PM2.5 Speciation Profiles and Emission Factors from Petroleum Industry Gas-Fired Sources

Stephanie Wien and Glenn England
GE Energy and Environmental Research, 18 Mason, Irvine, CA 92618
stephanie.wien@ps.ge.com and glenn.england@ps.ge.com

Karl Loos
Equilon Enterprises LLC, Westhollow Technology Center, P.O. Box 1380, Houston, TX 77251-1380

Karen Ritter
American Petroleum Institute, 1220 L Street Northwest, Washington, DC 20005

Daniel Gurney
U.S. Department of Energy National Petroleum Technology Office, Williams Center Tower One, One West Third St., Suite 1400, Tulsa, OK 74103

Jim McCarthy
Gas Technology Institute, 1700 S. Mount Prospect Road, Des Plaines, IL 60018-1804

Barry Liebowitz and Janet Joseph
New York State Energy Research and Development Authority, Corporate Plaza West, 286 Washington Avenue Extension, Albany, NY 12203-6399

Guido Franco
California Energy Commission, 1516 Ninth Street, Sacramento, CA 95814-5504

ABSTRACT

With the promulgation of the new National Ambient Air Quality Standards (NAAQS) for PM2.5 in 1997, the measurement of fine particulate matter from stationary sources becomes more important. A series of tests have been performed on three different natural and refinery gas-fired sources using traditional manual methods (in-stack cyclones and filter with iced-impinger train) and dilution tunnel sampling. The dilution tunnel mixes stack emissions with cleaned ambient air, cooling and diluting them to simulate what happens in the plume as emissions leave the stack. This type of sampling allows for extensive speciation of the PM2.5 fraction including elements, ions, organic and elemental carbon, semivolatile organic compounds (SVOCs) and volatile organic compounds (VOCs).

One result of particular interest is the low percentage of organic carbon (OC) accounted for by the SVOC results. At all locations, the sum of the SVOCs was less than 10 percent of the total OC measured using the dilution tunnel. Dilution tunnel sampling is able to provide a more complete speciation of SVOCs, however this large discrepancy indicates that further investigation is needed. Differences in organic aerosol emissions from natural gas versus refinery gas combustion have also been observed.

Results from these tests not only allow comparison of traditional manual methods to dilution sampling, but also allow comparison to ambient sampling results and utilization of data in atmospheric models, such as chemical mass balance models.

INTRODUCTION

New ambient air standards for particles 2.5 µm or less in diameter, referred to collectively as PM2.5, will motivate regulators to identify and control emission sources contributing to ambient PM2.5. Sulfates, nitrates, and carbon (elemental and organic) dominate PM2.5 composition in most urban and many non-urban areas; ammonium and elements also are present.[1, 2] Anthropogenic and natural combustion processes are generally believed to be the most significant sources of PM2.5.

The majority of primary emissions from combustion often is found in the PM2.5 or smaller size range, especially for devices equipped with particulate emission control equipment and for clean burning fuels such as gas. The predominant gaseous precursors of secondary particulate sulfates and nitrates are: sulfur dioxide (SO_2) and sulfur trioxide (SO_3); oxides of nitrogen (NO and NO_2, the sum of which is designated as NO_x); and ammonia (NH_3). Secondary organic aerosols formed from volatile organic carbon compounds also may be very significant in some areas, especially during the summertime when photochemical activity is high.[3]

Methods for identifying sources of ambient PM2.5 employ modeling approaches, which range from simple to complex. The chemical "fingerprint" of a source's emissions can be used to apportion the contribution of regional sources to local ambient PM2.5 using chemical mass balance models, one example of such methods. These relate the chemical speciation profile of ambient air samples to known sources in the modeled area; reliable results require complete speciation profiles for as many sources as possible.[4]

The quality of source emissions data which presently exist is often questionable because of: a lack of data for different process configurations to account for site-specific differences; data based on measurements using older, less sensitive or selective techniques; and/or incomplete profiles. Thus, there is a need for new source emission data for specific sources and locations using the latest measurement technologies to provide more reliable source apportionment results.[2,5] Existing emission factors for PM2.5, such as those provided by EPA in AP-42, are often based on an assumed size distribution applied to a total particulate factor instead of from direct measurement of PM2.5. One of the benefits of obtaining newer, more reliable data will be the development of better emission factors, which will aid facilities in the compilation of emissions inventories.

Combustion of gaseous fuels in steam boilers, process heaters, gas turbines and stationary reciprocating internal combustion engines accounts for a major fraction of fossil fuel combustion in the U.S.; most, if not all, petroleum refinery boilers and process heaters in the U.S. are gas fired. Petroleum refining uses the most energy of the major energy-consuming non-utility industries in the U.S., consuming 3.3 Quads of energy in 1994.[6] Many refineries are situated in or near areas where ambient PM2.5 levels are predicted to exceed the new NAAQS. To assure that source apportionment results in these areas are reliable, there is a need for reliable chemically speciated data on particulate emissions from gas combustion in petroleum industry operations.

