

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231274021>

Physical and Chemical Characterization of Residual Oil-Fired Power Plant Emissions

ARTICLE *in* ENERGY & FUELS · MAY 2009

Impact Factor: 2.79 · DOI: 10.1021/ef8011118

CITATIONS

8

READS

65

6 AUTHORS, INCLUDING:



[Matthew S Landis](#)

United States Environmental Protection A...

91 PUBLICATIONS 2,437 CITATIONS

SEE PROFILE

Physical and Chemical Characterization of Residual Oil-Fired Power Plant Emissions

Michael D. Hays,* Lee Beck, Pamela Barfield, Robert D. Willis, Matthew S. Landis, and Robert K. Stevens

United States Environmental Protection Agency, Office of Research and Development,
Research Triangle Park, North Carolina 27711

William Preston and Yuanji Dong

ARCADIS, Research Triangle Park, North Carolina 27711

Received December 18, 2008. Revised Manuscript Received February 24, 2009

Although the toxicity of oil combustion emissions is a significant public health concern, few studies characterize the emissions from plant-scale utility boilers firing residual oil. This study remedies that deficiency by diluting, sampling, and monitoring stack emissions from a 432 gigajoules (GJ) front-fired fossil fuel steam generator burning residual oil. Over a 3-day test period, continuous CO₂, SO₂, and NO_x emissions monitoring confirms a steady fuel feed rate, high combustion efficiency (3.4 kg of CO₂/kg of fuel oil burned), and evidence of a nocturnal soot-blowing event. The utility boiler emits fine aerosol (PM_{2.5}) at a rate of $53 \pm 2 \mu\text{g/kJ}$ (2 g/kg of oil burned). Vesicular coarse particles composed of C and S and spherical Al silicates with V and Ni inclusions are identified in a cyclone rinse using scanning electron microscopy and backscatter analysis. Ion chromatography results establish that the fine aerosol is predominantly sulfate ($44\% \pm 0.2\%$, w/w) which is likely coordinated to transition metals. From thermal optical transmittance measurements, less than 1% (w/w) of the fine aerosol is surmised to be carbonaceous. Low emissions of particle-phase carbon and contaminants interfered with the gas chromatography–mass spectrometry (GC-MS) analysis of polycyclic aromatic hydrocarbons and certain other semivolatile organic compounds. However, trace levels of branched-, cyclic-, and *n*-alkanes and organic acids are observed in the particle emissions. Sterane and hopane molecules are below the picogram level GC-MS detection limits. Future research determining the individual organic species in the particles emitted from this source will require real-time single particle measurements. Finally, application of EPA methods TO-11 and TO-15 shows that the total volatile nonmethane organic gas emissions from the plant-scale boiler vary between 6 and 28 mg/kg of fuel oil burned; greater than 50% of this mass is ascribed to oxygenated matter.

Introduction

Annually, the U.S. consumes roughly 26 billion liters of heavy fuel oil for electric power generation.¹ Although this represents just a slight fraction of the 1 billion metric tons of coal the U.S. burns annually for electricity, there is serious concern over the high toxicity of oil combustion particles, the excess relative health risks seen in susceptible populations living near oil combustion sources, and the conceivable formation of localized pollutant hotspots caused by emissions from large-scale oil-fired stationary sources.^{2,3}

Compositional data describing fossil fuel combustion emissions are sought to improve pollutant exposure estimates and our overall understanding of aerosol-related health effects.^{4,5}

They also serve to further develop anthropogenic emissions inventories and source–receptor⁶ and air quality models⁷ and to better predict the more recently observed emissions-related direct and indirect effects on climate.⁸ Yet few studies thoroughly characterize the physical and chemical properties of emissions directly from full-scale utility boilers firing heavy fuel oil.^{2,9–12} Access to plant stacks of this scale is normally restricted because of safety regulations and the exceedingly complex logistics and cooperation needed to support sampling efforts. Therefore, the emissions from pilot-scale refractory-lined com-

* To whom correspondence should be addressed. E-mail: hays.michael@epa.gov. Phone 919-541-3984. Fax 919-685-3346.

(1) U.S.D.O.E. Official Energy Statistics from the U.S. Government. <http://www.eia.doe.gov/> (accessed September, 2006).

(2) Ahlberg, M.; Berghem, L.; Nordberg, G.; Persson, S. A.; Rudling, L.; Steen, B. *Environ. Health Perspect.* **1983**, *47*, 85–102.

(3) Knox, E. G. *J. Epidemiol. Comm. Health* **2005**, *59*, 755–760.

(4) Ghio, A. J.; Silbajoris, R.; Carson, J. L.; Samet, J. M. *Environ. Health Perspect.* **2002**, *110*, 89–94.

(5) Grahme, T. J.; Schlesinger, R. B. *Inhalation Toxicol.* **2007**, *19*, 457–481.

(6) Kim, E.; Hopke, P. K. *Atmos. Environ.* **2008**, *42*, 6047–6056.

(7) Russell, A. G. *J. Air Waste Manage. Assoc.* **2008**, *58*, 289–302.

(8) IPCC, The physical science basis. Summary for policymakers. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Prepared by the IPCC. In 2007.

(9) Galbreath, K. C.; Toman, D. L.; Zygarlicke, C. J.; Huggins, F. E.; Huffman, G. P.; Wong, J. L. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1876–1886.

(10) Galbreath, K. C.; Schulz, R. L.; Toman, D. L.; Nyberg, C. M.; Huggins, F. E.; Huffman, G. P.; Zillioux, E. J. *J. Air Waste Manage. Assoc.* **2005**, *55*, 309–318.

(11) Northrop, P. S.; Levendis, Y. A.; Gavalas, G. R. *Energy Fuels* **1991**, *5*, 587–594.

(12) Olmez, I.; Sheffield, A. E.; Gordon, G. E.; Houck, J. E.; Pritchett, L. C.; J.A., C.; Dzubay, T. G.; Bennett, R. L. *J. Air Pollution Control Association* **1988**, *38*, 1392–1402.

bustors that simulate combustion conditions at the plant-scale or from smaller institutional-scale, water-tube, or fire-tube package boilers firing residual oil traditionally are better characterized.^{13–22} Moreover, several laboratory furnace studies have examined the effects of air-fuel ratios and dilution and fuel spray conditions on residual oil combustion emissions.^{9,23–26} And while all these studies use a variety of complex dilution, sampling, analytical, chemical, and particle sizing techniques to measure the physical and chemical properties of these emissions, it is uncertain how well this past testing mimics the gas- and particle-phase emissions from front-firing utility-scale boilers burning residual oil. This information gap potentially impedes a realistic environmental risk assessment of plant-scale oil combustion for power-generation; thus, it is imperative that emissions from oil combustion at this scale continue to be investigated.

