

PM2.5 EMISSION CHARACTERIZATION FOR STATIONARY SOURCE GAS COMBUSTION

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ABSTRACT

Reliable PM2.5 source apportionment will require accurate inventories of speciated emissions from stationary sources. Although gas combustion is typically thought of as a "clean" process, the enormous quantities of gas burned in boilers, process heaters, and engines could make even small emissions concentrations significant. This study shows that current methods for measuring emission factors and speciation profiles from gas fired sources may have significant artifacts leading to overestimation of emissions. Chemically speciated results using an improved test protocol for natural gas- and refinery gas-fired boilers and process heaters are presented.

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}. Combustion devices are believed to be the most significant source of PM2.5.

The majority of primary emissions from combustion is often 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 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 high³.

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 sources based on speciation profiles for all sources in the modeled area. Reliable results require complete speciation profiles for every source⁴.

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}.

GAS-FIRED COMBUSTION SOURCES

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 is the most energy-intensive of the major energy-consuming industries in the U.S., consuming 3.3 Quads of energy in 1994⁶. The majority of this was accounted for by combustion of gaseous fuels. There is widespread use of reciprocating engines and steam generators in exploration and production activities. Many refineries are situated in or near areas where ambient PM2.5 levels are predicted to exceed the new NAAQS.

Based on 1982 data gathered in southern California, petroleum industry equipment is believed to be a minor source of carbonaceous aerosols in ambient fine particulate matter⁷. Organic compounds may be present in emissions from gas-fired sources as products of incomplete combustion. Organic aerosols in the atmosphere result from semivolatile organic compounds ($>\text{C}_{20}$) present in the source combustion products and atmospheric reaction of volatile organic compounds ($>\text{C}_7$) to form heavier, condensable organics⁸. Tests for "air toxics" conducted over the past ten years provide a partial database of volatile and semivolatile organic compound emissions for several classes of petroleum industry sources. Recent pilot-scale tests indicate that the yield of selected organic compounds from gas combustion is extremely low under operating conditions representative of good operating practice normally found throughout the industry⁹. Emissions of BTX (the sum of benzene, toluene and xylene), formaldehyde, and PAH (the sum of 16 polycyclic

aromatic hydrocarbons) derived from pilot scale tests of a single refinery heater burner and field tests of petroleum industry boilers and process heaters reveals a range of emissions typically near or below detection limits, even when the most sensitive test methods available are used. Compared to boilers and process heaters, stationary reciprocating internal combustion engines (RICE) have relatively high average PAH emission factors – on the order of 0.1 lb per million Btu of gas fired. PAH emissions from asphalt blowing are slightly lower than stationary RICE. PAH emission factors for refinery boilers, process heaters, gas turbines, and coke calciners are approximately an order of magnitude lower. While these types of data may provide a clue to sources of ambient aerosol precursors, the tests usually looked only for specific compounds deemed toxic or carcinogenic, ignoring many other organic compounds such as fuel fragments that may contribute to ambient organic aerosols.

Tests of industrial gas-fired boilers and gas turbines in which particulate emissions measurements included both the filterable and condensable particles show that the condensable fraction is significant, sometimes exceeding the filterable fraction¹⁰. The contribution of the condensable fraction is even more pronounced for oil-fired sources. For example, tests of distillate oil-fired industrial boilers showed condensable particulate matter amounted to several times the filterable particulate. A comparison of fine organic carbon emissions from an oil-fired industrial boiler showed total condensable organic aerosol was 7 to 16 times higher than the filterable organic fraction.

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 and heated to a constant temperature (e.g., EPA Method 17 or Method 5).¹¹ Heating the filter avoids condensation of moisture and/or acid aerosols, depending on the temperature selected. These methods define primary particles that are filterable at the filter temperature.

Condensable 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).^{12, 13} Impinger methods for condensable particulate are subject to substantial artifacts¹⁴ that do not occur in atmospheric processes, especially when ammonia, sulfates and/or chlorides are present in the exhaust, and thus may not provide an accurate measure of primary condensable particles.

PM₁₀ and PM_{2.5} are commonly measured using in-stack cyclones or cascade impactors^{13, 15}, or occasionally using heated out-of-stack cyclones.¹⁶ 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 source apportionment studies for PM_{2.5}.

Source-level measurement methods also exist for secondary particle precursors. NO_x and SO₂ emissions can be characterized using continuous gas analyzer systems. SO₂ can be measured by high-temperature filtration of the sample to remove solid particles, followed by cooling to a temperature below the H₂SO₄ dew point (but above the moisture dew point) and subsequent filtration to remove condensed acid mist¹⁷. 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 which simulates conditions in the exhaust plume, then particles which 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

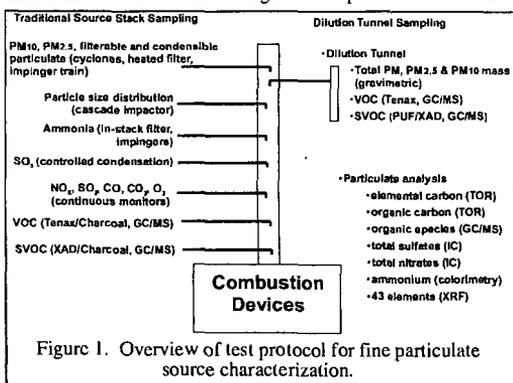
and minor gases are not necessary. Because of the comparatively low temperature of ambient air and diluted source samples, a greater range of sampling media such as Nylon and Teflon membrane filters can be used. This simplifies and extends the range of chemical speciation measurements.

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 are then taken to an analytical laboratory for analysis.

Hildemann et al.¹⁸ 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 others¹⁹ to generate detailed organic aerosol speciation data for several types of sources.

TEST APPROACH

Tests were performed on a gas-fired boiler and a gas-fired process heater in refineries. Both units were fired on refinery process gas. Both in-stack and dilution tunnel methods were included in the test matrix (Figure 1). The dilution tunnel used in these tests follows the Hildemann design discussed above. The diluted sample was passed through various collection media as illustrated in the figure. Volatile organic compounds 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 were collected on quartz filters followed by



polyurethane foam (XAD-4 sorbent, which 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. Ions were determined on quartz filters by ion chromatography. Organic and elemental carbon were determined on quartz filters by thermal optical reflectance.

Source-level sampling for total particulate, PM₁₀, PM_{2.5} and condensable particulate was performed concurrently and co-located with dilution tunnel sampling, providing a direct comparison between the results obtained with the two approaches. PM_{2.5} precursor measurements during the gas-fired unit tests included SO₂, NO_x and volatile organic compounds. In a separate test of a fluid catalytic cracking unit not reported here, particle size distribution was measured using *in situ* cascade impactors and PM_{2.5} precursor measurements also included SO₂ and NH₃.

