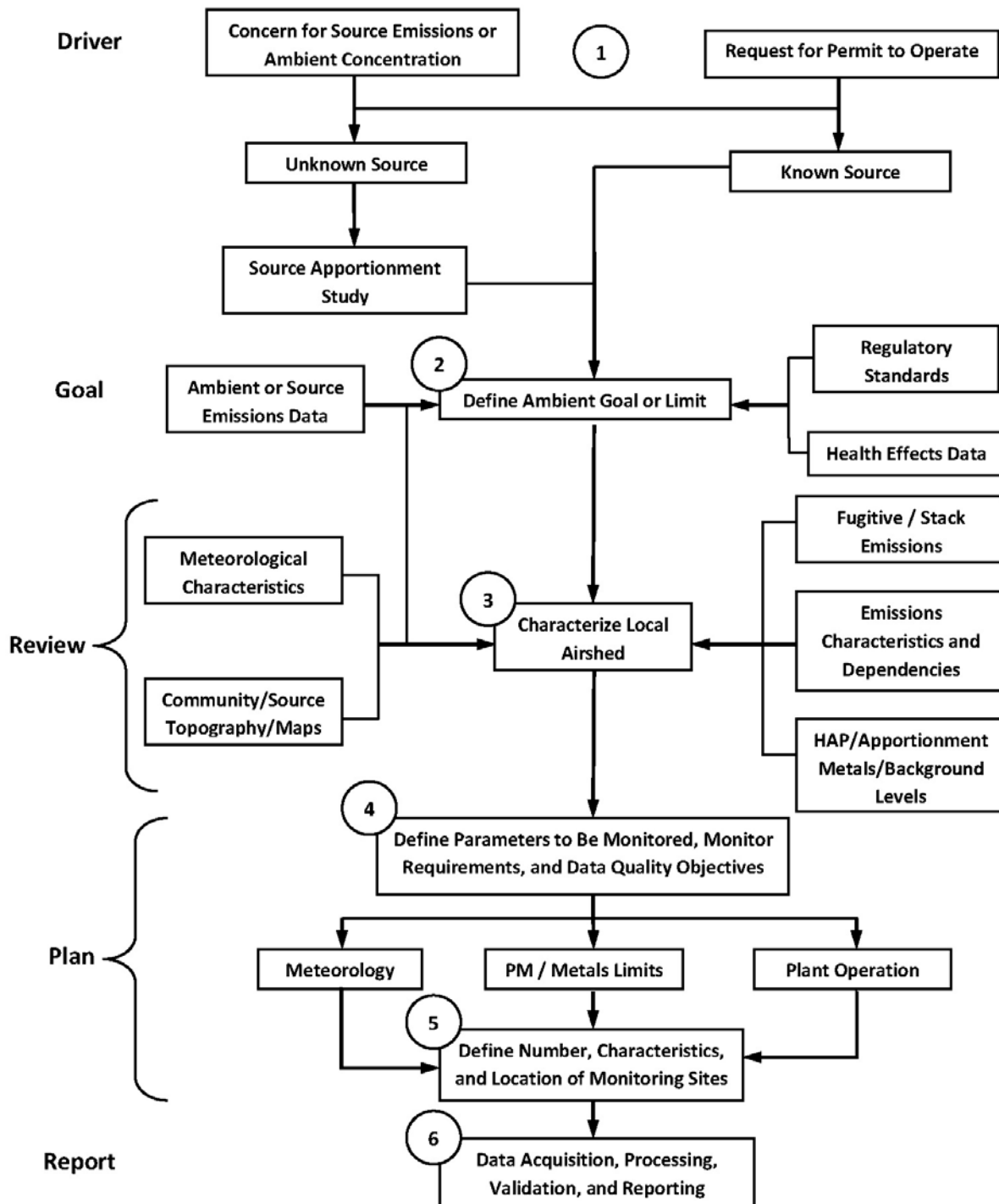


Figure 5. Flow diagram illustrating key steps in developing a fence-line monitoring plan for fugitive metals emissions

**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<sub>10</sub> arsenic measurements suggest that NIOSH health limits, set at 2 µg/m<sup>3</sup>, 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 ( $2.3 \mu\text{g}/\text{m}^3$ ) that exceeded the 15 minute ceiling ( $2 \mu\text{g}/\text{m}^3$ ) 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.

