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NICKEL, CHROMIUM, AND ARSENIC SPECIATION OF AMBIENT PARTICULATE MATTER IN THE VICINITY OF AN OIL-FIRED UTILITY BOILER

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Project Description

A yearlong project was initiated in August 2002 to identify and quantify the Ni, Cr, and As species occurring in ambient particulate matter (PM) and fine PM with aerodynamic diameters of less than 10 μm (PM_{10}) and 2.5 μm ($\text{PM}_{2.5}$) in an urban environment near an oil-burning power plant. Uncertainties in the chemical speciation of Ni, Cr, and As in ambient PM, PM_{10} , and $\text{PM}_{2.5}$ associated with oil-fired boilers greatly affect inhalation health risk estimates, primarily because of the great variability in cancer potencies for different chemical species. For example, nickel subsulfide (e.g., Ni_3S_2 and Ni_7S_6) and hexavalent chromium (Cr^{6+}) compounds are considered the most carcinogenic Ni and Cr species on the basis of available human epidemiology and animal studies [1–4].

The U.S. Environmental Protection Agency (EPA) has had to assess the inhalation cancer risks of Ni and Cr emissions from oil-fired utility boilers parametrically at various levels of Ni_3S_2 and Cr^{6+} because of considerable uncertainties in the available speciation analyses results [1]. EPA used similar conservative assumptions in classifying Ni and Cr as hazardous air pollutants (HAPs) for its integrated urban air toxics strategy and required Toxics Release Inventory reporting for utilities [5]. The emission of metals from oil-fired boilers, especially those that are listed as HAPs in the 1990 Clean Air Act Amendments (e.g., Ni, Cr, and As), may be regulated in the future. A regulatory decision based on overestimates of Ni_3S_2 and Cr^{6+} emissions and concentrations in ambient PM, PM_{10} , and $\text{PM}_{2.5}$ could adversely affect the electric utility industry and its consumption of fuel oils.

The EERC, working in conjunction with the University of Kentucky, is uniquely qualified to determine the Ni, Cr, and As species present in the vicinity of an oil-fired boiler on the basis of recent advances in methods to directly determine metal speciation in oil fly ash and ambient PM using x-ray absorption fine-structure spectroscopy (XAFS) [6–8]. The EERC previously evaluated the validity of Ni sampling and speciation methods used to obtain the Ni speciation results reported in EPA's study of HAP emissions from electric utility boilers [1, 2]. This work, completed in July 1999, indicates that the sequential extraction procedure used to infer the presence of Ni_3S_2 in residual oil fly ash underestimates the soluble Ni species (i.e., nickel sulfate [NiSO_4]) and overestimates the relatively insoluble Ni species (i.e., Ni-rich spinel, trevorite [NiFe_2O_4]) content [8]. XAFS analyses of two fly ash samples and an ambient PM sample from a 400-MW oil-fired power plant indicated that >95% of the total Ni occurs as a NiSO_4 and Ni-bearing spinel mixture [8]. The absence of Ni_3S_2 in measurements performed on emissions and ambient PM associated with this particular

utility boiler is contrary to EPA's conservative Ni risk assessment [1], where it was assumed that the Ni compound mixture emitted from oil-fired utilities is 50% as carcinogenic as Ni_3S_2 . This assumption appears to greatly overestimate the Ni cancer risk from oil-fired utilities. The Ni and Cr species in ambient PM near additional oil-fired utility boilers need to be directly analyzed to improve the metal species emission characteristics for oil-fired boilers.

In addition to resolving discrepancies in Ni and Cr speciation work, research is required to determine the speciation of As in ambient PM, PM_{10} , and $\text{PM}_{2.5}$. Arsenic is generally more abundant in residual oil fly ashes relative to Cr [6, 8]. Cancer risk assessments for As by inhalation are based on occupational exposure to trivalent arsenic (As^{3+}), which is 25–60 times more toxic than pentavalent arsenic (As^{5+}) [9–11]. Consequently, a meaningful health risk assessment of As must include information on the As speciation of ambient PM, PM_{10} , and $\text{PM}_{2.5}$.