The tests demonstrated that the dilution tunnel approach could be successfully applied to stationary industrial sources. 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 relatively generous sampling platforms available (a half-circle platform with two sample ports at the boiler site, and a full-circle platform with four sampling ports at the process heater site). However, there are many gas-fired sites where such generous access is not available since stack sampling of gas-fired sources is not universally required. Because of the limited space on the boiler site's platform, the dilution tunnel tests and in-stack method tests could not be performed concurrently; instead, they were performed on different days. Process operating data indicated similar process conditions during all tests. Better access was available at the process heater site, so these tests were performed concurrently. 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-STOCK 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 2). However, condensable particulate matter (CPM) as defined by EPA Method 202 was measured at much higher levels. Analysis of the impinger contents from the boiler test suggests a large fraction of the measured CPM can be accounted for in sulfates and chlorides (Figure 3); however, the mass of sulfates based on the impingers is much greater than that based on the dilution tunnel filters. It is believed the impinger results may be biased high due to dissolved SO_2 in the impingers. Due to differences in the fuel gas sulfur content, SO_2 concentration at the boiler site was approximately 8 ppm, while SO_2 at the process heater site was less than 0.3 ppm. The sulfate concentration in the impinger contents and CPM mass also was higher for the boiler than for the process heater site. 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 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.

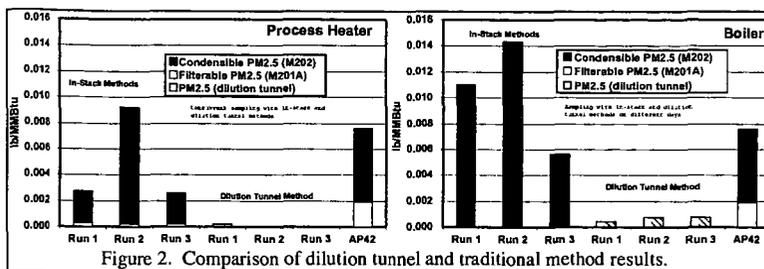


Figure 2. Comparison of dilution tunnel and traditional method results.

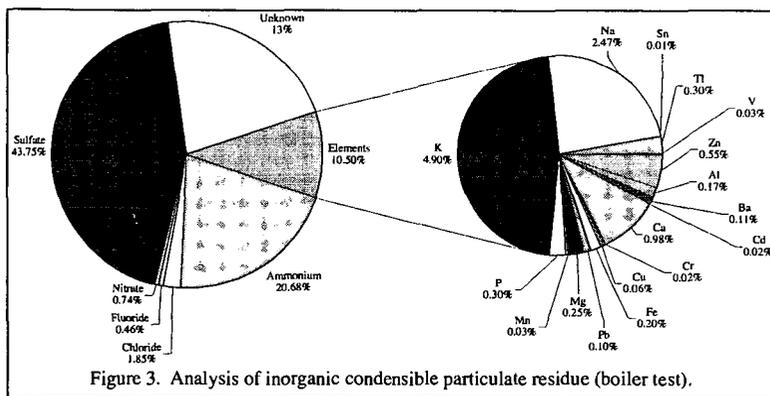


Figure 3. Analysis of inorganic condensable particulate residue (boiler test).

SUMMARY

The sampling methodology described in this paper should result in an improved characterization of source contributions to ambient PM2.5, especially for sources with low particulate concentrations. The test results suggest that traditional source testing methods may significantly overestimate particulate emissions, especially the ultrafine condensable particle fraction. This may be due to analytical method artifacts associated with application of methods designed for much higher particle concentrations. Since particle condensation mechanisms are dependent on both vapor concentration and temperature, dilution tunnel methods provide conditions that more closely represent true atmospheric condensation conditions compared to impinger condensation methods.

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PARTICULATE IMPACTS ON VISIBILITY AT THE GRAND CANYON FROM NORTHWESTERN MEXICO

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ABSTRACT

Project MOHAVE was a large study to investigate the causes of visibility impairment in the Grand Canyon National Park region. An episode with regionally elevated sulfate gave the highest concentrations of sulfate measured at Meadview just west of the Grand Canyon on September 1 and 2, 1992. The elevated sulfate concentrations extended south into northwestern Mexico. Based on wind profiler data, emissions from the power plant in the vicinity of Meadview, MPP, could not have been responsible for the regionally observed sulfur oxides. A CMB model developed during Project MOHAVE was used to apportion sulfur oxides at Meadview and other sampling sites throughout the study region for August 31 - September 2, 1992. The results indicate that the contribution of MPP to sulfate at Meadview was typical. However, transport of SO_x from northwestern Mexico was elevated throughout much of the region during this time period. This led to the large increase in sulfate concentrations at Meadview on September 1 and 2. In addition to this major episode, the results obtained with the CMB model indicate that particulate emissions originating from northwestern Mexico are frequently present during the summer at the Grand Canyon. These results indicate that Mexico can be a significant source of visibility reducing particles at the Grand Canyon.

BACKGROUND AND METHODS USED

Project MOHAVE¹ was a joint partnership research program between the U.S. Environmental Protection Agency, the National Park Service and Southern California Edison. An objective of the program was to establish the relative contribution of emissions from the Mohave Power Project, MPP, to visibility degradation in the Grand Canyon region.

Chemical mass balance receptor based apportionment techniques have been used to estimate the point sources and regional contributors to SO_x (SO_2 plus particulate sulfate) and fine particulate sulfate present in the study region^{2,3}. Source profiles of SO_x from the four coal-fired generating station closest to the Grand Canyon National Park and from the various regional sources which can impact the Grand Canyon have been developed using spherical aluminosilicate (SAS) particles present in coal-fired power plant emissions^{3,4}, fine particulate Se, As, Pb, and Br, and light absorption by fine particles^{3,4}. These source profiles allow the CMB discrimination among the various point and regional sources of SO_x in the southwestern United States^{2,3}.

Details of the identification of the various regional sources and the establishment of the source profiles used in the CMB analysis have been given^{3,4}. The profiles of emissions from the coal-fired generating stations nearest the Grand Canyon [Mohave Power Project (MPP), Navajo Generating Station and Reid Gardner Generating Station were established from both ambient and stack data^{3,4}. The eight regional sources present in the Grand Canyon region during the July-August 1992 summer intensive^{2,3} are summarized below. In addition, the profile of emissions from the coal-fired generating stations in Arizona to the southeast of the Grand Canyon was determined from the ambient data.

