



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

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### *Project Description*

X-ray absorption fine structure (XAFS) spectroscopy was used in an attempt to identify and quantify the As, Cr, Ni, and S species occurring in total suspended particulate (TSP) matter and fine particulate matter (PM) with aerodynamic diameters of less than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ) and 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ) in an urban environment near a residual (No. 6 fuel) oil-burning power plant. Uncertainties in the chemical speciation of As, Cr, and Ni in ambient PM,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  greatly affect inhalation health risk estimates, primarily because of the large variability in acute, chronic, and cancer-causing effects for different As, Cr, and Ni compounds. For example, nickel subsulfide (e.g.,  $\text{Ni}_3\text{S}_2$  and  $\text{Ni}_7\text{S}_6$ ) and hexavalent chromium ( $\text{Cr}^{6+}$ ) compounds are considered the most carcinogenic Ni and Cr species [1–4], and trivalent arsenic ( $\text{As}^{3+}$ ) compounds are 25–60 times more toxic than pentavalent arsenic ( $\text{As}^{5+}$ ) compounds [5–7].

TSP,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  were sampled continuously using a high-volume air sampler (HVAS), an automatic cartridge collection unit (ACCU), and a sequential air sampler (SAS), respectively, during August 26–31, 2002, from an urban air monitoring site in Davie, Florida. A utility boiler located approximately 11.2 km (7 miles) east of the Davie site was burning residual oil at peak load (400 MW) capacity for about 18 hours during the sampling period. Meteorological conditions and SCREEN3 dispersion model calculations indicated that the residual oil combustion plume from the boiler stack was probably a kilometer or more north of the site and was probably never present at or above the Davie monitoring site. The predicted maximum  $\text{PM}_{10}$  contribution concentrations from the oil-burning boiler unit were so low ( $\leq 4.0 \times 10^{-6} \mu\text{g}/\text{m}^3$ ) that even if the plume had impacted the Davie monitoring site, its contribution to the mass loadings on sampling filters would have been insignificant given that the actual sample loadings corresponded to average TSP,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  concentrations of 26.8, 10.4, and 6.3  $\mu\text{g}/\text{m}^3$ , respectively. An insufficient amount of  $\text{PM}_{2.5}$  was sampled to perform XAFS spectroscopy chemical speciation measurements. In addition, As and Cr contamination ( $\approx 200$  ppm) of glass-fiber sampling filters used in the HVAS, ACCU, and SAS prevented accurate As and Cr analyses of the TSP,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  samples. X-ray absorption near-edge structure (XANES) spectral measurements indicated that  $>97\%$  of the sulfur in Davie TSP,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  occurs as sulfate ( $\text{SO}_4$ )-based compounds. TSP and  $\text{PM}_{10}$  Ni concentrations of 86 ppm and  $\approx 140$  ppm corresponded to airborne Ni concentrations of 2.3 and  $\approx 1.5 \text{ ng}/\text{m}^3$ , respectively, which are very similar to the annual average ambient Ni concentration of 1.9  $\text{ng}/\text{m}^3$  estimated for Broward County, Florida, by the U.S. Environmental Protection Agency (EPA). These low Ni concentrations probably represent the atmospheric burden of “background” Ni derived from long-range transport via the North Atlantic trade winds. An x-ray

diffraction (XRD) analysis of Davie TSP indicated that halite (NaCl) and calcite (CaCO<sub>3</sub>), classic tracers for marine aerosols, were present.

XAFS and XANES results indicated that NiSO<sub>4</sub> · xH<sub>2</sub>O and a nickel oxide compound, most likely a Ni-containing oxide spinel compound similar in composition to NiFe<sub>2</sub>O<sub>4</sub>, were the dominant Ni species occurring in Davie, Florida, TSP. A small amount of NiS was also detected. Davie PM<sub>10</sub> lacked NiS, but NiSO<sub>4</sub> · xH<sub>2</sub>O was more abundant than in TSP, probably because of the greater surface area of PM<sub>10</sub> on which NiSO<sub>4</sub> · xH<sub>2</sub>O heterogeneously condensed or adsorbed. TSP and PM<sub>10</sub> Ni species concentrations were estimated using a XANES least-squares fitting procedure and by assuming, for calculation purposes, pure stoichiometric NiSO<sub>4</sub> · 6H<sub>2</sub>O, NiFe<sub>2</sub>O<sub>4</sub>, and NiS compounds. These species concentrations could be used to estimate an inhalation dose for evaluating the potential health risks associated with each Ni species.

### ***Goal***

Project objectives were to identify and quantify the As, Cr, Ni, and S species present in urban ambient TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> sampled near a residual oil-burning power plant. The overall goal was to provide a better understanding of the relationship between oil-based power system emissions and ambient air quality.

### ***Rationale***

The EPA assessed the inhalation cancer risks from residual oil-fired utility boilers assuming various Ni<sub>3</sub>S<sub>2</sub> and Cr<sup>6+</sup> emissions because of considerable uncertainties in existing speciation analysis results [1]. EPA used similar assumptions in classifying Ni and Cr as urban hazardous air pollutants (HAPs) for its integrated urban air toxics strategy and requiring Toxics Release Inventory reporting for utilities [8, 9]. The emission of metals from oil-fired boilers, especially those that are listed as HAPs in the 1990 Clean Air Act Amendments (e.g., As, Cr, and Ni), may be regulated in the future. A regulatory decision based on overestimates of As<sup>3+</sup>, Ni<sub>3</sub>S<sub>2</sub>, and Cr<sup>6+</sup> emissions and concentrations in ambient TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> could adversely affect the electric utility industry and its consumption of fuel oils.