This study aimed to chemically and physically characterize the surface-level emissions from a fossil fuel steam generator burning No. 6 fuel oil (also termed “residual” or “heavy” fuel oil). Continuous emissions monitoring (CEM) of CO₂, SO₂, and oxides of nitrogen is conducted because of the well-known effects of these gases on the atmosphere and climate. Coarse and fine particle matter (PM) and organic gas emissions are sampled and analyzed using a variety of techniques. Gas chromatography–mass spectrometry (GC-MS) is applied to speciate individual semivolatile organic constituents in the fine aerosol emissions; the elemental carbon and inorganic matter in fine PM are examined using thermal-optical-transmittance (TOT) and energy-dispersive X-ray fluorescence (ED-XRF), respectively. Microstructure and elemental composition of individual coarse particles are investigated using scanning electron microscopy (SEM) techniques. Analysis of low-pressure impactor substrates by ion chromatography produces particle size distributions of sulfate emitted from the plant-scale source. Oxygenated and hydrocarbon gas concentrations in the emissions are determined using widely practiced EPA methods TO-11 and TO-15. Finally, some of the challenging analytical and

Table 1. Residual Oil Fuel Use and Stack and Dilution Sampling Conditions for Each of the Three Days

	day 1	day 2	day 3
Fuel Use Data			
fuel burned (kg/min)	267.0	265.7	272.8
fuel energy per unit volume (GJ/L)	0.6		
Stack Conditions Measured			
barometric pressure (mm Hg)	762.0	765.3	764.0
static pressure (mm Hg)	−12.4	−16.0	−16.0
stack temperature (°C)	147.5	150.0	149.4
CO ₂ (%)	9.6	9.2	8.9
O ₂ (%)	9.4	9.9	10.2
N ₂ (%)	81.0	80.9	80.9
Calculated			
stack pressure (mm Hg)	760.9	764.0	762.8
moisture (%)	7.1	6.5	6.2
velocity (m/s)	15.9	16.5	16.3
wet volumetric flow @ STP (m ³ /min)	4938.1	5121.8	5067.5
DSS Conditions			
sampling time (min)	359.7	479.8	480.0
sampling flow rate (slpm)	19.4	20.8	21.3
dilution ratio	44.6	41.8	40.7

sampling issues that arise when testing a plant-scale oil boiler source for organic gases and aerosols are discussed.

Experimental Section

Plant-Scale Utility Boiler Firing Residual Oil. The boiler was a front-fired fossil fuel steam generator with a permitted capacity of 432 GJ. It burned No.6 residual fuel oil throughout testing (250 L/min), operating at roughly 51% of its permitted load with a 5-field electrostatic precipitator (ESP) as the only control device. Results of an analysis of the No.6 oil found C, 87.85; H, 7.34; O, 1.87; N, 0.57; S, 2.35; ash, 0.02—all values are given as percentages. Plant fuel use data and real-time plots of the fuel flow rate are given in Table 1 and Supporting Information Figure S1, respectively.

Stack Emissions Monitoring and Sampling. Plant emissions were collected using a modified version of the dilution sampling system (DSS) designed by Hildemann et al.²⁷ This system allowed the condensation and coagulation of particles to occur in a residence chamber prior to sample collection. The DSS probe withdrew sample from a stack port ($d = 20$ cm) positioned orthogonally to the emissions stream at least 40 m from any flow disturbance (i.e., the stack exit was ~ 40 m above the sampling port) and downstream of the ESP control. Static pressure at the sampling ports was slightly negative (< -25 mm water). Stack gas flow rates were determined daily using EPA Methods 1–2.²⁸ The measured sampling dilution ratio was $\geq 40:1$, which according to Chang et al.²⁹ was sufficient to obtain representative primary particles from stationary combustion sources. As a result of logistical and plant safety constraints, only three days of plant stack testing were permitted. Average stack, test, and dilution conditions for the 3-day test period (6–8 h of sampling for each test) are provided in Table 1. Over the 3 test days, CEM data from the plant were obtained every 6 min for CO₂ (infrared analyzer; ZRH, California Analytical Instruments), SO₂, and oxides of nitrogen (NO and NO₂ or NO_x) (Thermo Scientific). The NO–NO₂ analyzer was operated in NO_x mode; thus, the NO stack emission concentrations were approximated at 95% (v/v) for emission factor values reported henceforth.

The DSS sampling array configuration used for this study is described elsewhere.³⁰ Briefly, fine PM emissions were collected on Teflon and preconditioned (550 °C, 12 h) quartz fiber filters

(13) Bond, T. C.; Wehner, B.; Plewka, A.; Widensohler, A.; Heintzenberg, J.; Charlson, R. J. *Atmos. Environ.* **2006**, *40*, 3574–3587.

(14) Goldstein, H. L.; Siegmund, C. W. *Environ. Sci. Technol.* **1976**, *10*, 1109–1114.

(15) Huffman, G. P.; Huggins, F. E.; Shah, N.; Huggins, R.; Linak, W. P.; Miller, C. A.; Pugmire, R. J.; Meuzelaar, H. L. C.; Mohindar, S. S.; Manivannan, A. J. *Air Waste Manage. Assoc.* **2000**, *50*, 1106–1114.

(16) Linak, W. P.; Miller, C. A.; Wendt, J. O. L. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1532–1544.

(17) Linak, W. P.; Miller, C. A.; Wendt, J. O. L. *Proc. Combust. Inst.* **2000**, *28*, 2651–2658.

(18) Miller, C. A.; Linak, W. P.; King, C.; Wendt, J. O. L. *Combust. Sci. Technol.* **1998**, *134*, 477–502.

(19) Miller, C. A.; Ryan, J. V.; Lombardo, T. J. *Air Waste Manage. Assoc.* **1996**, *46*, 742–748.

(20) Chen, Y.; Shah, N.; Huggins, F. E.; Huffman, G. P. *Environ. Sci. Technol.* **2004**, *38*, 6553–6560.

(21) Galbreath, K. C.; Zygarlicke, C. J.; Huggins, F. E.; Huffman, G. P.; Wong, J. L. *Energy Fuels* **1998**, *12*, 818–822.

(22) England, G. C.; Watson, J. G.; Chow, J. C.; Zielinska, B.; Chang, M.-C.; Loos, K. R.; Hidy, G. M. *J. Air Waste Manage. Assoc.* **2007**, *57*, 79–93.

(23) Allouis, C.; Beretta, F.; D'Alessio, A. *Chemosphere* **2003**, *51*, 1091–1096.

(24) Costa, M.; Costen, P.; Lockwood, F. C. *Combust. Sci. Technol.* **1991**, *75*, 129–154.