The identified regional sources³ and their probable geographical origins^{2,3} include:

- SJ: Air masses from the San Joaquin Valley, CA area.
- LA: Air masses transported from the South Coast Air Basin and the San Diego, CA area.
- BC: Air masses for this source region originate from northcentral and northwestern Mexico.
- AZ: Characterized by air masses from the area generally south of the Grand Canyon.
- SE: Characterized by air masses from southeast of the Grand Canyon and Petrified Forest National Parks.
- NW: Days when the sampled air mass at a given site originated from the region north and west of the Grand Canyon established the NW region source profiles. The data were characterized by three distinctly different source regions. These included the profiles for NW1, a region which includes emission from coal-fired power plants (probably in northern Nevada) as evidenced by the elevated SAS/SO₂ ratio, a NW2 local region characterized by a high F_{Total}/SO_x ratio, and a LV profile in which SAS particles and F_{Total} are absent and which meteorological data suggest includes emissions from the Las Vegas urban area 100 km west of the MV sampling site, Figure 1.

The application of a hybrid CMB model² developed using regional profiles to the Project MOHAVE data accounted for all of the source profile species concentrations and for all of the SO₂ and sulfate. An episode of particular interest occurred at the end of the Project MOHAVE summer intensive. The concentrations of sulfate measured by IMPROVE at Meadview on September 1 and 2, 1992 were the highest concentrations reported at this site in six years of monitoring. During this period, the concentrations of SO₂ at Meadview were also high and about three times the sulfate concentrations. Some investigators have assumed this elevated SO₂ indicated that both SO₂ and sulfate at Meadview were dominated by emissions from the nearby Mohave Power Project, MPP. However, the concentrations of sulfate and SO₂ were also comparably high at all stations south of MPP⁶. We have used a combination of meteorological and CMB analyses to investigate the probable source of this regionally observed SO₂ and sulfate. The meteorological data indicate that MPP could not have been the dominant source of the SO₂ and sulfate present throughout the region during this episode⁶. The results indicate that the contribution of MPP to sulfate at Meadview was no higher than, but comparable to, that seen during the July - August 1992 Project MOHAVE Summer Intensive^{2,3,6}. However, transport of SO_x from the Baja California CMB source area was elevated throughout the region during this time period. This lead to the large increase in sulfate concentrations at Meadview on September 1 and 2.

THE SEPTEMBER 1 & 2 EPISODE

The Hybrid CMB model used to apportion sulfur oxides at Meadview and Hopi Point during the Project MOHAVE Summer Intensive period² was applied to IMPROVE data from the Meadview (MV), Las Vegas Wash (LVW), Cottonwood Cove (CC), Dolan Springs (DS), Essex (ES), Yucca (YU), Parker (PA), Wickenburg (WB) and Painted Desert (PD) sampling sites, Figure 2. These regionally distributed sites were all included in the CMB analysis because the IMPROVE data indicated they were all associated with a marked increase in SO₂ and sulfate on September 1 and 2. For most sites, the sulfate concentrations were higher than those measured during the Project MOHAVE 12 July through 30 August Summer Intensive. The source profiles previously developed as part of the CMB model^{2,3} were used without change. The paradigms previously used for the estimation of SO₂ and sulfate deposition and conversion, and for the regional and Meadview area specific transport times were also used without change². Details of this episode CMB analysis have been given⁶.

The CMB analysis results for sulfur oxide emission sources present in the study region for 2 September are given in Figure 2. As indicated, emissions from both LA and BC were generally present throughout the period at all sites. The impact from BC was greater than from LA for both SO₂ and sulfate. During the episode the highest concentrations of impacts from BC were found at Parker, Essex and Yucca. The highest impacts from LA were found at Essex and Yucca. High impacts for SO₂ (but not sulfate) from MPP were found at Cottonwood Cove, Dolan Springs, Las Vegas Wash and Meadview. Significant impacts from LV were found at Las Vegas Wash and Meadview. The site-to-site and day-to-day changes in sulfate and SO₂ are consistent with a southerly flow resulting in generally decreasing SO_x concentrations, but an increasing sulfate to SO_x ratio for the SO_x from the BC and LA source areas throughout the region. The sulfate impacts at Meadview from all sources for each sampling day are given in Table 1. The highest concentrations of sulfate from MPP were 0.69 µg/m³ at Dolan Spring on 1 September and 0.55 µg/m³ at Meadview on 2 September. All other estimated MPP sulfate impacts were

less than $0.4 \mu\text{g}/\text{m}^3$. In contrast, the highest estimated sulfate impact at Meadview from any source was $1.8 \mu\text{g}/\text{m}^3$ from BC on September 2.

RESULTS FROM THE PROJECT MOHAVE SUMMER INTENSIVE

The results obtained during the episode described above were consistent with the importance of the BC source in the Grand Canyon region during the Project MOHAVE Summer Intensive². These results are illustrated by the data in Figure 3 where are given the total sulfate present at the sampling site at Hopi Point in the Grand Canyon and the sulfate attributed to the BC source region during each day of the Project MOHAVE Summer Intensive. As indicated, sulfate from the BC region were frequently present at Hopi Point. When emissions from this source region were present, they often accounted for the majority of the sulfate. While concentrations as high as the $1.8 \mu\text{g sulfate}/\text{m}^3$ at Meadview on September 2 were not seen at Hopi Point during the summer intensive, concentrations from 0.5 to $1.5 \mu\text{g sulfate}/\text{m}^3$ were frequently seen. The BC region accounted for an average of 42% of the sulfate present at Hopi point during the Project MOHAVE summer intensive². Correlation of the CMB results with measured light extinction at Meadview indicated that light extinction due to anthropogenic emissions from the BC region, per unit of sulfate present from the source, was comparable to that for anthropogenic emissions from most other sources, but only about half that for emissions from the LA source region.⁷ However, the LA source region only accounted for 5% of the sulfate present at Hopi Point.² Thus, combination of the CMB and light extinction data obtained during Project MOHAVE suggest that emissions from northwestern Mexico were the dominant anthropogenic source of visibility impairing particulate material at Hopi Point in the Grand Canyon during Project MOHAVE.

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Table 1. Meadview Sulfate Source Apportionment, 31 August - 2 September 1992, $\mu\text{g}/\text{m}^3$.

Date	MPP	LV	LA	BC	Sulfate	
					Not Fit.	% ($\mu\text{g}/\text{m}^3$)
31 Aug	0.3	0.3	0.2	1.1	4.2	(0.1)
1 Sep	0.3	1.4	0.4	0.9	8.4	(0.2)
2 Sep	0.6	0.8	0.6	1.8	14.8	(0.6)

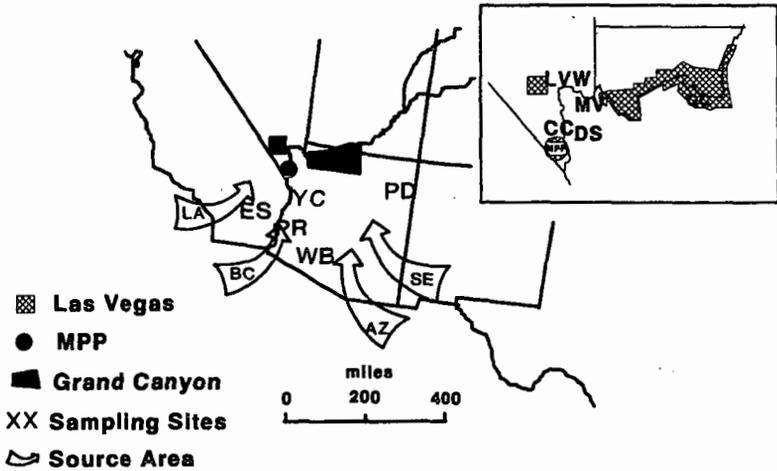


Figure 1. Location of the various sampling sites included in the CMB analysis for 31 August - 2 September 1992, and the expected origins of emissions from the sources included in the analysis; MPP, Las Vegas, LA, BC, AZ and SE.