SOURCE CHARACTERIZATION TEST METHODS

Source characterization approaches for particulate matter fall into two general categories: source-level sampling and ambient-level sampling. The general sampling and analytical principles for characterizing particulate mass, size, and composition are similar for the two types of measurements, but the specific approaches differ due to the differences in gas temperature, pollutant concentrations and background gas composition. In the context of regulatory enforcement, source-level sampling is currently the accepted approach for total suspended particulate and PM10 measurements for stationary sources, while ambient level sampling using dilution is the accepted approach for mobile source particulate emission measurements.

Source-Level Sampling

The most common approaches to source-level sampling for particulate employ an in-stack filter or a filter external to the stack that is heated to a constant temperature (e.g., EPA Method 17 or Method 5).[7] Heating the filter avoids condensation of moisture and/or acid aerosols, depending on the temperature selected. These methods define primary particles as those particles that are filterable at the filter temperature.

Condensible particulate is frequently defined as the amount of material collected in a series of impingers in an ice bath downstream of an in-stack filter and includes both fine particles which pass through the filter and vapors which condense at the temperature of the gas leaving the impingers (typically 60-70°F).[8,9] Impinger methods for condensible particulate are subject to substantial artifacts[10] that do not occur in atmospheric processes, especially when ammonia, SO_2, and/or hydrogen chloride (HCl) are present in the exhaust, and thus may not provide an accurate measure of primary condensible particles. Previous studies[10,11,12] have documented the bias caused by absorption of SO_2 in the impinger water and subsequent conversion to sulfate via the following mechanism:

$$SO_2 + H_2O \rightarrow SO_2 \,(\text{dissolved gas})$$
$$SO_2\,(g) + \text{time} + O_2 \rightarrow SO_4^=$$
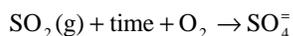
PM10 and PM2.5 are commonly measured using in-stack cyclones or cascade impactors[8,13], or occasionally using heated out-of-stack cyclones.[14] While these methods may provide regulatory agencies a means of enforcing emission limits defined using the same methods on a specific type of source, they may not be generally applicable to all source types and may be biased high or low due to interferences and artifacts. Further, the methods may allow subtraction of sulfate or chloride captured in the impingers as a matter of policy, which may not be appropriate when conducting health risk assessments or source apportionment studies for PM2.5.

Source-level measurement methods also exist for secondary particle precursors. NO_x and SO_2 emissions can be characterized using continuous gas analyzer systems. SO_3 can be measured by high-temperature filtration of the sample to remove solid particles, followed by cooling to a temperature below the H_2SO_4 dew point (but above the moisture dew point) and subsequent filtration to remove condensed acid mist.[15] Gaseous ammonia can be trapped in sulfuric acid impingers and subsequently analyzed by ion chromatography, although the sample must be filtered at stack temperature to avoid biases due to formation or decomposition of solid/liquid ammonium compounds. Gas-phase organic compounds usually are measured by using a sorbent trap, which strips organics from the gas onto the sorbent. The sorbent is subsequently analyzed by thermal desorption of the organic compounds into a gas chromatograph/mass spectrometer system for quantification and speciation.

Dilution Sampling

Ambient-level sampling for source characterization involves diluting the exhaust gas and subsequently sampling and analyzing the diluted gas using ambient air methods. This has at least one major advantage over source-level sampling in that results are directly comparable to ambient air measurements. If the dilution is performed in a manner that simulates conditions in the exhaust plume, then particles that would form in the plume are represented in the sample. Ambient air methods are similar in general principle to source-level measurements for combustion devices, but somewhat simpler because provisions in source-level methods to eliminate problems caused by the high gas temperature, high moisture content, higher pollutant concentrations and interfering major and minor gases are not necessary. The comparatively low temperature of ambient air and diluted source samples allows for the

use of a greater range of sampling media such as Nylon and Teflon membrane filters, simplifying and extending the range of chemical speciation measurements.

Dynamic dilution samplers for stationary source studies draw a hot exhaust gas sample continuously into a chamber where it is mixed with a continuous flow of conditioned ambient air or pure inert gas. The diluted sample is then drawn through multiple filters, sorbents or denuders, which strip particles and/or selected gases from the sample. These samples are then taken to an analytical laboratory for analysis.

Hildemann et al.[16] introduced a dilution sampler designed specifically for characterizing organic aerosols at very low concentrations. The key features of this system were: 1) it did not contain any plastic or rubber materials that could leach organics into the system or prevent thorough decontamination of the system; 2) it allowed for a relatively large sample size to facilitate detailed chemical analysis of organic compounds; 3) it allowed for dilution and cooling of the sample fully to ambient temperature; 4) the dimensions and the flow rates in the system were selected to minimize particle and vapor losses onto the walls; and 5) it provided for long sample residence times. Dilution ratios of at least 40:1 were used to assure adequate mixing between the sample stream and the dilution air, in addition to cooling the sample to essentially ambient temperature. An analysis of aerosol condensation, coagulation and nucleation rates in samples with low particle concentrations revealed that diffusion of condensing organic vapors to particle surfaces is relatively slow; hence, the design incorporates an additional residence time chamber providing a total of approximately 80-90 seconds residence time to facilitate condensation of low concentration aerosols. The design has been used by Hildemann and others[17] to generate detailed organic aerosol speciation data for several types of sources.