(25) Galbreath, K. C.; Zygarlicke, C. J.; Toman, D. L.; Huggins, F. E.; Huffman, G. P. *Combust. Sci. Technol.* **1998**, *134*, 243–262.

(26) Lee, S. W.; Pomalis, R.; Kan, B. *Fuel Process. Technol.* **2000**, *65–66*, 189–202.

(27) Hildemann, L. M.; Cass, G. R.; Markowski, G. R. *Aerosol Sci. Technol.* **1989**, *10*, 193–204.

(28) U.S.E.P.A. Measurement Science - Test Method Collections, <http://www.epa.gov/osa/fem/methcollectns.htm> (accessed April 2008).

(29) Chang, M.-C.; Chow, J. C.; Watson, J. G.; Hopke, P. K.; Yi, S. M.; England, G. C. *J. Air Waste Manage. Assoc.* **2004**, *54*, 1494–1505.

(30) Hays, M. D.; Beck, L.; Barfield, P.; Lavrich, R. J.; Dong, Y.; Vander Wal, R. L. *Environ. Sci. Technol.* **2008**, *42*, 2496–2502.

(Pall Life Sciences, 47 mm diamter 2.0 μm Teflo and Tissuquartz, respectively) positioned in parallel downstream of a PM_{2.5} cyclone. Gas-phase semivolatile organic compounds (SVOCs) were collected on polyurethane foam plugs (PUFs) located behind the quartz filters. An identically configured array sampled dilution air and was used to background correct the chemical emissions factors where appropriate. This check was likely more stringent than a field blank correction for passive deposition because filters were treated as field blanks but also collected compounds present in the dilution air, which was passed through the collection substrates at the same volumetric rate as the sampling emissions. The method of Turpin et al.³¹ later applied by Subramanian et al.³² was used to estimate the positive adsorption artifact on the quartz filters. Hereafter termed the Q-QBT method, it utilized a front quartz filter (Q_f) in parallel with a second quartz filter (Q_b) positioned downstream of a Teflon filter.

A 13-stage low pressure impactor (Dekati Inc.) interfaced to the DSS segregated and collected PM by size (from 0.03 to 10.0 μm). Because we were interested in characterizing the fine aerosol emissions and wanted to reduce the potential for coarse particle fragmentation and bounce from higher stages, a PM_{2.5} cyclone was placed upstream of the impactor. The aluminum foil discs lining the impactor stages were not greased because they were used for chemical analysis. Volatile organic compounds (VOCs) and oxygenated gas-phase compounds were measured using EPA Methods TO-15 and TO-11A, respectively.^{33,34}

Schematic diagrams of the dilution sampler (Figure S2), the sampling arrays (Figure S3), and the stack sampling location (Figure S4) used in the present study are provided in the Supporting Information. A more comprehensive dilution sampling discussion is also given.

Physical and Chemical Analyses of the Utility Oil Boiler Emissions. The general approach to sample collection and substrate analysis used for this study was described elsewhere.³⁰ Briefly, fine PM mass collected on the Teflon filters and the impactor liners was analyzed gravimetrically (Sartorius microbalance) following equilibration (25 °C at 40% RH for 24 h). The Teflon filters were subject to ED-XRF, which determined the elemental composition of the fine PM emissions from the boiler. An element was considered above detection limits if its concentration was greater than 3σ . The Teflon filter set was also subject to a leaching procedure that quantified separately the concentrations of water-soluble and acid extractable metals and ions using high-resolution inductively coupled plasma mass spectrometry and ion chromatography (IC), respectively. Results of these tests are forthcoming.

Determination of the organic and elemental carbon (OC and EC, respectively) in the fine PM collected on preconditioned quartz filters was attempted using TOT analysis (Sunset Laboratories) and NIOSH Method 5040.³⁵ A small section of each quartz filter was also analyzed by thermal extraction–gas chromatography–mass spectrometry (TE-GC-MS) in an attempt to measure individual nonpolar organic compounds in the fine PM sample. Details of the

TE-GC-MS conditions used were described previously.³⁶ In brief, a filter section was placed in a concentric quartz tube, spiked with a deuterated internal standard suite, heated stepwise (10 °C/min) over helium (20 L/min) to 300 °C, and held for 10 min. Vaporized organic matter was condensed and trapped in a quartz-packed programmable temperature vaporization (PTV) inlet being cryo-cooled (−100 °C) with liquid N₂. Following this step, the PTV inlet was flash heated (720 °C/min) to 300 °C, which transferred the organic matter to the GC-MS instrument for separation and detection as described below.

As a result of low organic carbon mass loadings, quartz filters were also composited across the three test days and extracted multiple times successively while undergoing mild sonication in a benzene/isopropyl alcohol/hexanes solvent mixture. Individual PUFs were extracted manually in a dichloromethane/hexanes/acetone mixture. Extracts were concentrated to ~200 μL with N₂. The quartz filter extract was split into two 100 μL fractions. One remained untreated while the other was derivatized with diazomethane to convert organic acids to their methyl ester analogues. All extracts were analyzed by GC-MS (Agilent 6890/5973, Palo Alto, CA).³⁷ In brief, extracts were injected into a hot (300 °C) split/splitless inlet operating in splitless mode. The carrier gas was He, and the column (HP 5MS; 30 m length, 0.25 mm i.d., and 0.25 μm 5% phenyl-methylpolysiloxane film thickness) flow rate was 1 mL/min. The GC oven temperature was held constant at 65 °C for 10 min and then ramped to 300 °C at a rate of 10 °C/min. The MS detector was operated in scan mode (50–500 amu). Enhanced Chemstation software (version D.02.00.275) was used for instrument control and data acquisition and analysis. The internal standard method was used for quantification. Select deuterated forms of target analytes from the following compound classes were used as internal standards: *n*-alkane (C₁₀–C₃₈), branched-alkane, cyclic alkane, polycyclic aromatic hydrocarbon, sterane, hopane, and carboxylic acid (*n*-alkanoic, alkeneoic, alkanedioic, and aromatic). Organic compound standards were prepared at the University of Wisconsin, Madison, Wisconsin State Laboratory of Hygiene. In addition to the dilution air checks used in background corrections, a series of field and laboratory method blanks were performed for quality control purposes.