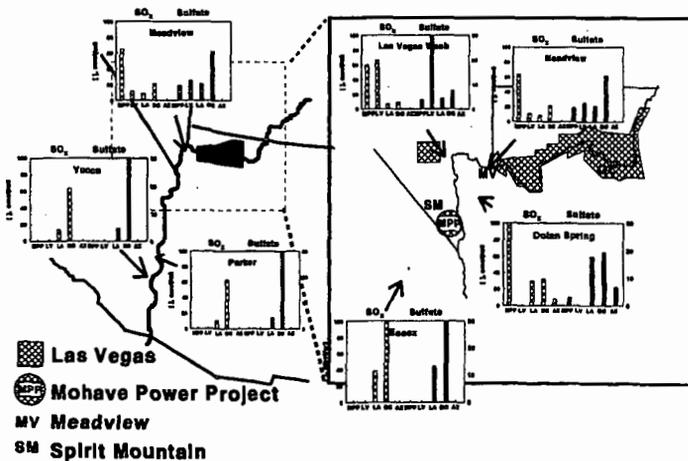


Figure 2. Results of the CMB analysis for SO_2 and sulfate (nmol/m^3) on 2 September 1992 at the sampling sites identified in Figure 1 for the sources identified in Figure 1.

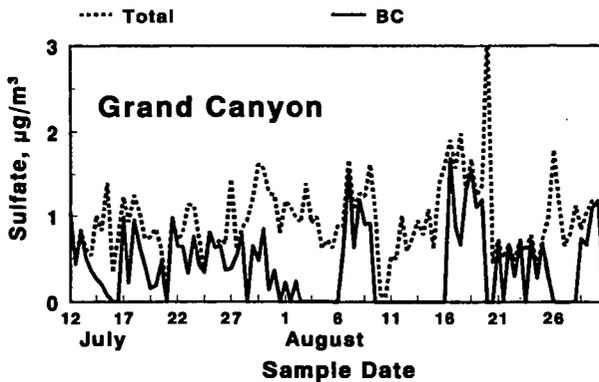


Figure 3. Total and BC sulfate at GC. Northern Mexico is often a major contributor to sulfate at the Grand Canyon.

PM_{2.5} SEMI-VOLATILE MATERIAL: PHILADELPHIA AND ATLANTA SUPERSITE RESULTS

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KEYWORDS: Fine particle sampling, semi-volatile organic material, ambient monitoring

ABSTRACT

Ammonium nitrate and semi-volatile organic material are significant components of fine particulate material in most urban atmospheres which are not properly identified during sampling with single filter samplers because of the loss of these materials from the collected particles during sampling. The composition of fine particulate material at the Philadelphia NARSTO and Atlanta Supersite studies was measured with two PC-BOSS diffusion denuder samplers and with a RAMS continuous monitor. Samples collected with the PC-BOSS were analyzed for sulfate, nitrate (including ammonium nitrate lost from collected particles during sampling), soot, organic material (including semi-volatile organic material lost from particles during sampling), crustal material, and mass. Significant amounts of semi-volatile organic material were present in the particles throughout both studies and semi-volatile organic material was not well measured with single filter samplers such as the a TEOM monitor or the PM_{2.5} FRM.

BACKGROUND

Human health endpoints associated with exposure to airborne particulate matter (PM) include increased mortality and morbidity from respiratory and cardiopulmonary disease^{1,2}. These effects are observed with exposure to concentrations substantially below the U.S. PM₁₀ ambient air quality standard. The observed exacerbation of health problems is believed to be associated more closely with exposure to fine particles than coarse particles. As a result, the U.S. Environmental Protection Agency has promulgated³ revised standards for PM, which establishes new annual and 24-hour fine particle standards with PM_{2.5} as the indicator. This recognition of fine and coarse particles as different classes of PM pollutants is an advance in the understanding and control of PM. However, ambient fine particulate matter is not a single pollutant, but a mixture of many chemical species. Major components include: sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic metals); organic material; elemental carbon (or soot); crustal components; and water. Stable species such as trace and crustal elements, and sulfate can be accurately measured by available technology. However, monitoring technologies for organic carbon, nitrate and particulate water are not as well established.

The collection of particulate matter containing ammonium nitrate on a filter results in displacement of the equilibrium, $\text{NH}_4\text{NO}_3 \cdot x\text{H}_2\text{O}(s) = \text{HNO}_3(g) + \text{NH}_3(g) + x\text{H}_2\text{O}(g)$, with the extent of loss of ammonium nitrate from particles being a function of sampling time, filter face velocity, composition of the fine particles being sampled, temperature, humidity and other factors. However, in the eastern United States there tends to be little nitrate in fine particles because of the high acidity of the aerosol.

A second fine particulate component for which significant losses during sampling on a filter have been documented is semi-volatile organic material. Preliminary studies in eastern sites have indicated that an average of about one-half of fine particulate organic material is lost due to the stripping of semi-volatile organic compounds from the particles during sampling. The hypothesis of the studies reported here is that fine particulate mass will be significantly under-determined in eastern urban environments using the proposed PM_{2.5} Federal Reference Method (FRM) because of the loss of semi-volatile material from the particles during sampling. It is postulated that fine particulate mass, including the semi-volatile fine particulate species, is an appropriate surrogate for the components of fine particles which have been associated with observed mortality and morbidity effects in epidemiological studies. Under-determination of these semi-volatile species will tend to over emphasize the importance of non-volatile fine particulate components such as sulfate. In addition, the need is recognized for both real-time and week-long sampling methods which accurately measure PM_{2.5}, including the volatile constituents ammonium nitrate and semi-volatile organic material. The studies reported here used a PC-BOSS diffusion denuder sampler for the determination and characterization of fine particulate

mass, including semi-volatile organic and nitrate species which can be lost from fine particles during sampling with a filter, and a RAMS for the continuous measurement of fine particles.