### ***Approach***

The Energy & Environmental Research Center (EERC), working in conjunction with the University of Kentucky, is uniquely qualified to determine the As, Cr, Ni, and S species present in the vicinity of an oil-fired boiler on the basis of recent advances in the direct determination of trace element species in fossil fuel combustion fly ash and ambient PM using XAFS [10–16]. 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 nickel subsulfide compounds in residual oil fly ash overestimates the relatively insoluble Ni species (i.e., Ni-rich spinel, trevorite [NiFe<sub>2</sub>O<sub>4</sub>]) content [12]. XAFS analyses of two fly ash samples and an ambient TSP sample from a 400-MW oil-fired power plant indicated that >95% of the total Ni occurs as a NiSO<sub>4</sub> and Ni-bearing spinel mixture [12]. The absence of nickel subsulfide compounds in emissions and ambient TSP associated with this particular utility boiler is contrary to EPA's Ni risk assessment [1], where it was assumed that the Ni compound mixture emitted from oil-fired utilities is 50% as carcinogenic as Ni<sub>3</sub>S<sub>2</sub>. This assumption appears to greatly overestimate the Ni cancer risk from oil-fired utilities. The Ni and Cr species in ambient TSP near additional oil-fired utility boilers need to be directly analyzed to improve our understanding of the relationship between oil-based power system emissions and ambient air quality.

In addition to resolving discrepancies in Ni and Cr speciation work, research is required to determine the speciation of As in ambient TSP, PM<sub>10</sub>, and PM<sub>2.5</sub>. Cancer risk assessments for As by inhalation are based on occupational exposure to As<sup>3+</sup> compounds, which are 25–60 times more toxic than As<sup>5+</sup> compounds [5–7]. Consequently, a meaningful health risk assessment of As must include information on the oxidation state of As in ambient TSP, PM<sub>10</sub>, and PM<sub>2.5</sub>.

**Progress**

**Site Description and Urban TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> Sampling**

Ambient TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> were sampled continuously during August 26–31, 2002, from an urban State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring System (NAMS) site located in Davie, Florida (26.08 N, 80.24 W). The Broward County Air Quality Division utilizes this urban (citywide scale, 4–50 km) site to determine representative PM<sub>10</sub> and PM<sub>2.5</sub> concentrations in an area of high population density. According to the Broward County Planning Services Division [17], the 2002 population density of Broward County was 3837 persons/mi<sup>2</sup>.

The locations of major PM<sub>10</sub> point sources in relation to the sampling site and a wind rose diagram, created from hourly average wind speed and direction measurements from the Fort Lauderdale International Airport, for the sampling period are shown in Figure 1. The PM<sub>10</sub> emission estimates in Figure 1 are based

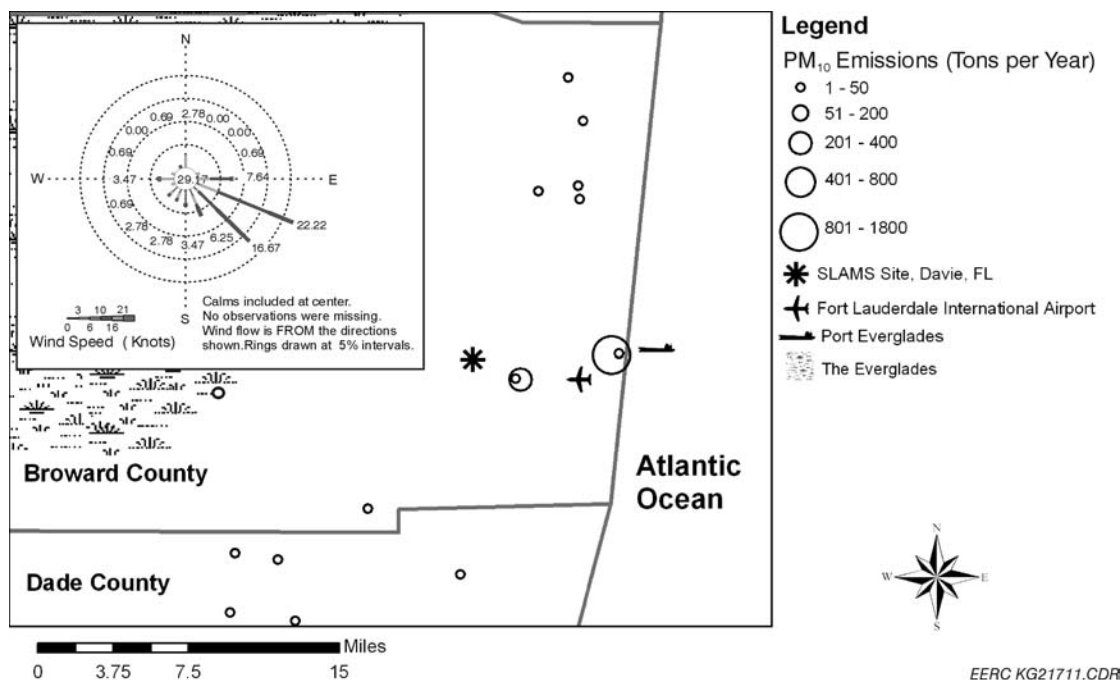


Figure 1. Davie, Florida, SLAMS/NAMS Site, Major PM<sub>10</sub> Point Source, Fort Lauderdale International Airport, and Port Everglade Locations and a Wind Rose Diagram for the Sampling Period