In an attempt to produce particle size distributions of sulfate and other chemical ions, the impactor foils were subject to IC.³⁰ IC analysis of the liners immediately followed their extraction with water. The IC was calibrated at multiple levels for NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ cations and Cl[−], Br[−], NO₂[−], NO₃[−], PO₄^{3−}, and SO₄^{2−} anions. The gravimetric and sulfate size distributions produced using the impactor data were inverted using the model of Dong et al.³⁸

The PM_{2.5} cyclone was rinsed in an effort to sample its particle catch. Samples were analyzed by SEM (LEO 440, Leo Electron Microscopy, Ltd.) coupled with an energy-dispersive X-ray (EDX) analysis system (IMIX, Princeton Gamma-Tech). Particles were dispersed over a clean section of polycarbonate filter (0.1 μm pores) affixed to a carbon sticky tab and attached to an SEM stub. Images were collected both from particles on the surface of the polycarbonate filter as well as particles on the surrounding carbon sticky tab. A second sample was analyzed via Computer-Controlled SEM-EDX (CCSEM) analysis (R.J. Lee Instruments Ltd.) in a dedicated search for heavy metals. The brightness threshold in the backscatter mode was set to reject lighter particles. Metals included in the search were Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, La, Ba, Hg, and Pb. The EDX detection limit for these metals in individual particles is estimated to be on the order of a few wt %. The sample was analyzed for 5 h during which a total of 326 particles containing

(31) Turpin, B. J.; Huntzicker, J. J.; Hering, S. V. *Atmos. Environ.* **1994**, 28, 3061–3071.

(32) Subramanian, R.; Khylstov, A. K.; Cabada, J. C.; Robinson, A. *Aerosol Sci. Technol.* **2004**, 38, 27–48.

(33) U.S.E.P.A. Compendium Method TO-11A; Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC); EPA/625/R-96/010b (NTIS PB99-172355); U.S. Environmental Protection Agency, Center for Environmental Research Information, Office of Research and Development: Cincinnati, OH, 1999.

(34) U.S.E.P.A. Compendium Method TO-15; Determination of Volatile Organic compounds (VOCs) In Air Collected in Specially-Prepared Canisters And Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS); EPA/625/R-96/010b (NTIS PB99-172355); U.S. Environmental Protection Agency, Center for Environmental Research Information, Office of Research and Development: Cincinnati, OH, 1999.

(35) Cassinelli, M. E.; O'Connor, P. F. NIOSH Method 5040 In *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed.; Cassinelli, M. E.; O'Connor, P. F., Eds.; The Centers for Disease Control and Prevention: Atlanta, GA; 1998; 2nd Supplement to DHHS (NIOSH) Publication No. 94-113.

(36) Hays, M. D.; Smith, N. D.; Kinsey, J.; Dong, Y.; Kariher, P. H. *J. Aerosol Sci.* **2003**, 34, 1061–1084.

(37) Hays, M. D.; Geron, C. D.; Linna, K. J.; Smith, N. D.; Schauer, J. J. *Environ. Sci. Technol.* **2002**, 36, 2281–2295.

(38) Dong, Y.; Hays, M. D.; Smith, N. D.; Kinsey, J. *J. Aerosol Sci.* **2004**, 35, 1497–1512.

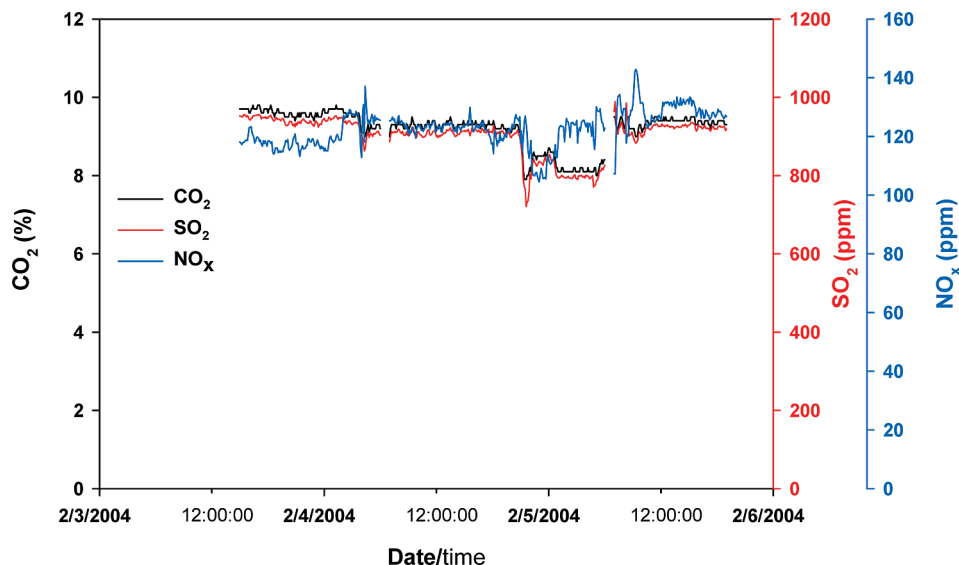


Figure 1. Continuous emissions measurements of CO₂, SO₂, and NO_x.

metals were identified. All particles and spectra were manually reviewed to confirm the presence of heavy metals.

Results and Discussion

Continuous Emissions Monitoring of the Plant Stack Gases. The steady fuel feed rate, feedstock, and combustion conditions at the plant over the test period produces relatively consistent CO₂ ($9.2 \pm 5\%$), SO₂ (902 ± 48.6 ppm), and NO_x (123 ± 6.0 ppm) stack emissions, Figure 1. Mass balance calculations show that greater than 90% of the carbon in the fuel is released as CO₂ at a rate of roughly one metric ton per minute or 3.4 kg of CO₂/kg of fuel oil burned. Greater than 90% of the sulfur in the fuel is emitted as SO₂, an acid gas; the SO₂ emission factor is nearly 50 g/kg of fuel burned. Fuel-based emission factors for NO and NO₂, derived assuming [NO] = 95% (v/v), are 3.0 ± 0.2 g/kg of fuel burned and 0.2 ± 0.01 g/kg of fuel burned, respectively. Soot-blowing with compressed air appears evident from the small stepwise decrease in CO₂ and SO₂ emissions accompanied by the rise in NO_x observed over the 2/4/2004–2/5/2004 test period in Figure 1. Soot blowing removes soot from the boiler surface to improve heat transfer efficiency between the flame and the boiler water. Nitrogen oxides are critical to tropospheric O₃ production, acid deposition, and radiative forcing.³⁹ NO_x production via nitrogen fixation (i.e., thermal NO_x—nitrogen would be in abundance from the compressed air) presumably explains the rise in NO_x, whereas a dilution effect from the added compressed air lowers the CO₂ and SO₂ concentrations in the stack emissions.