TEST PROCEDURES

Tests were performed on a gas-fired boiler and a gas-fired process heater in two separate refineries and a gas-fired steam generator in an oil field. The boiler and heater were fired on refinery process gas and the steam generator was fired on natural gas. Both in-stack and dilution tunnel methods were included in the test matrix. The in-stack method train was based on EPA Preliminary Method PRE-004, which includes in-stack PM10 and PM2.5 cyclones, an in-stack 47 mm quartz filter, and an EPA Method 202 impinger train for collection of condensible particulate (Figure 1). The sample inlet is a stainless steel nozzle on the PM10 cyclone sized to provide near-isokinetic sampling and accurate cut size for the PM10 and PM2.5 cyclones at the chosen sampling rate.

The dilution tunnel used in these tests follows the Hildemann design discussed above (Figure 2), where the diluted sample is passed through various collection media as illustrated in the figure. The sample inlet was a stainless steel probe and buttonhook nozzle sized to provide near-isokinetic sampling for the sample rates selected for each test. Volatile organic compounds (VOCs) were collected on Tenax sorbent, and analyzed by gas chromatographic separation and flame ionization detection of individual hydrocarbons for peak quantification, and/or combined mass spectrometric/Fourier transform infrared detection for peak identification. Semivolatile organic compounds (SVOCs) were collected on Teflon-impregnated glass fiber filters followed by polyurethane foam (PUF)/XAD-4/PUF sorbent. These cartridges were extracted and analyzed by electron impact gas chromatography/mass spectrometry, using Fourier transform infrared detection, mass selective detection, and multiple ion detection for compound identification and quantification. Elements were determined on Teflon membrane filters by energy dispersive X-ray fluorescence (XRF). Ions were determined on quartz filters by ion chromatography. Organic carbon (OC) and elemental carbon (EC) were determined on quartz filters by thermal optical reflectance (TOR).

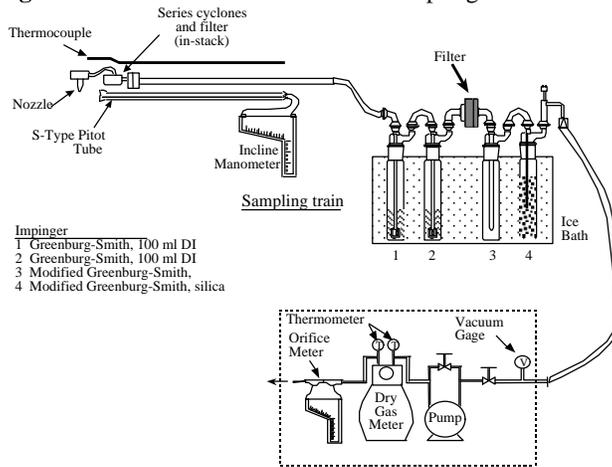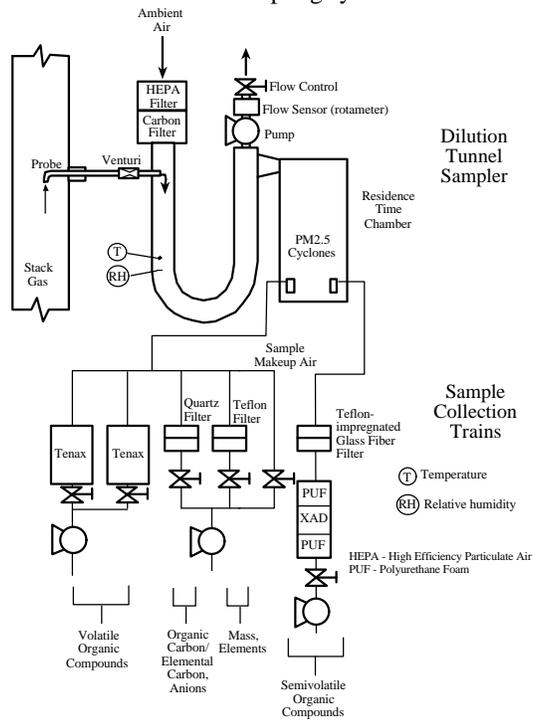**Figure 1.** EPA Method PRE-004/202 sampling train.

Impinger
1 Greenburg-Smith, 100 ml DI
2 Greenburg-Smith, 100 ml DI
3 Modified Greenburg-Smith,
4 Modified Greenburg-Smith, silica

Figure 2. Dilution tunnel sampling system.