EXPERIMENTAL

Samples were collected at the NARSTO summer 1999 sampling site at the Baxter Water Treatment Plant in Philadelphia PA during July, and at the EPA Supersite program at the Georgia Power facility in Atlanta GA during August. The two diffusion denuder samplers intercompared in these two studies were:

1. PC-BOSS

The combination of the technology used in the BIG BOSS sampling system⁴ and the Harvard particle concentrator has resulted in the Particle Concentrator-Brigham Young University Organic Sample System⁵. The system has been optimized to meet the following criteria; 1. Removal of at least 75% of the gas phase material before the sampled aerosol is passed through the diffusion denuder. 2. Efficiency >99% for the removal of SO₂, HNO₃, and gas phase semi-volatile organic material in the minor flow. 3. Determination of particulate mass, carbonaceous material and nitrate with a diffusion denuder sampler.

The inlet to the sampler is a Bendix cyclone with a particle cut of 2.3 μm aerodynamic diameter at an inlet flow of 150 L/min. The cyclone is followed by a virtual impactor particle concentrator. The particle concentrator separates most of the gas phase material into the major flow and leaves particles larger than the cut point (about 0.1 μm) along with a significantly reduced fraction of the gas phase material in the minor flow. The minor flow (25% of the total 150 L/min flow) containing concentrated particles enters the BOSS diffusion denuder^{4,6}. The denuder is comprised of 17 (4.5 x 58 cm) strips of Schleicher and Schuell charcoal impregnated filter paper which are separated at the long edges by 2-mm glass rods. This gives a diffusion denuder with both high efficiency and high capacity. The denuder is followed by two parallel filter packs. The filter pack containing a 47 mm quartz filter (Pallflex, pre-fired) followed by a 47 mm charcoal impregnated filter (3M EMPORE Carbon) is used to determine fine particulate nitrate and carbonaceous material, including semi-volatile organic material lost from the particles during sampling. The second filter pack contains 47 mm Teflon (Gelman Teflo) and nylon (Gelman Nylasorb) filters to determine mass, acidity, ammonium ion, sulfate and nitrate, including any nitrate lost from particles during sampling.

2. RAMS

The RAMS (Real-time Ambient Mass Sampler) is based on the modification of a TEOM monitor to allow for the determination of fine particle mass, including the volatile species⁵. Gas phase compounds which can be absorbed by a charcoal impregnated filter (CIF) are removed by a series of denuders and a Nafion dryer. The resulting airstream is then sampled by a TEOM monitor with a "sandwich" filter containing an R&P TX40 and an S&S CIF filter to collect particles and any ammonium sulfate or semi-volatile organic material lost from the particles during sampling. An active blank system with a filter at the inlet is used to correct for any inefficiency in the denuder and dryer for the removal of gas phase material.

RESULTS

The RAMS blank corrected data are illustrated in Figure 1 for both Philadelphia and Atlanta. Also shown in Figure 1 are conventional TEOM monitor data for the same time periods. As indicated, the concentrations of PM_{2.5} measured by the RAMS is generally either equal to or greater than that measured by the TEOM monitor. The time periods when greater PM_{2.5} mass is measured by the RAMS are those when measurable concentrations of semi-volatile material (dominated by semi-volatile organic material) are measured by the RAMS, but not the TEOM monitor.

The results obtained for the continuous determination of PM_{2.5} with the RAMS have been validated by comparison with results obtained from the PC-BOSS integrated samples to determine the mass of fine particulate material retained on a filter⁵ and the semi-volatile organic material and ammonium nitrate lost from the filter during sampling with a PC-BOSS⁵. Results obtained with RAMS and PC-BOSS denuder sampler show that PM_{2.5} mass, including semi-volatile fine particulate nitrate and organic species can be continuously and accurately monitored with the RAMS. The linear regression of RAMS vs PC-BOSS results give a slope of 1.02±06 (n=7) for the Philadelphia data and comparable results for Atlanta. The average composition of the fine particles collected during the time period shown in Figure 1 at Philadelphia is shown in

Figure 2. As indicated, an average of 35% of the $PM_{2.5}$ was lost from particles during sampling at Philadelphia. These species were not measured by either the TEOM monitor or a single filter sampler. The results obtained at Atlanta were similar, Figure 1.

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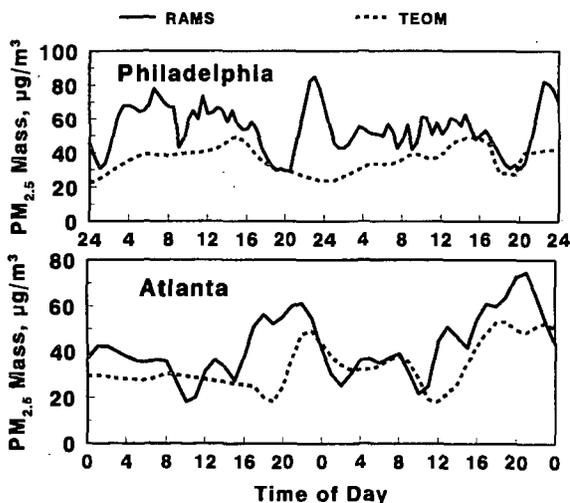


Figure 1. Comparison of 2 h running average of RAMS and TEOM monitor data at Philadelphia. The higher mass measurements with the RAMS is due to the determination of semi-volatile fine particulate material.

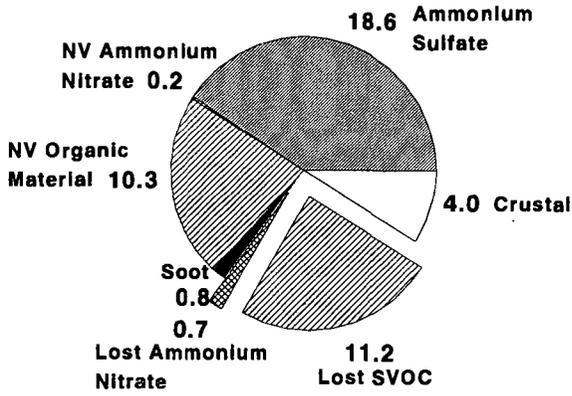


Figure 2. Composition of Philadelphia PM_{2.5}. The ammonium nitrate and SVOC lost from particles during sampling are collected by the RAMS, but not a TEOM monitor.

CHARACTERIZATION OF FINE PARTICULATE MATTER IN OHIO

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ABSTRACT

As a result of recent changes in the air quality standards for particulate matter, an exhaustive study was undertaken to measure PM_{2.5} in Ohio. The ambient results reported here are from an ongoing field experiment in Ohio that began in January of 1999. The ambient monitoring is part of a comprehensive health based study evaluating the impact of air pollution on pediatric health in Ohio. This is among the first of its kind in Ohio, with continuous ambient air monitoring at several sites to characterize fine particulate matter concentrations within the region using Tapered Elemental Oscillating Microbalance (TEOM) samplers. Two locations in Columbus, Ohio were chosen, one in the urban corridor and the other in a suburban location. A third location in rural Athens, Ohio was also established. In addition to the continuous monitors, filtered samples were gathered for chemical analysis of the particulate matter using an x-ray fluorescence spectrometer and an ion-chromatography unit. A spatial homogeneity in the mass concentration time-series data was noted. Sulfate was the largest component of the PM_{2.5} comprising approximately 40% of the total mass

INTRODUCTION

In 1997, the United States Environmental Protection Agency (EPA) implemented new National Ambient Air Quality Standards (NAAQSs) for ozone (O₃) and particulate matter (PM). These standards were based on multi-year scientific assessments that linked health effects to present air pollution levels. The standards, which tighten the requirements for attainment, will have significant economic and social impact for Ohio. For example, under the PM_{2.5} standard, estimates have indicated that 26 counties in Ohio will be in non-attainment. In comparison, one county in Ohio does not currently meet the NAAQSs for PM₁₀.