on 2001 statistics from the Florida Department of Environmental Protection. Point sources in the vicinity of the Davie site include residual oil- and gas-burning power plants, cement kiln operations, and municipal waste incineration facilities. Significant mobile sources of TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> near the Davie site include motor vehicle, aircraft, and marine vessel traffic. Marine vessels are also potential Ni emission sources because most burn distillate and residual-grade fuel oils which generally contain significant Ni contents [18, 19]. Approximately 5400 ships call at Port Everglades a year [20]. The wind rose diagram in Figure 1 indicates that winds were predominantly marine in origin and that mobile and point sources east-southeast and southeast from the Davie site probably contributed to TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> during the sampling period. Two meteorological processes that occurred during the sampling period were synoptic southeast and easterly winds associated with the tropical North Atlantic trade winds and the formation of deep convective thunderstorm cells. Tall (12–16 km) convective thunderstorms were generally generated during the afternoon when moist air from the ocean breeze was carried aloft by the hot air masses rising off the southern peninsula of Florida. In contrast to low-altitude frontal storms, these tall convective thunderstorms scavenge PM from the middle and upper troposphere.

### Plume Dispersion Modeling

The two largest PM<sub>10</sub> point sources indicated in Figure 1 are power plants located east and southeast of the Davie monitoring site. The power plant closest to the Davie, Florida, sampling site was burning natural gas during August 26–31, 2002, which probably did not produce significant As, Cr, Ni, and S emissions. The power plant east of the Davie site, however, was burning residual oil from approximately 8:00 a.m. to 5:00 p.m. at peak boiler load capacity on August 27 and 28, 2002, in one of its four 400-MW units. The combustion of residual oil is especially known as a source of Ni-bearing TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> [21–23]. A dispersion model, SCREEN3, was used to estimate the potential effect of PM<sub>10</sub> emissions from the easternmost residual oil-burning power plant on air quality at the Davie, Florida, sampling site. A graphical summary of the output from the SCREEN3 model is shown in Figure 2. Each trace in Figure 2 represents maximum concentration values for a receptor height of 1.83 m (equivalent to the height of sampling equipment employed at the Davie site) at various distances from the stack. Peak maximum concentration values vary with distance from the stack and wind speed. The Davie monitoring site is approximately 11.2 km (7 miles) from the oil-burning boiler unit stack (Figure 1). The maximum predicted PM<sub>10</sub> concentration contributed by the oil-burning unit at this distance was  $3.96 \times 10^{-6} \mu\text{g}/\text{m}^3$ , associated with a mean wind speed of 1 m/s. The average, hourly-observed wind speed between 8:00 a.m. and 5:00 p.m. on August 27 and 28, 2002, was 3.57 and 2.31 m/s, respectively. Rounding these averages to the nearest half increment, the estimated maximum PM<sub>10</sub> contribution concentrations are  $1.21 \times 10^{-6}$  and  $2.38 \times 10^{-6} \mu\text{g}/\text{m}^3$  at mean wind speeds of 3.5 and 2.5 m/s, respectively.

It should be noted a significant limitation of SCREEN3 is that it does not account for wet or dry deposition. Wet deposition was probably significant during the 2-day period because afternoon thunderstorms and rain showers occurred in the area on both days. During these events, significant amounts of PM<sub>10</sub> were probably removed from the plume, resulting in significantly lower PM<sub>10</sub> concentrations at relatively large distances downwind from the stack. Landing et al. [24] determined that Ni is effectively washed out of the Florida air shed during rainfall events. Consequently, the maximum concentration estimates from the model are greatly overestimated for periods during the afternoon rain events.

The predicted maximum PM<sub>10</sub> concentrations pertain to situations when the Davie monitoring site was directly downwind from the stack, along the center line of the plume. The Davie monitoring site is directly downwind of the stack when the wind was from 87.5° (compass direction). As indicated in the wind rose diagram presented in Figure 1, hourly observations between 8 a.m. and 5 p.m. for August 27 and 28, 2002, provide no evidence of winds from this direction. However, this does not preclude the possibility of such