PM2.5 precursor measurements during the gas-fired unit tests included SO_2, NO_x and volatile organic compounds. Table 1 presents a matrix of the sampling rates, dilution tunnel residence time and dilution ratios for each test.

Table 1. Approximate sampling rates, residence times and dilution ratios.

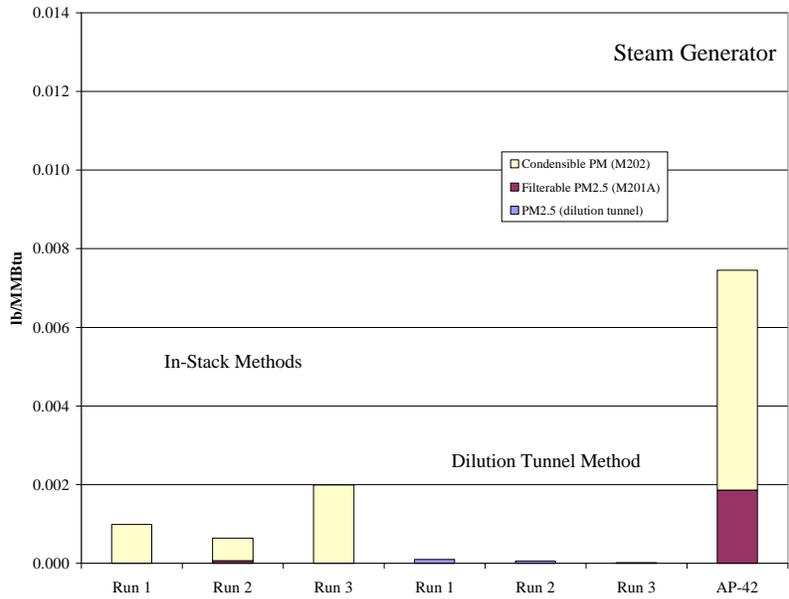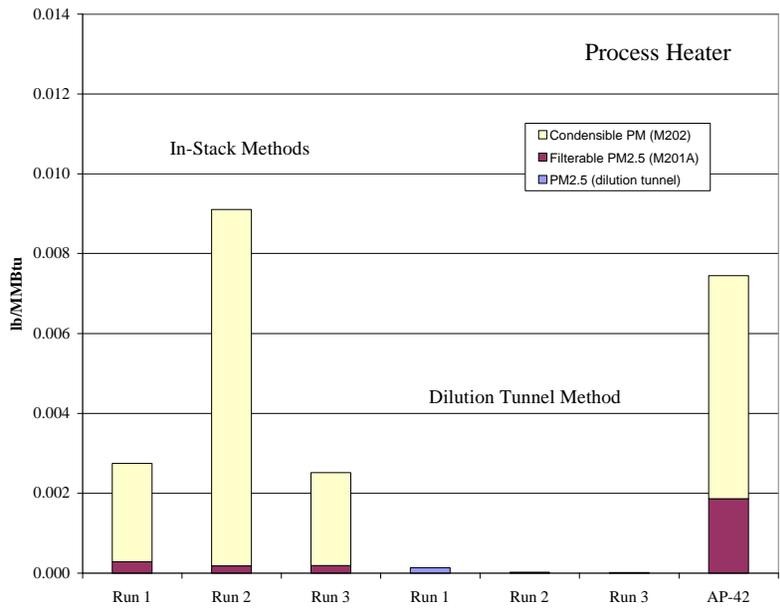| Unit	Sampling Rate (dscfm)		Dilution Ratio	Dilution Tunnel Residence Time
	Method PRE-004	Dilution Tunnel		
Boiler	0.4	1.4	6	80
Process Heater	0.4	1.4	8	80
Steam Generator	0.3	0.7	20	80

One of the practical challenges to the tests was limited space on the stack sampling platform for placement of the dilution tunnel and ancillary equipment. These sites were selected in part due to the size of the available sampling platforms; however, there are many gas-fired sites where such generous access is not available because stack sampling of gas-fired sources is not universally required. The boiler site's platform only covered 180 degrees of the stack; due to the limited space the dilution tunnel tests and in-stack method tests could not be performed concurrently. Instead, they were performed on different days, with process operating data indicating similar process conditions during all tests. Better access was available at the process heater and steam generator sites, so these tests were performed concurrently. Concurrent sampling, when possible, and co-located probes allow for a direct comparison between the results obtained from the two approaches. Each test run at both sites was six hours in duration, with a total of three runs for each measurement. In addition to stack samples, a single ambient air sample was collected near the combustion air inlets at each site for comparison.

PRELIMINARY COMPARISON OF IN-STACK AND DILUTION TUNNEL RESULTS

The amount of filterable particulate collected using the in-stack methods was essentially near or below the overall method detection limit (Figure 3). However, condensible particulate matter (CPM) as defined by EPA Method 202 was measured at much higher levels.