There is limited data on PM_{2.5} concentrations and its constituents in Ohio. The few historical studies (1,2,3) that have been conducted were health-based studies centered on areas with historically high levels of air pollutants, such as Steubenville, Ohio. This paper presents findings from an ambient PM_{2.5} monitoring campaign that is part of a large on-going health based study in Columbus and Athens, Ohio.

The field experiment, which began in February of 1999, consists of three longitudinal studies involving a rural location (Athens, Ohio), and two urban settings (both within Columbus, Ohio). Two contrasting sites in Columbus were established -- one urban (south central side of Columbus), and one suburban (New Albany, OH). Columbus, like numerous other metropolitan areas in the state and across the nation, has historically met the NAAQS for ozone and PM₁₀ but has the potential for non-attainment under the new PM_{2.5}, and O₃ standards. The rural site (Athens Ohio) was chosen due to its proximity to the background site established by Ohio EPA for PM₁₀ and recently PM_{2.5}. Athens is also being utilized as a background site for the Upper Ohio River Project (4), a comprehensive PM fine and precursor gas monitoring program centered in Pittsburgh that was initiated in early 1999.

MATERIALS AND METHODS

Data is collected simultaneously from three monitoring sites that typify urban, rural, and a downwind suburban location. These sites will aid in the characterization of fine particulate spatially and temporally. PM_{2.5} measurements are obtained with TEOM series 1400a monitors manufactured by Ruprecht and Patashnick Co. The TEOM is a real time gravimetric instrument that draws ambient air through a filter at a constant flow rate and measures PM concentrations continuously. The TEOMs are equipped with automatic cartridge collection units (ACU) fitted with 47 mm filter packs. Samples are collected on Teflon filters. At each site, seven hour (8:30 a.m. -3:30 p.m.) samples are collected Monday thru Friday. The outdoor monitoring regime is tied to simultaneous indoor and personal

monitoring conducted as part of the health based study. Particle mass is determined using an electronic microbalance. The Teflon filters are equilibrated prior to weighing under controlled conditions (22.5 ± 2.5 C and $35 \pm 5\%$ relative humidity). The filters are then subjected to elemental analysis by energy dispersive x-ray fluorescence (XRF). This non-destructive technique is capable of identifying and quantifying elements in the periodic table from atomic number 9 (fluorine) to atomic number 92 (uranium). The samples are then analyzed for water soluble ions by ion chromatography. The water soluble species measured include five anions (fluoride, chloride, nitrate, phosphate, and sulfate) and five cations (sodium, ammonium, potassium, magnesium, and calcium). Meteorological parameters such as temperature, wind speed, wind direction, relative humidity, and precipitation are also measured hourly at each site.

RESULTS/DISCUSSION

The first phase of this project is currently being analyzed. Detailed statistical analysis will be presented at the Particulate Matter and Fossil-Fuel Combustion Symposium - 2000 American Chemical Society Meeting in San Francisco, March 26-31, 2000. Site characterization of the $PM_{2.5}$ and its constituents both temporally and spatially will be evaluated. In addition, the influences of meteorological parameters on total mass and chemical constituents of the $PM_{2.5}$ will be examined.

Daily averaged TEOM data for February through the middle of May are contrasted in Figure 1 for the three sites -- New Albany (suburban, Columbus), Koebel (central urban, Columbus) and East (rural, Athens). What is striking about the preliminary analysis is the uniformity in the data between the sites. New Albany and East (which are approximately 80 miles apart) show very similar temporal profiles over the entire sampling period. Koebel (central urban location) which experienced higher concentrations, potentially influenced by local sources, also had similar temporal patterns. This uniformity is further demonstrated in Figure 2 which presents the diurnal changes in $PM_{2.5}$ for June 2nd thru the 6th. Again all three sites show similar patterns in the concentration profile. Table 1 lists the results of the daily averaged $PM_{2.5}$ concentrations for February and March. As expected Koebel (urban) had a slightly higher average concentration followed by New Albany (suburban) and East (rural). Preliminary analysis by ion chromatography on the filter samples for February and March at East indicates that SO_4^{2-} is the primary water-soluble fraction, comprising on average 40% of the total $PM_{2.5}$ mass.

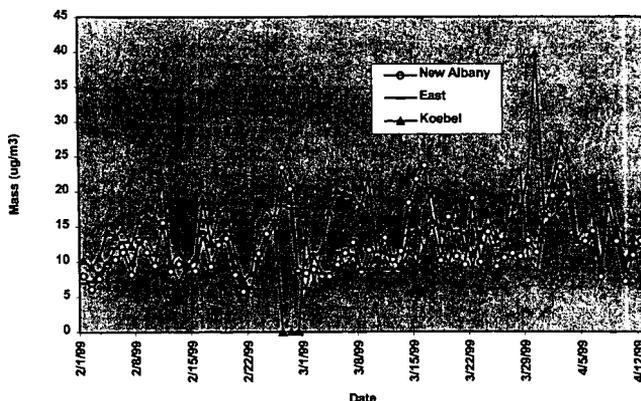


FIGURE 1. Daily average variations in $PM_{2.5}$ concentrations (TEOM) for Koebel (urban Columbus), New Albany (suburban Columbus), and Athens (rural).

CONCLUSIONS

Detailed analysis of the data is currently ongoing. However, preliminary review of the data indicates spatial homogeneity in the $PM_{2.5}$ concentration. This uniformity is experienced in

the daily average concentrations and in the diurnal patterns experienced at each site. SO_4^{2-} was found to comprise 40% of the $\text{PM}_{2.5}$ concentration at the rural site.