Fine Particulate Matter Mass and Mass Size Distribution. The PM_{2.5} emissions rate for the utility boiler is 53 ± 2 μg/kJ (or 2 g/kg of fuel burned). Possibly due to diffusion loss, the cascade impactor produces a somewhat lower emissions rate of 41 ± 2 μg/kJ. Similar values are published for power generation² and firetube package boilers¹⁸ firing heavy fuel oil. Experiments conducted in a refractory-lined combustor resulted in a lower PM_{2.5} emissions rate of 25 μg/kJ,¹⁷ which corresponds better to the AP-42 document emissions factor value of 28 ± 10 μg/kJ for boiler sources rated at 1 GJ/h or more.⁴⁰ A

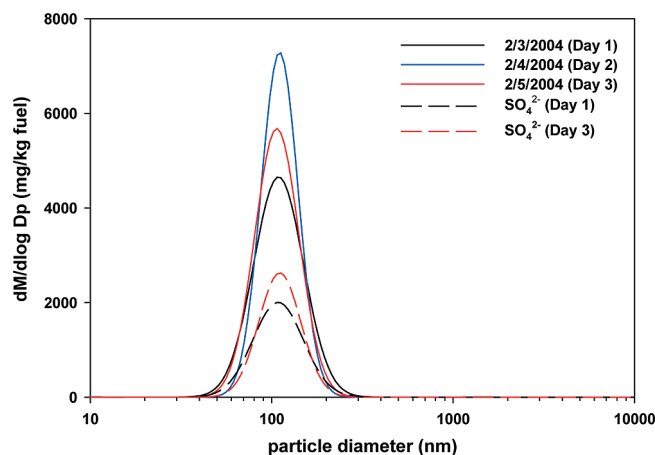


Figure 2. Size distributions of PM_{2.5} mass (solid lines) and sulfate (dashed lines). Data were inverted using the model of Dong et al.³⁸

significantly more modern (by 40 years), smaller institutional-scale oil boiler operating with no particle control technology produces an appreciably lower mass emission factor of 0.5 g/kg.¹³

The submicrometer particle mass size distributions are shown in Figure 2. The utility boiler is a source of ultrafine and accumulation mode particles. The single log-normal mode particle size distributions for each day are centered at ~100 nm, again reflecting the steady-state boiler operation during testing. Particles with aerodynamic diameters less than 140 nm predominate in institutional boiler and refractory-lined combustor emissions.^{13,16} The former and fire tube package boilers are also sources of coarse particle matter or cenospheres thought to be produced from supermicrometer spray droplets formed in the fuel atomizer.^{14,18} From the impactor data, verification of a coarse mode aerosol is uncertain given that the PM_{2.5} cyclone is upstream. It is the SEM images and backscatter analysis of particles in the cyclone catch that provide evidence of coarse and larger modes with a variety of morphologies and heavy metal compositions, Figure 3. There are lacy and pumice-like particles, with vesicles composed of C and S with less V, Al, Si, Fe, and Ni, and spherical aluminum silicate particles with V and Ni. The results also show some Fe combustion spheres rich in S. No particles are found containing As, Se, or Hg, although these may be present below the detection limit. Previous SEM studies observe coarse mode vesicular particles

(39) Richter, A.; Burrows, J. P.; Nuss, H.; Granier, C.; Niemeier, U. *Nature (London)* **2005**, 437, 129–132.

(40) U.S.E.P.A. Office of Air Quality Planning and Standards-Clearinghouse for Emission Inventories and Emission Factors. <http://www.epa.gov/ttn/chief/index.html> (accessed April 2008).

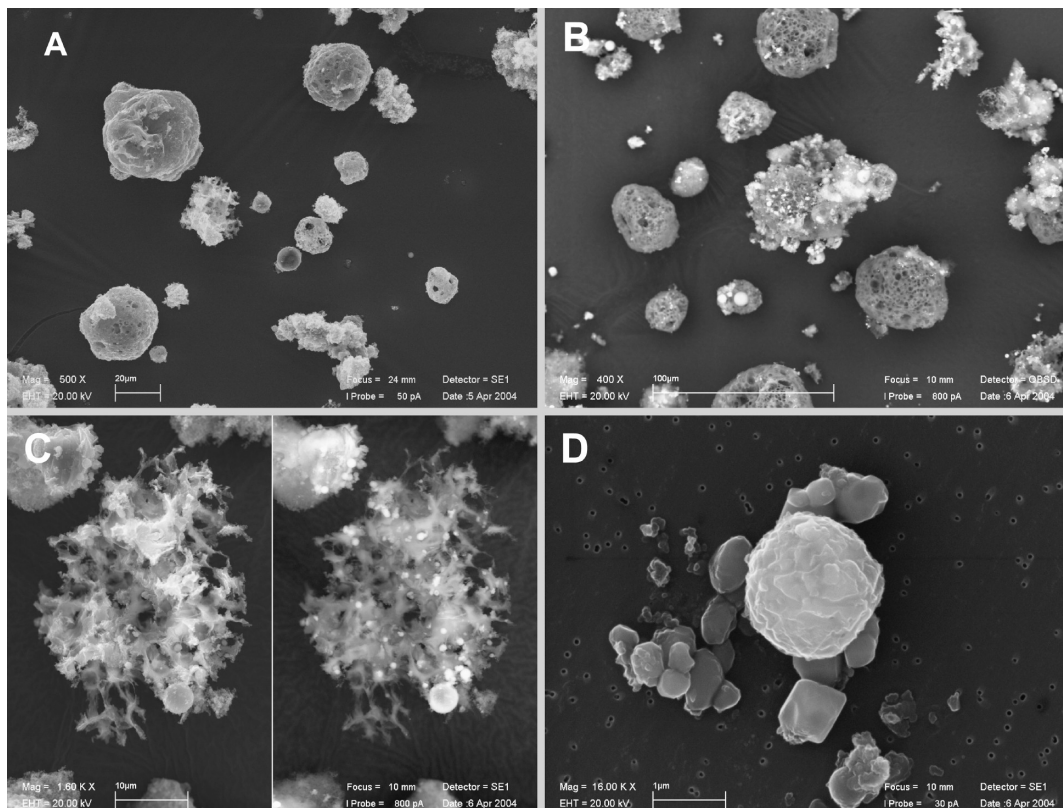


Figure 3. SEM micrographs of oil boiler particles with aerodynamic diameters $\geq \text{PM}_{2.5}$ collected from the $\text{PM}_{2.5}$ cyclone rinse. (A) Secondary electron (SE) image showing representative particle morphologies for coarse and larger size fraction. The rounded, vesiculated particles are very common in the coarse and larger size fraction. Typically, these are composed primarily of C and S with smaller amounts of V, Al, Si, Fe, and Ni. Size is indicated by a scale bar in the lower left of the figure. (B) Backscatter image (BSE) showing a field of coarse particles. The BSE image brightness is related to atomic number such that heavier elements appear brighter. The bright 1–2 μm spheres are spherical aluminum silicate (SAS) particles. SAS particles show varying concentrations of S, K, Ca, Ti, V, Fe, and Ni. Vanadium and Ni are present in most particles. (C) “Lacy” particles are observed frequently in the coarse fraction. These are composed of C and S, with lesser amounts of Al, Si, and V. The left image was acquired in the SE mode, and the right image was acquired in the BSE mode. The BSE image reveals numerous SAS particles embedded in the lacy structure. (D) SE image of rough quartz sphere surrounded by particles rich in Ca and S. The 0.1- μm features in the background are pores in the polycarbonate substrate.