**Figure 3.** Comparison of dilution tunnel and traditional method results.

Process Heater

In-Stack Methods

Dilution Tunnel Method

lb/MMBtu

Condensible PM (M202)
Filterable PM2.5 (M201A)
PM2.5 (dilution tunnel)

Run 1 | Run 2 | Run 3 | Run 1 | Run 2 | Run 3 | AP-42

0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000

Steam Generator

In-Stack Methods

Dilution Tunnel Method

lb/MMBtu

Condensible PM (M202)
Filterable PM2.5 (M201A)
PM2.5 (dilution tunnel)

Run 1 | Run 2 | Run 3 | Run 1 | Run 2 | Run 3 | AP-42

0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000

It is believed the impinger results may be biased high due to dissolved SO_2 in the impingers, based on previous work.[10,11,12] Due to differences in the fuel gas sulfur content, SO_2 concentrations at the different sites varied from 0.3 ppm to 8 ppm. The sulfate concentration in the impinger contents and total CPM mass also was higher for the boiler than for the process heater site. It should be noted that the impinger trains at the heater and boiler sites were not purged with nitrogen after sampling because, according to Method 202, a purge is not required if the impinger catch pH is greater than 4.5. The purge was performed at the steam generator site, however, and a subsequent reduction in CPM mass was observed, as shown in Figure 3.

Total PM2.5 mass obtained with the dilution tunnel was much lower than the total filterable matter plus CPM mass obtained with the in-stack methods. The dilution tunnel should capture all of the filterable matter plus any aerosols that condense under simulated plume conditions. The striking difference between the dilution tunnel and in-stack method results and the observations noted above suggest that EPA Method 202 results are significantly biased. The values of total particulate for the boiler and the heater agree qualitatively with results reported by EPA in its emission factor database for natural gas combustion in external combustion devices. However, assuming the EPA results were obtained using the same methods, a similar bias may be present in those data.

CHEMICAL SPECIATION PROFILES

Figure 4 shows the profiles of chemically speciated emissions from the process heater, boiler and steam generator as measured by the dilution tunnel. The concentrations of many elements detected in the stack samples and ambient air samples were similar. Also, many of the 40 elements included in the XRF analysis (Al, Ag, As, Au, Ba, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Ga, Hg, In, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Rb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, U, V, Y, Zn, Zr) were found at levels near or below the minimum detection limits of the analytical methods. In Figure 4, the concentrations of elements detected in the ambient air have been subtracted from their concentration in the stack samples to better characterize the contribution of the source. The standard deviation of the data is indicated on each graphic to indicate the confidence level of the averages; a standard deviation greater than the average indicates a high level of uncertainty. Elements that were not detected are not shown for clarity.