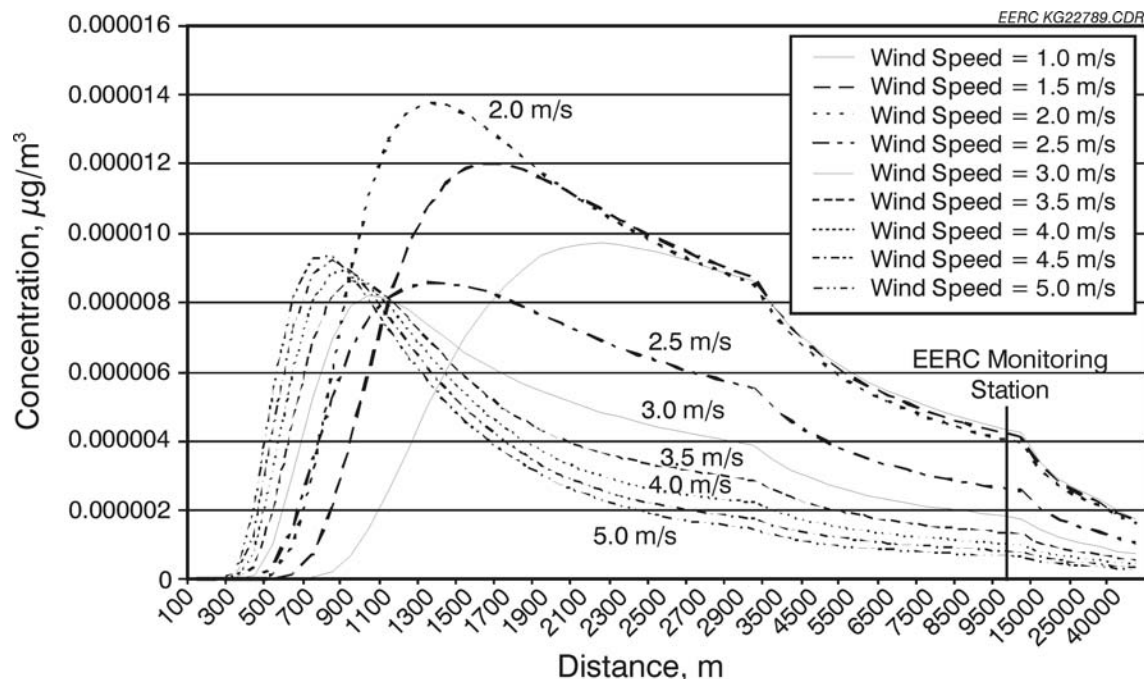


Figure 2. Estimated Concentration Maximums for  $PM_{10}$  along Plume Center Line at Various Distances from the Stack; Calculations Based on Atmospheric Stability of P-G Class 2

winds. A significant amount of time exists between observations when the wind may have been from this general direction (i.e., between  $80^\circ$  and  $95^\circ$ ), or another possibility is that higher-altitude winds near the stack height could have been from these directions. Upper air soundings from Miami International Airport indicated that the winds became more westerly with height.

In summary, the presence of a residual oil combustion plume at or above the Davie monitoring site during August 27 and 28, 2002, was very unlikely. Winds were mostly out of the southeast so the center line of the plume was probably a kilometer or more north of the site. In addition, the maximum predicted  $PM_{10}$  contribution concentrations from the oil-burning boiler unit were so low ( $\leq 4.0 \times 10^{-6} \mu\text{g}/\text{m}^3$ ) that even if the plume had impacted the Davie monitoring site, its contribution to the total TSP,  $PM_{10}$ , and  $PM_{2.5}$  mass loadings would have been insignificant.

#### TSP, $PM_{10}$ , and $PM_{2.5}$ Mass Loadings and As, Cr, Ni, and S Concentrations

Filter mass loading information was used to calculate average concentrations of airborne TSP,  $PM_{10}$ , and  $PM_{2.5}$  of 26.8, 10.4, and  $6.3 \mu\text{g}/\text{m}^3$ , respectively. An insufficient amount of  $PM_{2.5}$  was sampled to quantify As, Cr, and Ni and perform speciation measurements. Compared in Table 1 are the average measured (in duplicate) and certified As, Cr, and Ni concentrations for National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 1648 (Urban TSP) and measured As and Cr concentrations for a filter blank, as well as Ni concentrations for a filter blank and TSP collected at the Davie, Florida, site. As and Cr measurement results for SRM 1648 were acceptable with relative percent differences from the NIST certified values of  $\ll 10\%$ . However, the measured Ni concentration for SRM 1648 is biased 22% high relative to the NIST-certified Ni concentration. As and Cr contamination ( $\approx 200$  ppm) of glass-fiber sampling filters used in the HVAS, ACCU, and SAS prevented As and Cr analyses of the TSP,  $PM_{10}$ , and  $PM_{2.5}$

**Table 1.** Trace Element Analyses of NIST SRM 1648, Filter Blanks, and Davie, Florida, TSP, ppm

	NIST SRM 1648			Davie, FL, SLAMS/NAMS		
	Measured	NIST Certified	RPD <sup>1</sup>	Filter Blank	Urban TSP and Filter	Urban TSP <sup>2</sup>
As	120	115 ± 10	4.4	170	NR <sup>3</sup>	NA <sup>4</sup>
Cr	410	403 ± 12	1.7	205	NR	NA
Ni	100	82 ± 3	22	31	150	86

<sup>1</sup> Relative percent difference of the measured value from NIST certified value.

<sup>2</sup> Corrected concentration.

<sup>3</sup> Analyzed but not reported because filter blank contamination concentration was greater than that in TSP.

<sup>4</sup> Not applicable.

samples. Similar to As and Cr, the filter blank contained significant Ni but was much less than the Ni concentration of Davie TSP. The Ni concentration of Davie TSP is apparently much greater than SRM 1648. However, after the Ni contamination in the filter blank is accounted for and it is assumed that, similar to SRM 1648 the Ni measurement is biased 22% high, the corrected Ni concentration of Davie TSP presented in Table 1 is very similar to the SRM 1648 Ni concentration.

### XRD Analysis

A blank HVAS filter and the HVAS filter from Davie were analyzed using XRD to identify crystalline components of TSP. Halite and calcite were identified in Davie TSP. Halite and calcite are known tracers of marine aerosols.