in oil boiler emissions; they comprise primarily graphitic carbon, and smaller-sized S and metal particles at their surface and likely in their vesicle cavities.^{2,15}

Elemental Composition of Fine Particle Emissions. ED-XRF analysis of the $\text{PM}_{2.5}$ collected on the Teflon filters shows S as the predominant element. The $\text{PM}_{2.5}$ emissions comprise $\sim 13\% \pm 0.1\%$ (w/w) S on average (0.3 g S/kg of fuel), accounting for roughly 0.1% of the S in the oil. Recall that much of the S in the oil is released as SO_2 . Sulfur enrichments vary (10% vs 3%) in power plant and refractory-lined combustor soot produced while burning residual fuel oil containing 2% S.^{2,16} Olmez et al.¹² observed 12% S in fine PM from utilities burning 0.5% S residual oil. The trace elements quantified by ED-XRF are shown in Table 2. These explain less than 0.1% of the $\text{PM}_{2.5}$ mass, although several are of toxicological importance. Compared with published values,^{2,12,18} the oil soot examined in the present study is lower in Ca, V, Fe, Ni, and Zn by as much as 3 orders of magnitude. The metal compositions in oil combustion PM are likely to differ rather substantially with the boiler construction materials and fuel source.⁴¹ Also, in the present study, certain metal-bearing PM was likely removed downstream in the ESP. Note that the individual test runs from which the reported values in Table 2 are derived are provided in Supporting Information Table S1.

The coordination of SO_4^{2-} with transition metals—Ni, Fe, Zn, and Pb—predominates in oil boiler $\text{PM}_{2.5}$ emissions.^{9,15,42} Experimental IC results (Table 2) for the impactor stages show roughly 80% (w/w) of the sulfur in the form of water-soluble sulfate ($44\% \pm 0.2\%$ (w/w) SO_4^{2-} in $\text{PM}_{2.5}$), which compares well to the SO_4^{2-} values given in the Olmez et al.¹² study. IC detects significantly less NH_4^+ (0.1%, w/w), Ca^{2+} (0.03%, w/w), and K^+ (0.1%, w/w) ions in the fine aerosol that may also partly balance the SO_4^{2-} ; these ions were detected across only the bottom five impactor stages corresponding to $d_{50} = 30\text{--}265$ nm (the 50% particle size collection efficiency) and a propagated analytical uncertainty of 7% or less. X-ray diffraction has identified crystalline CaSO_4 and CaSO_4 dihydrate among amorphous Ca-bearing inorganic phases in a variety of residual oil fly ashes.⁹ The SEM image in Figure 3D provides evidence of Ca–S rich fine particles in the cyclone catch. Elemental S, organo-S, and sulfide (e.g., Ni–S) compounds in these particles presumably explain the 20% S fraction that is not SO_4^{2-} .^{2–15,30} SEM substantiates that the coarse particles contain crystallized FeS_2 (pyrite) and possibly FeSO_4 . The size distributions of sulfate ion in the boiler emissions for two of the three test days are given in Figure 2; they are in phase with the PM mass size distributions and correspond well to those obtained for the refractory-lined combustor.¹⁷ Evidently, water-soluble metal sulfates are present in ultrafines and in accumulation mode

(41) Federer, J. I.; Tenner, V. J. *Effects of alternate fuels report No. 7: Analysis of failure of a mullite-based refractory brick in an industrial oil-fired burner*; Research Report, Oak Ridge National Laboratory: TN; 1979; p 32.

(42) Pattanaik, S.; Huggins, F. E.; Huffman, G. P.; Linak, W. P.; Miller, C. A. *Environ. Sci. Technol.* **2007**, *41*, 1104–1110.

Table 2. Composition of Fine PM Emissions from a Utility-Scale Oil Boiler Firing No. 6 Oil^a

chemical	concentration ($\mu\text{g/kg}$ of fuel)		chemical	concentration ($\mu\text{g/kg}$ of fuel)	
total carbon	5997.5	(4096.2)	ions		
element			potassium	1062.3	(208.3)
sulfur	270564.3	(38383.7)	ammonium	1793.3	(181.4)
calcium	73.1	(41.3)	calcium	573.4	
titanium	138.4	(21.6)	sulfate	270564.3	(38383.7)
manganese ^b	7.9	(0.9)	chloride	183.0	
nickel ^b	100.5	(36.2)	unexplained mass	980000	(128000)
selenium	10.8	(3.3)			
tellurium	50.2	(17.2)			
cesium	46.4	(3.2)			
chlorine	678.5	(155.9)			
scandium	61.3	(17.9)	ratios		
vanadium	167.8	(86.3)	SO ₂ /PM mass	20.9	(2.1)
iron	60.5	(32.6)	NO/PM mass	1.4	(0.2)
zinc	15.5	(5.4)	NO ₂ /PM mass	0.1	(0.02)
antimony	50.2	(9.1)	CO ₂ /PM mass	1625.1	(158.3)
iodine	46.4	(3.2)			
lanthanum	108.0	(10.6)			

^a Relative standard deviations are given in parentheses. Element values represent an average of three separate test days, four filters each day ($N = 12$). The relative standard deviations (RSDs) are in parentheses. ^b Present on EPA's original air toxics list. Unexplained mass uncertainty is calculated using error propagation analysis. NO and NO₂ values were measured as NO_x and approximated as 95% (v/v) and 5% (v/v), respectively. Unexplained mass is ascribed to unmeasured oxygen, hydrogen, and other heteroelements.

particles emitted from utility-scale residual oil boilers. In the atmosphere, particle surface SO₄²⁻ induces secondary organic aerosol formation by catalysis.⁴³ It follows that metals coordinated to SO₄²⁻ also likely reside at or near the particle surface with their own possible implications on atmospheric reaction chemistry and health. The Mg²⁺, Br⁻, NO₂⁻, NO₃⁻, and PO₄³⁻ ion concentrations in the PM were below the IC detection limit range of ~20–30 ppb.