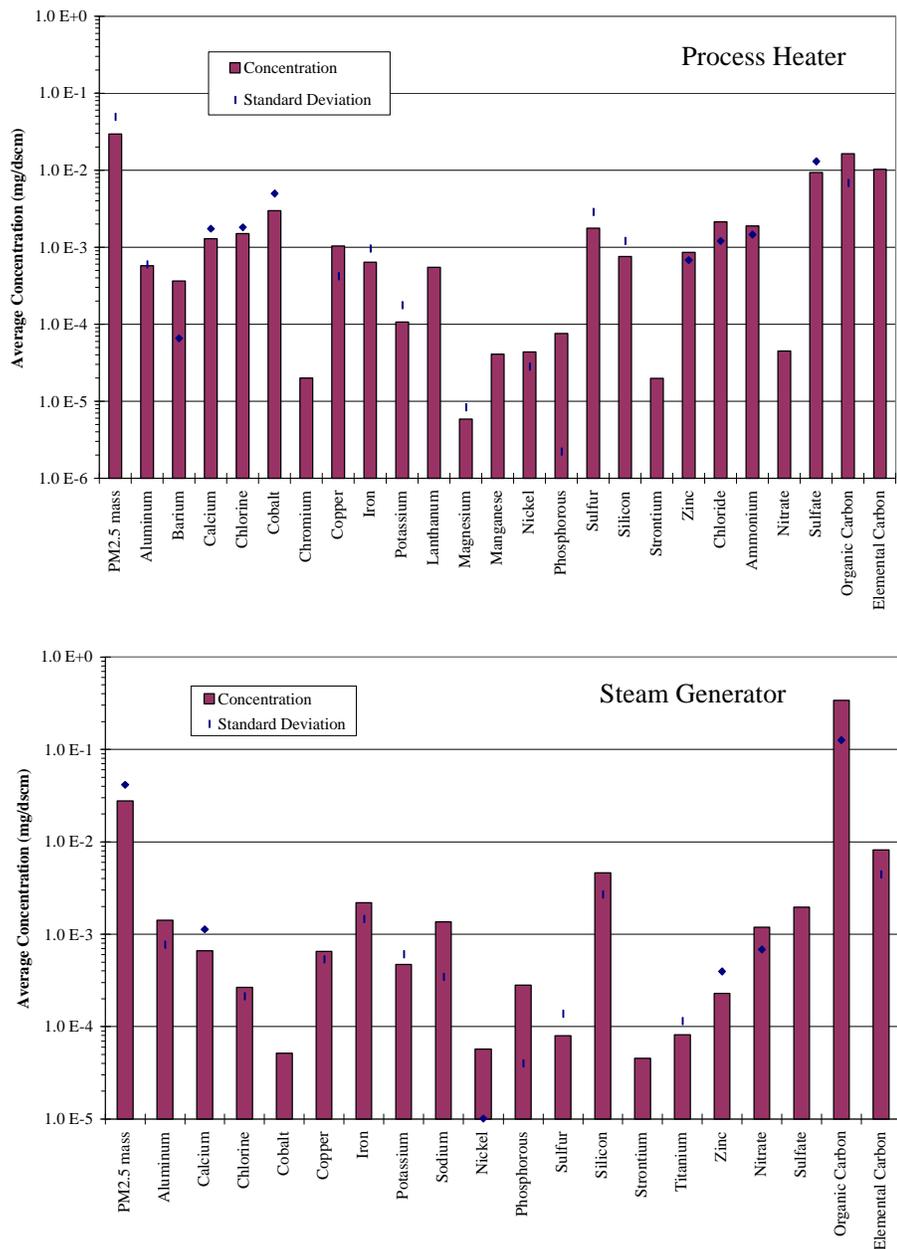**Figure 4.** Chemical speciation profiles.
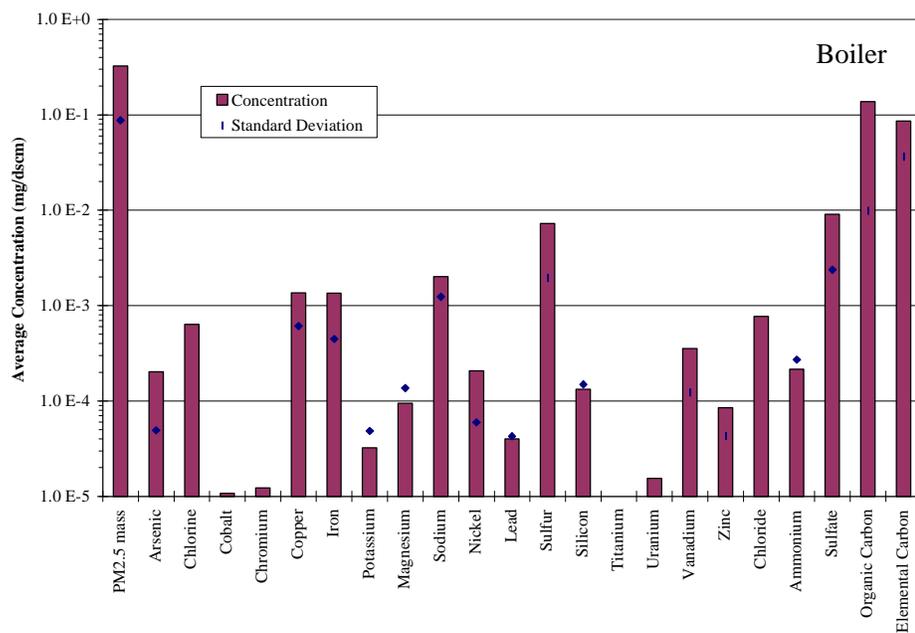
Figure 5 shows the relative contributions of all constituents by expressing each as a percent of the total primary PM2.5, as measured by the dilution tunnel. The in-stack particulate mass results are included for comparison. Total carbon (elemental plus organic), as measured by TOR, dominated PM2.5 primary emissions. Sulfates were the next most prevalent substance in both profiles. Sulfur and sulfates are present in approximately a 1 to 3 ratio, indicating most of the sulfur can be accounted for as sulfate. The predominance of other elements differs among the three different sites, and probably reflects differences in total particulate concentration, refinery fuel gas composition, ambient particulate

speciation, and process conditions. Silicon, copper and iron were among the highest of the detected elements at the sites, even though in most cases these were only slightly above ambient levels.