### Sulfur K-Edge XAFS Spectroscopy Analyses

Presented in Figure 3 are unprocessed S K-edge XAFS spectra for the ACCU (PM<sub>10</sub>) and SAS (PM<sub>2.5</sub>) filter blanks and filters containing Davie TSP, PM<sub>10</sub>, and PM<sub>2.5</sub>. A spectrum for a blank filter from the HVAS is not presented in Figure 3 because it was not analyzed for S using XAFS spectroscopy. Although the PM<sub>10</sub>- and PM<sub>2.5</sub>-containing filters exhibit much smaller x-ray absorption intensities than the TSP-containing filter, the absorption intensities for these samples are significantly greater than the absorption signals for the corresponding blank filters. Hence, the S absorptions are primarily caused by the PM<sub>10</sub> and PM<sub>2.5</sub> trapped within the filters. Sulfur XANES spectra for the SAS filter blank and the filters containing TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> are presented in Figure 4. A XANES spectrum for the ACCU filter blank is not included in Figure 4 because the S K-edge absorption signal was too weak to be processed. The XANES features in Figure 4 are insensitive to differences in S concentration because of the data reduction process used to create the XANES spectra. The energy location of the S peaks in Figure 4 is consistent with the presence of SO<sub>4</sub> compounds. The XANES S species detection limit is approximately 3% of the total S present, thus >97% of the S in Davie TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, and SAS filter blank is present as SO<sub>4</sub>-based compounds. An ion chromatography analysis of a water extract from Davie TSP indicated that it contains 1.61 wt% SO<sub>4</sub>.

### Nickel K-Edge XAFS Spectroscopy Analyses

Presented in Figure 5 are Ni K-edge XAFS spectra for the HVAS (TSP), ACCU (PM<sub>10</sub>), and SAS (PM<sub>2.5</sub>) filter blanks and filters containing Davie TSP, PM<sub>10</sub>, and PM<sub>2.5</sub>. Also included in Figure 5 is a Ni K-edge XAFS spectrum collected when no sample was in the x-ray beam path. The relative Ni absorption intensity relationships are PM<sub>10</sub> > TSP > PM<sub>2.5</sub> + filter and beam blanks indicating that Ni is mostly concentrated in PM<sub>10</sub>. Duplicate graphite furnace atomic absorption spectroscopy (GFAAS) analyses of Davie TSP indicated that it contains 86 ppm Ni (Table 1). Ni absorption is generally proportional to Ni

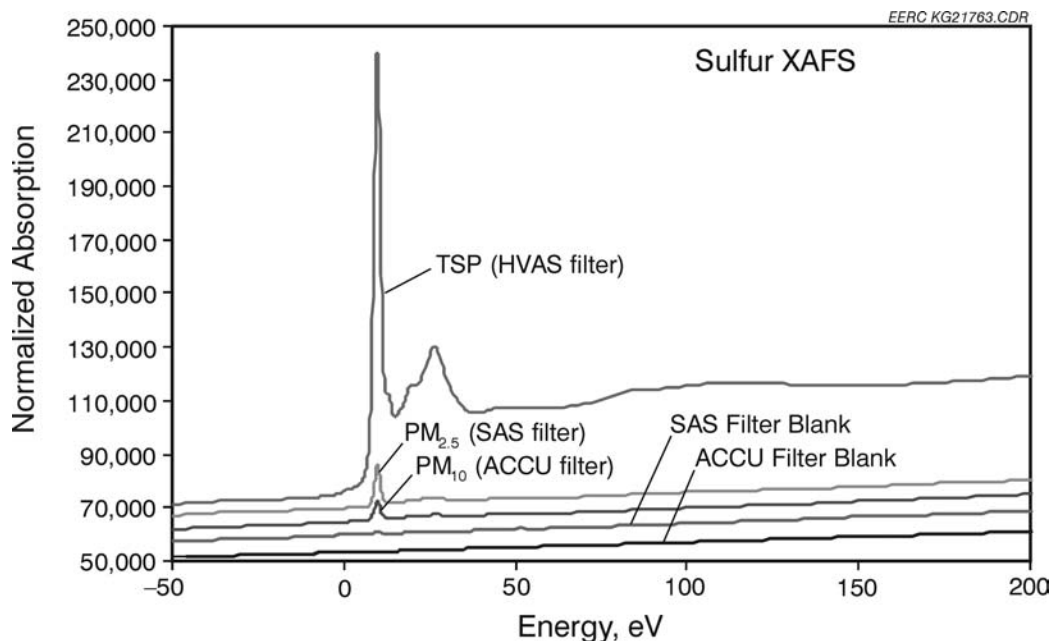


Figure 3. Sulfur K-Edge XAFS Spectra of ACCU ( $PM_{10}$ ) and SAS ( $PM_{2.5}$ ) Filter Blanks and Filters Containing Davie TSP,  $PM_{10}$ , and  $PM_{2.5}$ ; Value of 0 on the Abscissa Corresponds to the Actual S K-Edge Absorption Energy of 2472 eV