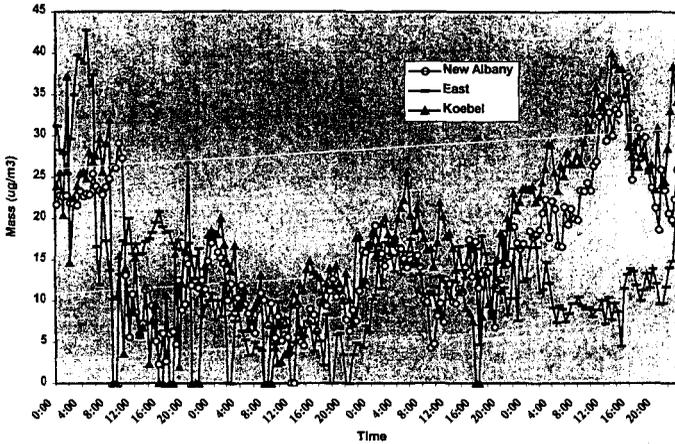


FIGURE 2. 30-minute average variations in $\text{PM}_{2.5}$ concentrations: June 2-6, 1999 for Koebel (urban Columbus), New Albany (suburban Columbus), and Athens (rural).

Table 1. Summary of the Daily Averaged $\text{PM}_{2.5}$ and Sulfate Concentrations for February and March 1999*

Site	Total Mass mean \pm SD	SO_4^{2-} mean \pm SD
New Albany (suburban)	11.8 \pm 4.1	
Koebel (urban)	14.7 \pm 5.1	
East (rural)	11.6 \pm 3.6	4.7 \pm 2.2

* Filter samples are collected five days per week (Monday thru Friday). Concentrations expressed as $\mu\text{g}/\text{m}^3$.

ACKNOWLEDGMENTS

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ENVIRONMENTAL IMPACT OF HEAVY METALS CONTAINED IN FLY ASH EMITTED FROM THE THAI LIGNITE-FIRED POWER PLANT

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ABSTRACT - In this work, the highly hazardous heavy metals (HM) are the focus of an assessment of the environmental impact of the Mae Moh Power Plant (Northern Thailand) fired with Thai lignites. The synergetic environmental impacts associated with the high sulfur content in the fuel (average value of 3.3% and maximum up to 7.0%) and the presence of a large number of heavy metals (As, Ba, Ce, Co, Cr, Cs, Ni, U, Rb, Sr, Th, etc) in the fly ash have been assumed in the model. Using data on the fly ash emission and HM content in the fly ash, the amount of heavy metals emitted from the lignite-fired boilers of the Mae Moh Power Plant was predicted. Calculation of the approximate rates of HM depositions was then conducted and the predicted values were compared with the corresponding element contents in regional soils. For various scenarios of power plant operation conditions and affected area, the environmental impact of heavy metals on that area was estimated. The results show the dangerous tendency of the HM accumulation in soil organic matter under certain conditions.

KEYWORDS: Environmental impact, heavy metals, Thai lignite-fired boilers.

INTRODUCTION

The power production sector of the Thai economy is the strongest emitter of suspended particulate matter (SPM) into environment. Annually, more than 1 Mton, or 80 % of the total SPM emission (referred to as fly ash), is discharged into the atmosphere from solid fuel-fired units, whereas the share of the SO_x emission from power generation accounts for 60 - 65 %. The contribution share of other pollutants (NO_x, CO₂, CO) formed in utility and industrial boilers is much lower (Chungpaibulpatana et al., 1997).

At present, Thai lignite is the major solid fuel used for power generation in Thailand, and this tendency will remain during the next 10-15 years. Lignite, like any other coal, structurally consists of aromatic rings connected by bridges of carbon, sulfur, nitrogen, and other heteroatoms. Coals also contain "grains" of mineral matter, basically consisting of aluminosilicates (or clays), sulfides, carbonates, oxides (usually quartz) and chlorides. Besides, heavy metals (HM) are incorporated into the coal structure as either organometallic compounds or inorganic materials, closely associated with the fuel matter. During combustion the mineral compounds are converted to oxides. Fly ash from conventional combustion boilers consists of conventionally seven oxides (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O and K₂O) as well as traces of HM. When fluidized-bed combustion is used, some other compounds (for example, MgCO₃ and CaSO₄) are contained in fly ash leaving the stacks of the power plant.

Almost all chemical elements have been found in various types of coals (including lignites). As for fly ash, the content of various elements in it may vary in the range from the parts per trillion level (ppt) to more than 50 wt. %. The content of heavy metals (HM) for different solid fuels varies from less than 0.5 ppm (for Cd, Hg) up to several thousands ppm (for Ba, Zn) as indicated by Tillman, 1994.

In this work, the highly hazardous HM were the focus of an assessment of environmental impact of the Mae Moh Power Plant fired with Thai lignites.

MATERIALS AND METHODS

Presently, the Mae Moh Power Plant consumes almost all of the lignite used for power generation in Thailand and represents, in effect, the only source of HM emission from the power sector in the country. After the year 2010, Thai lignites will be gradually replaced with imported higher quality coals, which are planned to be fired in new power producing utilities (Chungpaibulpatana et al., 1997).

Thai lignite can be classified as a high sulfur, low-rank coal. Moreover, as time goes by, the fuel quality is being deteriorated. The lignite supplied to the Mae Moh Power Plant from different mines is currently characterized by a low content of carbon (20 - 35 %), a medium moisture content (26 - 35 %), a variable ash content (17 - 41 %), and a high sulfur content (1.7 - 3 %). The nitrogen content varies from 0.8 to 1.25 %, the oxygen content from 7 to 10.7 %, and hydrogen content from 1.8 to 3.2 %. The lignite's lower heating value is estimated to be 10.4 MJ/kg (averaged).

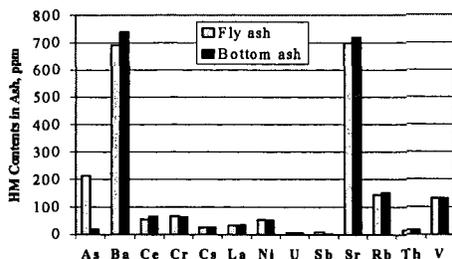


Fig.1. Variability of heavy metals measured in fly and bottom ash of Thai lignite

The most important data used to approach the objectives in our work were found in a paper devoted to determining the X-ray fluorescence analysis of fly and bottom ash (Fig.1) collected from units of the Mae Moh Power Plant (Ratanasthien et al., 1993). As may be seen in Fig.1, data referred to bottom ash confirm that the HM contents are of the same order as ones for fly ash, except for arsenic.

To estimate the emission of ash, we first estimated the total amount of ash (per annum) formed from fuel combustion in steam boilers installed at the power plant. Meanwhile, the SPM emission is associated with ash particles that enter the atmosphere with flue gas, i.e. those that pass through the ash removal equipment arranged downstream from the boilers and remain in the (waste) flue gas. The relevant data (Chungpaibulpatana et al., 1997) for the period of 1990 – 2030 are given in Fig. 2.

At present, the SPM emission is rather high and can be estimated to be about 1/3 of the total ash emission, indicating a low efficiency of ash collecting units used at the power plant. Since new power plants aimed at firing imported coals will be equipped with highly efficient ash collecting devices, the SPM emission is mostly associated with firing lignite, and the data can be used in our work (as given in Fig. 2) for estimating the HM emission from the power plant.