Goal

The overall goal is to provide a better understanding of the relationship between oil-based power system emissions and ambient air quality. Specific objectives are as follows:

- Identify and quantify the chemical compounds of Ni, Cr, and As present in the ambient PM, PM_{10} , and $\text{PM}_{2.5}$ near an oil-burning power plant.
- Assess Ni, Cr, and As species distributions as functions of particle type and size.
- Evaluate the stabilities and transformations of Ni, Cr, and As species in ambient air.

Rationale

The Ni, Cr, and As species present in the urban ambient PM, PM_{10} , and $\text{PM}_{2.5}$ sampled near an oil-burning power plant will be identified and quantified. These speciation results will be used to evaluate the hypothesis that the metal emissions from oil-fired utility boilers do not contribute Ni_3S_2 , Cr^{6+} , and As^{3+} to urban ambient PM, PM_{10} , and $\text{PM}_{2.5}$.

Approach

The following three activities are ongoing to achieve the project objectives:

- 1) Sampling
- 2) Analyses
- 3) Data reduction, interpretation, and reporting

The first activity was completed in August 2002; urban ambient PM, PM_{10} , and $\text{PM}_{2.5}$ near an oil-fired power plant were sampled using EPA Compendium Methods [12]. The second activity involves preparing and analyzing the samples using a variety of complementary analytical methods. Most of the analytical effort in the second activity is devoted to identifying and quantifying the chemical species of Ni, Cr, and As. The third activity involves the preparation of a conference presentation, final technical report, and peer-reviewed journal article based on the project results. In addition, the physicochemical properties of the identified species will be tabulated and compared to similar existing information for primary oil combustion PM (i.e., fly ash) sampled from the power plant to evaluate species transformations in ambient air.

Progress

Ambient PM, PM₁₀, and PM_{2.5} were sampled continuously August 26–31, 2002, from an urban State and Local Air Monitoring Stations (SLAMS) site in the vicinity of an oil-burning power plant. Relatively large amounts (0.2 gram) of bulk PM and much smaller amounts of PM₁₀ (≈ 2 mg) and PM_{2.5} (< 2 mg) were collected. Figure 1 shows the location of the SLAMS sampling site and its spatial relationship relative to major PM₁₀ and PM_{2.5} emission point sources [13]. Also presented in the figure are wind rose diagrams derived from meteorological data collected from two airports in the vicinity of the sampling site. The wind rose diagrams indicate the percentage of time that the wind was blowing from a given direction and the wind speed during the 6-day sampling period. Based on the predominantly easterly to southeasterly wind flows, the most likely local PM₁₀ and PM_{2.5} emission point sources to have contributed to the samples collected include the oil-burning power plant and a paving mixtures and blocks operation.

Urban PM, PM₁₀, and PM_{2.5} samples were analyzed during October 18–22, 2002, by the University of Kentucky using XAFS and at the National Synchrotron Light Source at Brookhaven National Laboratory, New York. Preliminary XAFS data reduction procedures indicate that Ni and Cr were present in sufficient concentrations in all three samples to obtain good x-ray absorption spectra; however, As was below the detection limit (≈ 2 ppm). XAFS is being used to directly determine the speciation of Ni and Cr in ambient PM, PM₁₀, and PM_{2.5} samples. In addition, automated scanning electron microscopy is being used to investigate the particle-size distributions and particle-type associations of various Ni and Cr species. The physicochemical properties of the identified Ni and Cr species will be tabulated and used as a basis for evaluating species stability and transformations in ambient air. Such information is crucial for properly assessing health effects and risks posed by stack emissions of Ni and Cr from oil-fired boilers and other emission sources.

Status

Ongoing analysis, data reduction, and interpretation activities will continue until the spring of 2003. Reporting aspects of the project are anticipated to be completed during June 2003.

Potential Users/Technology Transfer

Knowledge of the relationship between oil-burning power system emissions and ambient air quality will ultimately result in a more realistic inhalation-based risk assessment for oil-fired boilers. Such an assessment is necessary for EPA to properly address public health risks and regulatory decisions. The Utility MACT (Maximum Attainable Control Technology) Working Group, formed under the Clean Air Act Advisory Committee Subcommittee for Permits/New Source Reviews/Toxics, is interested in the outcome of this project because of the pending MACT regulations for coal- and oil-fired electric utility steam generating units that are being developed pertinent to section 112(d) of the Clean Air Act. According to an existing settlement agreement, MACT regulations are to be proposed by December 15, 2003, and promulgated by December 15, 2004.