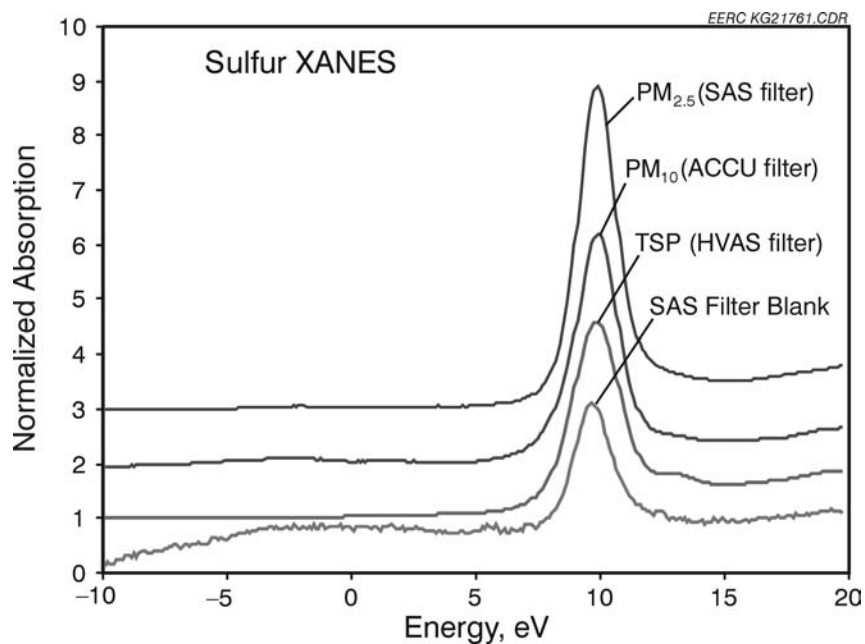


Figure 4. Sulfur XANES Spectra of SAS Filter Blank and Filters Containing Davie TSP,  $PM_{10}$ , and  $PM_{2.5}$ ; Value of 0 on the Abscissa Corresponds to the Actual S K-Edge Absorption Energy of 2472 eV

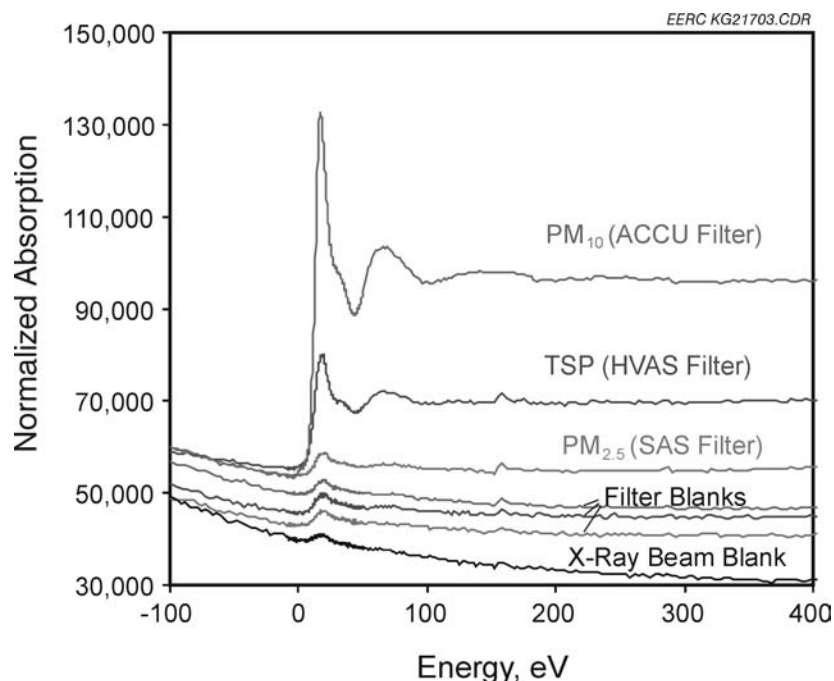


Figure 5. Ni K-Edge XAFS Spectra of HVAS, ACCU, and SAS Filter Blanks and Filters Containing Davie TSP, PM<sub>10</sub>, and PM<sub>2.5</sub>; Value of 0 on the Abscissa Corresponds to the Actual Ni K-Edge Absorption Energy of 8333 eV

concentration; thus the Davie PM<sub>10</sub> sample is estimated to contain approximately 140 ppm Ni. These Davie TSP and PM<sub>10</sub> Ni concentrations correspond to airborne Ni concentrations of 2.3 and  $\approx 1.5$  ng/m<sup>3</sup>, respectively, which are very similar to the annual average ambient Ni concentration of 1.9 ng/m<sup>3</sup> estimated for Broward County by EPA [25]. These Ni concentrations are much lower in comparison to average urban ambient air Ni concentrations which range from 5 to 50 ng/m<sup>3</sup> and are more representative of Ni concentrations found in remote and rural areas [26–29]. The low airborne Ni concentrations at the Davie, Florida, air-monitoring site probably represent the atmospheric burden of “background” Ni derived from long-range transport via the southeast and easterly North Atlantic trade winds (Figure 1).

The Ni K-edge absorption signals from the filters containing Davie TSP and PM<sub>10</sub> were sufficiently intense to process and create the XANES spectra presented in Figure 6. Spectra from the Ni XANES database, described previously in the experimental section of this report, were compared to the spectra shown in Figure 6 using a least-squares fitting procedure. Estimates, based on the least-squares fitting, of the Ni species compositions of Davie TSP and PM<sub>10</sub> are provided in Table 2. Davie PM<sub>10</sub> contains a much greater proportion of NiSO<sub>4</sub> · xH<sub>2</sub>O relative to TSP, probably because of the greater surface area of PM<sub>10</sub> on which NiSO<sub>4</sub> · xH<sub>2</sub>O heterogeneously condensed or adsorbed.