Carbon Composition of Fine Particle Emissions. The aerosol emission factor is a function of the primary organic aerosol concentration in the diluted emissions stream. Organic aerosol emissions for the residual oil boiler tested here were collected at 2.4 $\mu\text{g}/\text{m}^3$ or less, which is representative of atmospheric dilution.⁴⁴ The TOT analysis results show a carbonaceous particle emissions rate of 6.0 ± 4.1 mg/kg or 0.2 ± 0.1 $\mu\text{g}/\text{kJ}$, Table 2. Less than 1% of the residual oil-fired boiler aerosol matter is surmised to be carbonaceous. The ESP and highly efficient combustion in the utility oil boiler, as evidenced by the CO₂ data, may account for the low emissions of carbonaceous fine aerosol. EC (5.4 ± 5.1 mg/kg) exceeds OC (1.8 mg/kg [>0 for a single test day only]) in the sample by roughly a factor of 4 on average. However, particle-phase OC-EC split values are subject to high uncertainty because of the high concentration of organic vapors adsorbed onto the quartz filters; Table 2 reports only total carbon values as a result. The results of the material balance shown in Table 2 indicate that the Q-QBT artifact correction is overestimated as approximately 50% (w/w) of the particle phase is unexplained. Nonetheless, the high EC values are consistent with ¹³C nuclear magnetic resonance (NMR) data showing residual oil particles containing condensed graphitic structure with a rather low aliphatic content and C/H ratio.¹⁵ Moreover, high resolution transmission electron microscopy (HR-TEM) studies of primary residual oil soot nanoparticles and larger carbonized char particles show turbostratic carbon structure likely to be detected as EC by TOT.^{20,45}

Speciation of Semivolatile Organic Aerosol Matter Using GC-MS Techniques. Despite the TOT analysis confirm-

ing an organic carbon deficiency in the aerosol emitted from the plant, we attempted to study its organic composition using SE- and TE-GC-MS techniques. In large part, these attempts were disrupted owing to the degradation of the dimethylpolysiloxane column stationary phase. This reproducibly impaired certain organic compound and deuterated internal standard responses in this study. We deduced that the interference was unique to the vapors adsorbed on the Q_f and specific to the chemistry of the plant aerosol emissions. However, identifying the individual chemical constituents responsible for this result proved elusive. While determination of polycyclic aromatic hydrocarbon (PAH) concentrations is uncertain as a result of this setback, deuterated *n*-alkane standard recoveries, although low (17–33%), allow estimation of normal, branched, and cyclic alkane compound concentrations in the plant aerosol, Table 3. The scarcity of such estimates makes it important to provide them. They are relatively low, likely due to the plant combustion efficiency and ESP control alluded to earlier. Per unit of fuel mass burned, a residential oil furnace aerosol contains higher *n*-alkane concentrations than the plant-scale boiler by as much as an order of magnitude.³⁰ Roughly 47% of deuterated cholestane internal standard is recovered, but sterane and hopane molecules are below picogram detection limits.⁴⁶ These organic molecular markers continue to be specific to mobile sources. Straight chain hydrocarbons with molecular weights exceeding 478.0 amu and anteiso- and iso-alkanes in the oil boiler emissions are also below TE- and SE-GC-MS detection limits. Recovery of two of the six deuterated organic acid internal standards (19–24%) from the methylated composite extract permits concentration estimates to be made for a C₄-dioic acid and the C₈–C₁₄ *n*-alkanoic acids, Table 3. Generally, the GC-MS identifies organic species in the oil boiler plant aerosols that are ubiquitous in airborne aerosols and combustion source emissions as well.⁴⁷ We should note for quality control checks with blank quartz filters that standard recovery is inversely proportional to filter quantity and systematically higher than what is observed if oil boiler soot is present.

For a single test day, multiple sets of four PUFs in series are analyzed for gas-phase SVOC content. PAH (e.g., naphthalene,

(43) Jang, M.; Czoschke, N. M.; Lee, S.; Kamens, R. M. *Science* **2002**, 298, 814–817.

(44) Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. A.; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. *Science* **2007**, 315, 1259–1262.

(45) Hays, M. D.; VanderWal, R. L. *Energy Fuels* **2007**, 21, 801–811.

(46) Lavrich, R. J.; Hays, M. D. *Anal. Chem.* **2007**, 79, 3635–3645.

(47) Schauer, J. J.; Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R. *Atmos. Environ.* **1996**, 30, 3837–3855.

Table 3. Summary of Volatile and Semivolatile Organic Species Emitted from a Plant-Scale Boiler Firing Residual Fuel Oil^a

		concentration ($\mu\text{g/kg}$ of oil burned)			
SUMMA-collected VOCs		DNPH-collected polars		SVOCs by GC-MS	SE TE
<i>n</i> -alkanes		<i>aldehydes and ketones</i>		<i>n</i> -alkanes	
<i>n</i> -C ₃	49.6	formaldehyde ^b	329.1 (320.9)	octadecane	1.0
<i>n</i> -C ₄	314.1	acetaldehyde ^b	4217.8 (6038.2)	docosane	4.5
<i>n</i> -C ₉	32.6 (29.2)	acetone	2247.2 (1736.6)	tricosane	18.3
<i>n</i> -C ₁₁	151.1 (188.5)	propionaldehyde ^b	538.9 (691.5)	tetracosane	1.1 12.7 (3.7)
<i>n</i> -C ₁₂	204.9 (267.3)	butyraldehyde	1117.6	pentacosane	0.5 7.1 (0.1)
<i>branched alkanes</i>		methyl ethyl ketone ^b	291.3 (485.1)	hexacosane	1.4 3.7 (0.4)
3-methylpentane	258.1 (366.6)	benzaldehyde	46.0 (53.7)	heptacosane	2.3 (0.8)
2,2-dimethylbutane	178.8 (282.3)	valeraldehyde	138.5 (226.8)	octacosane	0.1 2.3
<i>halogenated compounds</i>		<i>p</i> -tolualdehyde	81.8	nonacosane	1.4 (1.8)
chloromethane ^b	33.1	hexaldehyde	407.0	triacontane	0.7 (0.8)
dichloromethane	140.5	2-butanone	152.3 (194.6)	hentriacontane	1.2
<i>n</i> -alkenes		glyoxal	498.0 (435.5)	dotriacontane	0.4
ethylene	45.3	methylglyoxal	673.6	tritriacontane	0.3
propylene	89.6 (79.8)	acetophenone ^b	93.1 (86.4)	<i>branched and cyclic alkanes</i>	
iso-butene, 1-butene	274.7 (268.8)	octanal	192.5 (320.6)	nonadecylcyclohexane	0.3 (0.1)
isoprene	22.7	nonanal	1470.6	squalene	2.5 (2.3)
<i>trans</i> -2-hexene	143.5			pristine	0.3
<i>cyclic compounds</i>				2,6-dimethylnaphthalene	2.1
α -pinene	316.9 (150.4)			<i>organic acids</i>	
<i>aromatics</i>				butanedioic acid	55.7
benzene ^b	2245.1 (2312.9)			octanoic acid	29.2
diethylbenzenes	76.7 (41.5)			nonanoic acid	11.6
<i>N</i> -bearing				decanoic acid	26.6
acetonitrile ^b	406.0 (538.3)			dodecanoic acid	205.1
				tetradecanoic acid	101.2
				pentadecanoic acid	3.8