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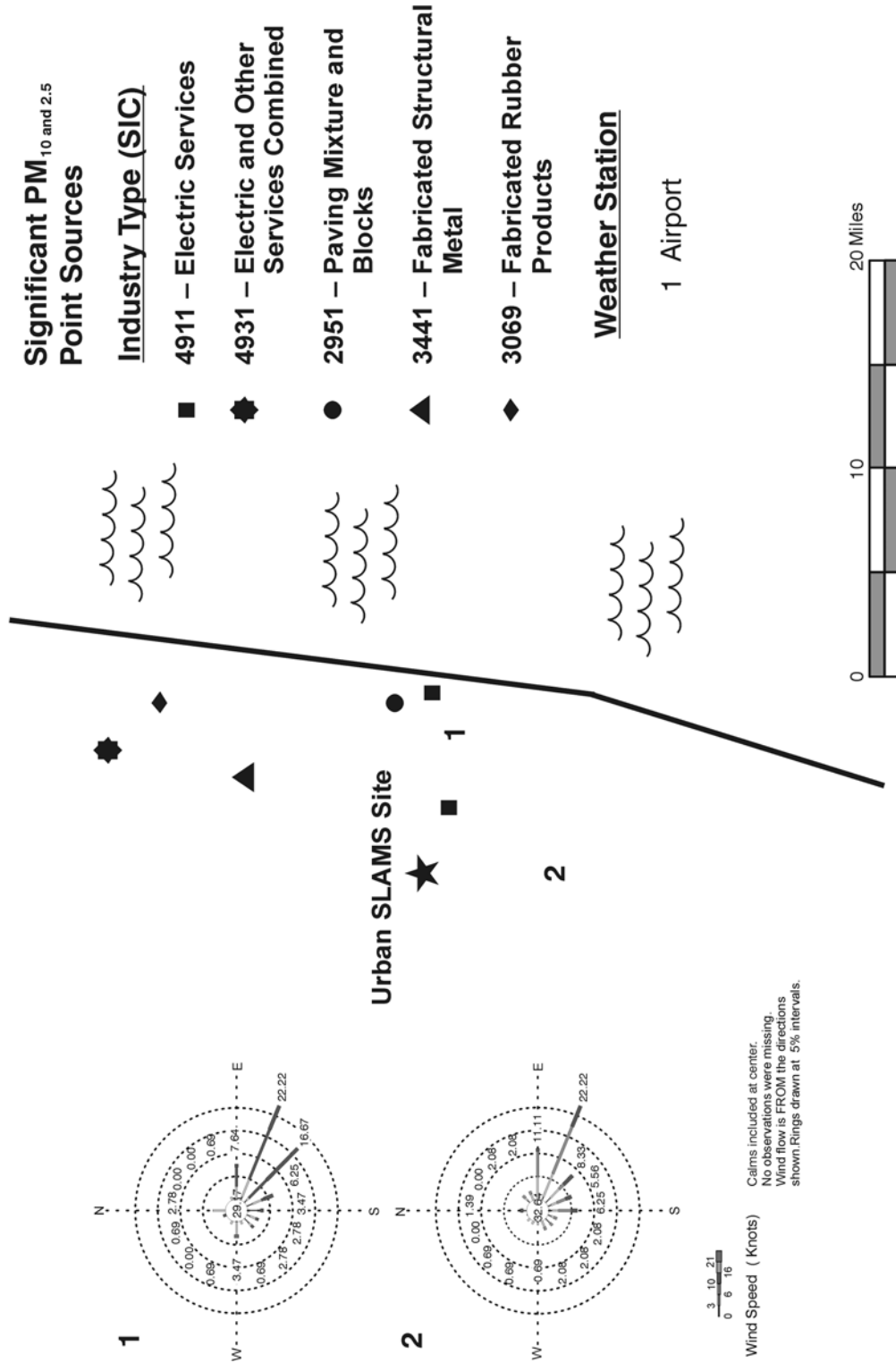


Figure 1. Sampling Site and Major PM₁₀ and PM_{2.5} Emission Point-Source Locations and Wind Rose Diagrams for Airport Locations 1 and 2

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