The Ni speciation results in Table 2 were used to calculate the concentrations of Ni compounds in Davie TSP and PM<sub>10</sub> and ambient air. The calculations were performed assuming pure stoichiometric nickel hexahydrate (NiSO<sub>4</sub> · 6H<sub>2</sub>O), NiFe<sub>2</sub>O<sub>4</sub>, and NiS compounds. Results of the calculations are presented in Table 3. The results in Table 3, especially those for PM<sub>10</sub>, can be used to estimate an inhalation dose and are,

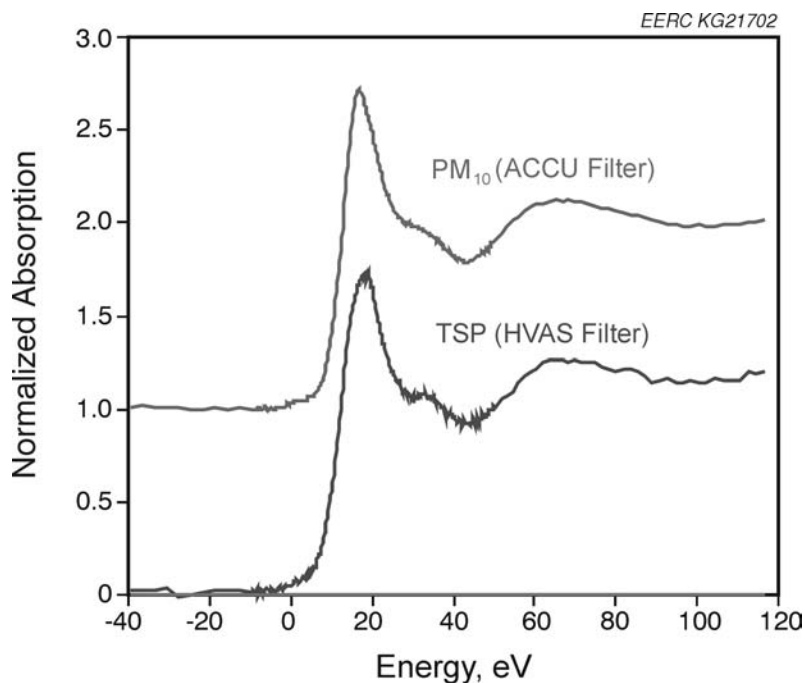


Figure 6. Ni K-Edge XANES Spectra of the Filters Containing Davie TSP and PM<sub>10</sub>; Value of 0 on the Abscissa Corresponds to the Actual Ni K-Edge Absorption Energy of 8333 eV

**Table 2.** XANES Ni Speciation Results for Davie TSP and PM<sub>10</sub>, % of total Ni

Ni Species	TSP	PM <sub>10</sub>
NiSO <sub>4</sub> · xH <sub>2</sub> O	40	78
NiFe <sub>2</sub> O <sub>4</sub>	50	22
NiS	10	<5

**Table 3.** Ni Species Concentrations for Davie TSP and PM<sub>10</sub>

Ni Species	TSP		PM <sub>10</sub>	
	Filter, ppm	Airborne, ng/m <sup>3</sup>	Filter, ppm	Airborne, ng/m <sup>3</sup>
NiSO <sub>4</sub> · 6H <sub>2</sub> O	154	4.1	489	5.1
NiFe <sub>2</sub> O <sub>4</sub>	172	4.6	123	1.3
NiS	13	0.4	<11	<0.1

therefore, more useful than those in Table 2 for evaluating the potential health risks associated with individual Ni species.

### **Status**

In addition to the CATM annual report, presented herein, and final technical report, preliminary Ni analysis results from this project were presented at the American Association for Aerosol Research PM Meeting, Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health; the appropriate literature citation is:

Galbreath, K.C.; Crocker, C.R.; Nyberg, C.M.; Ralston, N.V.C.; Huggins, F.E.; Huffman, G.P. Nickel Speciation of Urban Particulate Matter. Presented at the American Association for Aerosol Research PM Meeting, Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health, Pittsburgh, PA, March 31–April 4, 2003.

Most of the Ni analysis results from this project were also published in a Metals in Perspective column of the *Journal of Environmental Monitoring* at the request of the column editors: Dr. Adriana Oller and Dr. Hudson Bates; the appropriate literature citation is:

Galbreath, K.C.; Crocker, C.R.; Nyberg, C.M.; Huggins, F.E.; Huffman, G.P.; Larson, K.P. Nickel Speciation Measurements of Urban Particulate Matter: Method Evaluation and Relevance to Risk Assessment. *Journal of Environmental Monitoring* **2003**, 5, 56N–61N.

### **Quality Assurance/Quality Control**

The EERC is committed to delivering consistent and high-quality research. An organizationwide quality management system (QMS), authorized and supported by EERC managers, is in effect and governs all programs within the organization. The EERC established and formalized a QMS in August 1988. A quality manual defines the requirements and the organizational responsibilities for each major element of the QMS and references the supporting documents needed to provide a comprehensive program. Compliance with this manual and its supporting documents ensures that the EERC adequately fulfills governmental and private clients' requirements relating to quality and compliance with applicable regulations, codes, and protocols. Additionally, the CATM program at the EERC has a quality assurance (QA) plan in effect that addresses trace metal research [30]. The CATM QA plan has been reviewed and accepted by EPA. The project reported on herein has complied with the quality manual, the CATM QA plan, and all revisions. An independent QA auditor has reviewed all aspects of QA/quality control (QC) associated with this project and report.

#### **Quality Objectives**

The following quality objectives were established to evaluate data validity:

- Mass loading of a TSP-, PM<sub>10</sub>-, or PM<sub>2.5</sub>-containing filter must be at least 10  $\mu\text{g}$  greater than its original mass prior to sampling.
- Analyte concentration of a TSP-, PM<sub>10</sub>-, or PM<sub>2.5</sub>-containing filter must be greater than the analyte concentration of a corresponding blank filter.
- Measured metal analyte concentrations of SRM 1648 must be within  $\pm 10\%$  of the NIST certified value.