^a Standard deviations are given in parentheses. Compounds with single values were detected on one test day only. All VOC concentrations are background corrected using dilution air. ^b Compound is on the original EPA list of hazardous air pollutants. TE-GC-MS results are for nonpolar compounds. Organic acids are detected and quantified as methyl esters using SE-GC-MS. SE-GC-MS results are for a three day test composite and thus represent an average; relative analytical uncertainty is generally in the range of 20%. TE-GC-MS values represent a two-day test mean. All SE- and TE-GC-MS concentrations are background corrected using dilution air and backup quartz filters. Results for individual test days are provided in Table S1, Supporting Information.

phenanthrene, anthracene, etc.) and mono- and disubstituted alkyl PAH are below the GC-MS detection limits. Phthalates, branched-alkanes, and C₁₂–C₃₆ *n*-alkanes are detected in the emissions following background correction. However, their concentrations in the front PUFs are consistently less than 75% of the total load, indicating breakthrough. Thus, PUF sampling for quantification of SVOCs emitted from the plant scale boiler was inconclusive. The high CO₂ to semivolatile organic gas ratio, while better mimicking the atmospheric environment (by increasing SVOC gases while decreasing SVOC solid or liquid matter), apparently also vexed the filter–PUF sampling at the site. To partly correct this difficulty, future plant-scale oil boiler emissions research will include the deployment of field instrumentation that measures the chemical compositions of single particles in real-time.

Volatile Organic Compounds. Eight of the 35 VOC compounds identified and quantified in the plant emissions are classified as hazardous air pollutants, Tables 3 and S1 in Supporting Information. Total volatile nonmethane organic gases emitted from the plant-scale boiler vary between 6 and 28 mg/kg of fuel oil burned. A similar emissions factor range is reported for a residential boiler firing No. 2 distillate fuel.³⁰ From their tests on a 250 MW oil boiler, Ahlberg et al.² report VOC emissions of benzene (110–290 $\mu\text{g/kg}$), ethylene (83–170 $\mu\text{g/kg}$), formaldehyde (310–470 $\mu\text{g/kg}$), and acetaldehyde (560–810 $\mu\text{g/kg}$). Their narrow emissions ranges are likely due to constant burning conditions. The relatively higher ethylene and lower benzene in their emissions suggest a fuel composition that differs from the one used in the present study.

On average, more than 50% of the VOC emissions mass is oxygenated, Table 3. Oxygen-bearing compounds are likely combustion reaction products because residual fuels comprise primarily hydrogen saturated aliphatic, aromatic, olefin, and

cyclic alkane groups. The high combustion efficiency of the boiler is again evidenced by the lack of paraffin, olefin, and aromatic matter in the emissions. Only four organic gases, benzene, acetone, propionaldehyde, and α -pinene, are detected for all three test days. While there is concern over the α -pinene not being of anthropogenic origin,⁴⁸ it is possible that a changing fuel composition explains the day-to-day variation in emissions of benzene, acetone, and propionaldehyde. Many of the individual organic gases emitted are measured near the estimated method quantification limits and are present in the ambient dilution air. These measurement conditions in part influence the wide emissions ranges observed here for the organic gases. However, it is clear from these results that regional air quality models must consider a wide range of possible organic gas emissions scenarios over temporally short periods (24-h) to accurately capture the influence that oil boiler plant stacks have on the atmosphere and ultimately on human health.

Several of the volatile aromatic hydrocarbons in the plant boiler emissions are aerosol precursors. In the atmosphere, oxygenated VOCs may photolyze, react with, and form OH radical or undergo acid-catalyzed polymerization following hydration and formation of acetal or hemiacetal compounds.^{43,49} The photooxidation of benzene and diethyl benzene can yield aromatic acids, ketones, aldehydes, nitrophenols, or ring fragmentation products via various epoxide and peroxy radical intermediates; several of these contribute to particle nucleation and growth events and are considered potentially toxic.^{50–52}

Conclusions

This study examined the gas- and particle-phase emissions from heavy oil combustion for electricity generation. Combustion at the plant-scale was efficient; greater than 90% of the

carbon and sulfur in the oil was converted to CO₂ and SO₂, respectively. Although an ESP was used for particle control at this plant, its heavy oil combustion emissions contained ultrafine, fine, and coarse mode aerosols. SEM-EDX examination showed the coarse mode particles had vesicular, spherical, and lacy microstructures with varying concentrations of S, K, Ca, Ti, V, Fe, and Ni. Results from ED-XRF, IC, GC-MS, and TOT analyses showed primarily sulfate, with lower concentrations of carbon and Ti, Fe, Mn, Ni, and Zn transition metals in the oil boiler particles. Preliminary evidence suggests these metals may reside at or near the particle surface when coordinated to sulfate in particles with diameters of less than 100 nm. Use of conventional filter sampling and analytical techniques precluded a thorough rendering of organic PM_{2.5} composition. In sum, roughly 45–50% w/w of the fine aerosol mass is speciated in the present study. As much as 30% of the mass unaccounted for may be due to an earlier noted overprediction ascribed to

the Q-QBT artifact correction method.³⁰ In the future, use of more sensitive organic analysis methods—such as those developed for measuring atmospheric aerosol composition in near real-time—will be required. The VOCs emitted were mostly oxygenates from combustion. Their individual emission rates varied considerably, owing partly to concentrations being measured near the method quantification limits. Several of these and the heavy metals detected in the oil boiler particles are listed as air toxics. Finally, if the physical and chemical properties of particles are determining factors, pilot-scale refractory combustors seem to provide a reasonable approximation of what occurs at the plant-scale.

Acknowledgment. The authors extend their gratitude to Thomas Balicki and David Profitt of ARCADIS for assisting with the sampling effort. The cooperation and assistance of the plant staff during the planning and testing phases of this research is also much appreciated.

Supporting Information Available: Real-time fuel-use flowcharts and further details on the stack testing and dilution sampling are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

EF8011118

(48) Geron, C. D.; Rasmussen, R.; Arnts, R. R.; Guenther, A. *Atmos. Environ.* **2000**, *34*, 1761–1781.

(49) Atkinson, R. *Atmos. Environ.* **2000**, *34*, 2063–2101.

(50) Forstner, H. J. L.; Flagan, R. C.; Seinfeld, J. H. *Environ. Sci. Technol.* **1997**, *31*, 1345–1358.

(51) Martin-Reviejo, M.; Wirtz, K. *Environ. Sci. Technol.* **2005**, *39*, 1045–1054.

(52) Suh, I.; Zhang, R.; Molina, L. T.; Molina, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 12655–12665.