Figure 5. Chemical speciation profiles as percent of primary PM2.5.
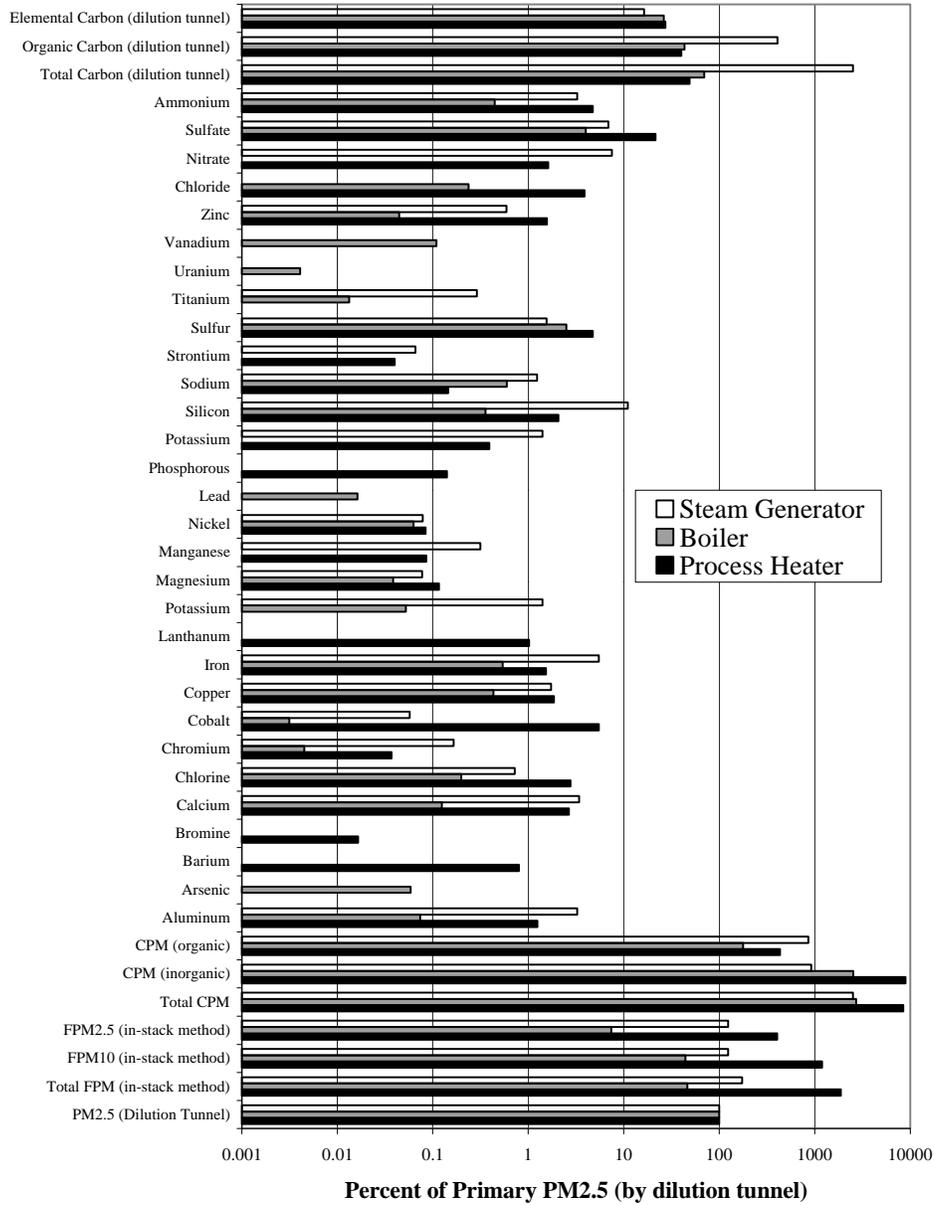
Although carbon dominates in the PM2.5 speciation profile, the percentage of organic carbon accounted for in the SVOC measurements is very small. Figure 6 shows the emission factors for organic carbon, the sum of detected SVOC species and the amount of OC unaccounted for by the speciated measurements. As seen in the figure, the amount of unspeciated OC ranged from 94 to 98 percent. This

large difference can be explained at least in part by the difference in analytical methods (the TOR method defines OC somewhat arbitrarily) and the presence of organic species that are not quantifiable by the methods used in this project. This gap in the speciation of OC has been observed to varying degrees in other studies of similar scope.[18]

Figure 6. Organic carbon speciation.
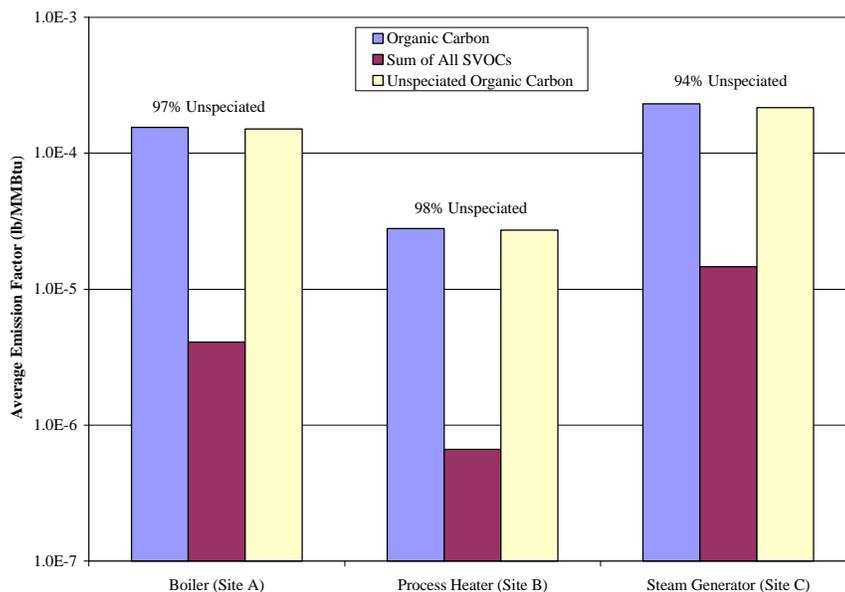
CONCLUSIONS