#### **Measurement/Data Acquisition**

The following equipment and EPA Compendium Methods [31] were used to sample ambient TSP, PM<sub>10</sub>, and PM<sub>2.5</sub>:

- Tapered electronic oscillating microbalance, Rupprecht & Patashnick Model 1400a (EPA Compendium Method IO-1.3)
- ACCU, Rupprecht & Patashnick
- SAS, Rupprecht & Patashnick Model 2025 (EPA Compendium Method IO-2.3)
- HVAS and General Metal Works (EPA Compendium Method IO-2.1)

TSP was collected on Gelman Scientific Type A/E glass-fiber filters, whereas PM<sub>10</sub> and PM<sub>2.5</sub> were collected on Whatman GF/C glass-fiber filters. Field filter blank samples were collected for QC purposes. Meteorological conditions (e.g., temperature, wind speed and direction, and relative humidity) were also recorded during the sampling period. However, late in the sampling campaign, lightning struck the weather mast at the Davie site, and the recorded meteorological data were lost.

#### **As, Cr, Ni, and S Analyses**

Urban TSP, PM<sub>10</sub>, and PM<sub>2.5</sub> samples and filter blanks were prepared using American Society for Testing and Materials Method D6357. As and Ni were analyzed using GFAAS, whereas Cr was analyzed using inductively coupled-atomic emission spectroscopy. Analysis quality was evaluated by analyzing NIST SRM 1648. The S concentration of TSP was determined by performing a water extraction and analyzing the extract by ion chromatography.

#### **XRD**

XRD analyses were performed on the Davie TSP sample to identify crystalline phases. XRD patterns were collected over 5°–70° 2θ with a Philips X'Pert theta-theta x-ray diffractometer system operating at 40 kV and 50 mA (graphite monochromatized Cu K-α radiation, 0.02° 2θ steps, 3 sec/step). Incident beam optics consisted of a programmable divergence slit fixed at ¼° and a 15-mm wide-beam mask. Diffracted beam optics consisted of an antiscatter slit programmed for an automatic 10-mm irradiated length, programmable receiving slit set to a height of 0.35 mm, soller slits, and a secondary monochromator. Diffraction peaks were identified using a Minerals Data Incorporated JADE+ processing software utilizing the ICDD PDF-2 inorganic and organic powder diffraction database, Sets 1–45 on CD-ROM.

#### **XAFS Spectroscopy**

XAFS spectroscopy was performed at the As, Cr, Ni, and S K-absorption edges at beam-lines X-18B and X-19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York, during October 18–22, 2002. The NSLS was operated at a constant voltage of 2.85 GeV, and the current generally decayed from 290 to 175 mA between fills every 12 hours. As, Cr, and Ni XAFS spectra were collected in fluorescence geometry using a multielement Ge array detector. Sollor slits and the appropriate 6 μm Z-1 filter were used to enhance the signal-to-noise ratio of the XAFS spectra. As and Ni XAFS spectra were generated by rotating a double Si (220) crystal monochromator from about 100 eV below the K-edge to about 500 eV above. Cr and S XAFS spectra were produced on beam-line –19A using a Si (111) channel cut crystal. S XAFS spectra were collected from about 72 eV below and 250 eV above the S K-edge using a PIPS detector without soller slits or a filter. Multiple scans, typically between 3 and 5 scans, were combined to produce the overall spectrum.

K-absorption edge locations were defined by the major peaks in the first derivative XAFS spectra using metallic nickel (Ni<sup>0</sup>) and Cr<sup>0</sup> foils or by the major XAFS peak for S<sup>0</sup> (diluted 20× in boron nitride) and a thin

smear mount of  $\text{As}_2\text{O}_3$ . Ni and As calibration spectra were acquired simultaneously in absorption geometry behind the fluorescence experiment. S and Cr calibration spectra were usually acquired in separate analyses.

As, Cr, Ni, and S XAFS spectra were analyzed using the procedures described by Brown et al. [32], Lee et al. [33], and Koningsberger and Prins [34]. First, the energy scale was calibrated with respect to the zero-point of energy defined by the calibration standard spectrum. Then the XAFS spectrum of the unknown sample was divided into separate XANES and extended XAFS regions. XANES spectra of reagent-grade compounds and synthesized compounds, acquired in previous investigations [10–16], were used essentially as “fingerprints” for identifying chemical species. For example, the following Ni compounds are included in this spectral database:  $\text{Ni}^0$ , NiS,  $\text{NiS}_2$ ,  $\text{Ni}_3\text{S}_2$ – $\text{Ni}_7\text{S}_6$  mixture, “green” NiO,  $\text{Ni}(\text{OH})_2$ ,  $\text{NiSO}_4 \cdot x\text{H}_2\text{O}$ ,  $\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{NiCO}_3$ ,  $\text{NiFe}_2\text{O}_4$ ,  $(\text{Mg},\text{Ni})(\text{Al},\text{Fe})_2\text{O}_4$ ,  $\text{MgNiO}_2$ ,  $(\text{Mg}_{0.2},\text{Ni}_{0.8})_2\text{SiO}_4$ , and  $(\text{Mg}_{0.85},\text{Ni}_{0.15})_2\text{SiO}_4$ .

### **Assessment and Validation**

Acceptable project data and results were identified using the quality objectives presented in the previous section of this report.

### ***Potential Users/Technology Transfer***

Knowledge of the relationship between residual 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 and state agencies to properly address public health risks and regulatory decisions. EPA and the Utility Maximum Achievable Control Technology (MACT) Working Group, formed under the Clean Air Act Advisory Committee Subcommittee for Permits/New Source Reviews/Toxics, should be interested in the project results presented herein 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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