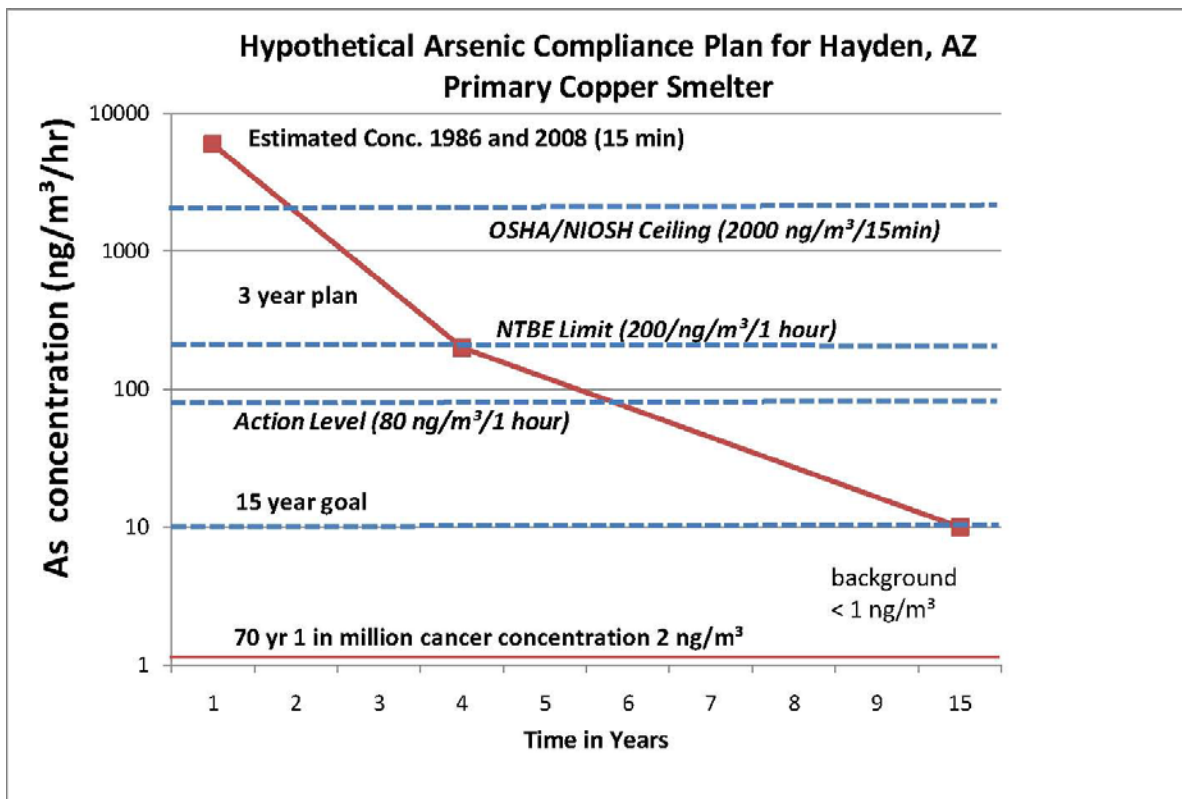
Clearly, the goals of these applications and resulting monitoring plans will be significantly different for each of these illustrated examples based in part on differences in their primary drivers. For example, the arsenic exposure drivers are more urgent than the health concerns of the ferrous metal 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<sup>19</sup> 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<sub>10</sub> arsenic, PM<sub>10</sub> 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<sup>3</sup> for TSP lead, 200 ng/m<sup>3</sup> for PM<sub>10</sub> 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<sub>2</sub>, SO<sub>2</sub>, HCl, Cl<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2.5</sub> 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 identifying 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<sub>10</sub> arsenic, the indicator in this case should remain as PM<sub>10</sub> arsenic. In this case, continuous measurement of PM<sub>10</sub> 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<sub>10</sub> 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<sub>2.5</sub> 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<sub>10</sub>, PM<sub>2.5</sub>) 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<sup>3</sup> 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<sub>2.5</sub> arsenic. Historic data shows that 85% of arsenic is in the PM<sub>2.5</sub> fraction. This smaller particle size should improve the source apportionment study by eliminating coarse particle interference.

Specific plan limits include an Action Level set at 80 ng/m<sup>3</sup>/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<sup>3</sup>/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<sup>3</sup>/1 hour.

Existing monitoring sites: Current monitoring sites exist in the two communities. Two PM<sub>2.5</sub> 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<sub>2.5</sub> 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  $2.3 \mu\text{g}/\text{m}^3$ . 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  $\text{PM}_{10}$  arsenic since the recorded episode was a  $\text{PM}_{10}$  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<sub>10</sub> 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  $1.5 \mu\text{g}/\text{m}^3$  and now is struggling to meet the new lead NAAQS at  $0.15 \mu\text{g}/\text{m}^3$ . 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  $43 \mu\text{g}/\text{m}^3$ , which



averaged over a month is  $0.060 \mu\text{g}/\text{m}^3$  representing 40% of the NAAQS of  $0.150 \mu\text{g}/\text{m}^3$ . 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  $0.15 \mu\text{g}/\text{m}^3$ , 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  $1 \mu\text{g}/\text{m}^3$  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  $\text{PM}_{10}$  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  $0.15 \mu\text{g}/\text{m}^3$ , 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  $1 \mu\text{g}/\text{m}^3$  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  $\text{PM}_{10}$  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<sup>3</sup>

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

**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 from 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 PM<sub>2.5</sub> and PM<sub>10</sub>*. 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 TSD- *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.
22. Noll, K. E. and T. L. Miller. *Air Monitoring Survey Design*, Ann Arbor Science, Ann Arbor, MI, 1977

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## 15.0 Glossary of Definition, Abbreviations, and Symbols

**Ambient Limit:** Average Ambient Concentration of a regulated species that cannot be exceeded 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 ratio of the difference between a reference value and the FLM Measured Value 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.