Measured emissions of primary fine particulate from the gas-fired boiler, process heater, and steam generator were extremely low. Traditional source testing methods and dilution tunnel methods yielded different results for total PM2.5 mass. Sampling and analytical artifacts appear to be significant in traditional source test methods, especially the ultrafine condensible particle fraction. Laboratory results indicate a significant bias from gaseous SO_2 in the sample, even for the extremely low SO_2 concentrations present in this study. Also, since particle condensation mechanisms are dependent on vapor concentration and residence time in addition to temperature, dilution tunnel methods provide conditions that more closely represent true atmospheric condensation conditions and therefore are believed to yield more representative source emission results. In addition, dilution sampling provides an opportunity to speciate PM2.5 more fully than traditional in-stack methods, allowing for the development of better speciation profiles for combustion sources.

ACKNOWLEDGEMENTS

REFERENCES

1. U.S. Environmental Protection Agency. Data from the IMPROVE Network, ISSN: 0737-53, 1996.
2. Cheng, L.; Sandhu, H.S.; Angle, R.P.; Myrick, R.H. *Particulate Matter in Calgary and Edmonton*; Proceedings of the AWMA International Specialty Conference on Emerging Air Issues for the 21st Century: The Need for Multidisciplinary Management; Air and Waste Management Association, Pittsburgh, PA, April 1997.
3. Rogge, W.F.; Mazurek, M.A.; Hildemann, L.M.; Cass, G.R.; Simoneit, B.R.T. "Sources of fine organic aerosol: 1. Charbroilers and meat cooking operations," *Environ. Sci. Technol*. 1991, 26, 1112-1125.
4. *Receptor Model Technical Series, Volume III: CMB 7 User's Manual*; U.S. Environmental Protection Agency. U.S. Government Printing Office: Washington D.C. 1990; EPA-450/4-90-004.
5. Watson, J.; *Physics and Chemistry of Fine Particles*; Air and Waste Management Association Specialty Conference on PM2.5: A Fine Particulate Standard, Long Beach, CA, January 1998.
6. U.S. Department of Energy; Energy and Environmental Profile of the U.S. Petroleum Refining Industry, Office of Industrial Technology, 1995.
7. United States Code of Federal Regulations, Title 40, Part 60, Appendix A.
8. United States Code of Federal Regulations, Title 40, Part 51, Appendix M.
9. South Coast Air Quality Management District; *Determination of Particulate Matter from Stationary Sources Using a Wet Impingement Train*; Method 5.1, Source Test Manual, 1989.
10. Filadelfia, E. J.; McDannel, M. D. "Evaluation of False Positive Interferences Associated with the Use of EPA Method 202." Presented at the 89th Annual Air and Waste Management Association Meeting and Exhibition, Nashville, Tennessee, June 1996.
11. Corio, L.A.; Sherwell, J. "In-Stack Condensible Particulate Matter Measurements and Issues." *J. Air & Waste Management Assoc*. 2000, 50, 207-218.
12. DeWees,W.G.; Steinsberger, K.C.; *Method Development and Evaluation of Draft Protocol for Measurement of Condensible Particulate Emissions*; U.S. Environmental Protection Agency. U.S. Government Printing Office: Washington D.C. 1990; EPA-450/4-90-012.
13. U.S. Environmental Protection Agency, 1999. Pre 4-Draft Method for Determination of PM10 and PM2.5. Emissions Measurement Center, http://www.epa.gov/ttn/emc/prelim.html (accessed June 1999).
14. U.S. Environmental Protection Agency; Source Assessment Sampling System. Method 0020, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA SW-846, Third Edition, 1986, as amended May 1998.
15. Technical Assistance Document for Monitoring Sulfuric Acid Vapor from Stationary Sources; U.S. Environmental Protection Agency. U.S. Government Printing Office: Washington D.C. 1985; EPA-600-4/85-005.
16. Hildemann, L.M.; Cass, G.R.; Markowski, G.R. "A dilution stack sampler for organic aerosol emissions: Design, characterization and field tests." *Aerosol Sci. Technol*. 1989, 10, 193-204.
17. McDonald, J.; Zielinska, B.; Fujita, E.; Chow, J.; Watson, J.; Sagebiel, J.; Hayes, T.; Sheetz, L.; Batie, S. "*Chemical Speciation of PM2.5 Emissions from Residential Wood Combustion and Meat Cooking*." Presented at the Air and Waste Management Association Specialty Conference on PM2.5: A Fine Particulate Standard, Long Beach, CA, January 1998.
18. Hildemann, L. M., Klinedinst, D. B., Klouda, G. A., Currie, L. A. and Cass, G. R. "Sources of urban contemporary carbon aerosol." *Environ. Sci. Technol*. 1994, 9, 28.