The Mae Moh Fuel-Power Complex (including the power plant) is located in Northern Thailand. The area is bound between 15°N to 20.5°N and 97.5°E to 101.5°E. The climate characteristics of the region (Climatological Division, 1994) and also the vegetation and soil properties of Northern Thailand were used for calculation of pollutants deposition rates and comparison with natural HM content in different soil/ecosystem combinations.

In the case of Thai lignite firing, the synergetic environmental impacts are associated with the presence in the fuel of high quantity of sulfur (1.7 – 3.0 %, in some samples up to 7.0 %) and large number of heavy metals (As, Ba, Ce, Co, Cr, Cs, Ni, U, Rb, Sr, Th, etc). Upon deposition, the synergetic environmental impacts of sulfur and HM are related to the acceleration of biogeochemical migration of most HM under acid conditions. The acidification of tropical soils due to sulfur acidity loading will undoubtedly facilitate the accumulation of many heavy metals in food chains in both terrestrial and aquatic ecosystems (Bashkin & Park, 1998).

The general concept of atmospheric transport and deposition computational method is that the concentration of any substance in air is calculated from its emissions, subsequently transported by (averaged) wind flow and dispersed over the area of interest due to atmospheric turbulence. Basically, the removal of the substances from the atmosphere by wet and dry deposition and photochemical degradation is described in general model algorithms. Meantime, transportation and dispersion of HM in the atmosphere are assumed to be similar to as for other air pollution compounds, for instance, such as SO₂ and the smog compounds (Dutchak et al., 1998).

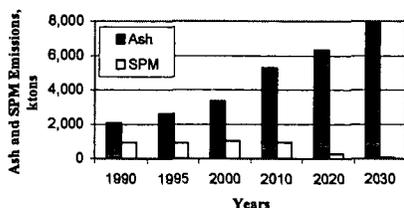


Fig.2. Emissions of ash and SPM (per annum) from the power sector in Thailand

The RAIN-ASIA computational model has been previously applied for the area in the North of Thailand scaled with the $1^{\circ} \times 1^{\circ}$ grid for different time/fuel scenarios based on sulfur deposition predicted data (World Bank, 1994). Some new results have been reconsidered recently using the updated input data (Kozlov& Towprayoon, 1998). Much more detailed studies were carried out by Doolgindachbaporn, 1995, and Ross et al., 1998, for the Mae Moh valley where the power plant is located. The resolutions were from 5 to 10 km cells. Differing in some details, these models indicate the area of most polluted zone as 134 – 179 km², averaged 159 km².

Due to lack of the comprehensive computational model for the HM depositions in the Mae Moh valley, we assume the following two assumptions in selecting the impacted area around the Mae Moh Power Plant:

1. The area of HM dispersion is assumed to be similar to that described in RAIN-ASIA for sulfur deposition, i.e., 20 $1^{\circ} \times 1^{\circ}$ Lola grid cells ranged between 16°N – 20°N and 98°E – 103°E. The total area is as much as 12321 km².
2. The area of HM dispersion is selected to be similar to that described by Doolgindachbaporn (1995) and Ross et al. (1998) for the Mae Moh valley only. The total area is (approximately) 159 km².

These assumptions allow us to estimate the boundary limits for depositions of heavy metals emitted from the Mae Moh Power Plant.

RESULTS AND DISCUSSION

In our study we will consider the toxic metals (according to US EPA classification), namely As, Ba, Cr, Ni and Sb, and also some others, whose emissions are expected to be high. The predicted values on HM emissions are represented in Table 1.

Obviously, HM emissions depend on both emission of SPM from the power plant and HM content in fly ash. The prevailing values of emissions were found for Barium and Strontium, the amounts of those by the year 2000 were estimated to be 716.22 and 726.6 tons/year, respectively.

The emissions of Vanadium, Rubidium, and Arsenic ranged between 120 and 220 tons per year. Relatively small emissions were found for Cesium, Chromium, Nickel, Cerium and Lanthanum (26 – 70 ton/year). The smallest values were found for Uranium, Thorium, and Antimony, they ranged from 5 to 9 tons per year.

However, the environmental impact of the HM depends not only on their emission. Mainly, it is associated with the deposition rates (which depend on the impacted area), relative increase in HM content in soil and some other factors. As mentioned above, two case studies (associated with different impacted areas assumed in computations) have been considered in our work to estimate the dispersion of HM over the area near the power plant.

In the first case study, the total amount of emitted HM was assumed to deposit proportionally to sulfur compounds dispersion over the (maximum) area of 12321 km². The selected year is referred to 1995. According to our assessment, if the impacted area were selected to be 12321 km², in the most polluted $1^{\circ} \times 1^{\circ}$ Lola grid cells, 100°E – 18°N, the deposition rates of HM would

Table 1. Predicted Values of HM Pollution from Power Generation in Thailand, tons

Element	1981	1986	1990	1995	2000	2010
As	29.394	84.561	201.285	196.599	221.094	204.054
Ba	95.22	273.93	652.05	636.87	716.22	661.02
Cr	9.177	26.4005	62.8425	61.3795	69.027	63.707
Ni	7.3554	21.1601	50.3685	49.1959	55.3254	51.0614
Sb	1.1868	3.4142	8.127	7.9378	8.9268	8.2388
Ce	7.4658	21.4777	51.1245	49.9343	56.1558	51.8278
Cs	3.588	10.322	24.57	23.998	26.988	24.908
La	4.5264	13.0216	30.996	30.2744	34.0464	31.4224
U	0.8570	2.46537	5.86845	5.73183	6.44598	5.94918
Rb	19.872	57.168	136.08	132.912	149.472	137.952
Sr	96.6	277.9	661.5	646.1	726.6	670.6
Th	2.3598	6.7887	16.1595	15.7833	17.7498	16.3818
V	18.078	52.007	123.795	120.913	135.978	125.498

have varied from 174 g/km²/year (U) up to 19665 g/km²/year (Sr). The intermediate values are shown for As (5984 g/km²/year), Cr (1868 g/km²/year) and Ni (1497 g/km²/year).

In the second case study the total amount of emitted HM was assumed to disperse evenly over the minimum area of 159 km². If the minimum impacted area were assumed to be 159 km², the values of HM deposition rates would vary from 40,500 g/km²/year (for U) to 4,064,200 g/km²/year (for Sr). The depositions of the most dangerous elements are shown to be equal to 1,236,450 g/km²/year for As, 386,100 g/km²/year for Cr and 309,000 g/km²/year for Ni. No doubt these values are of the great environmental concern for human and ecosystem health.

In spite of the very rough estimation, the predicted values of HM deposition rates are useful for comparison with their natural content in soils of North Thailand. Many considered heavy metals (Ba, Cr, Ni, Cs, La, V) are active biogeochemical migrants and they accumulate in the upper humus soil layer in much more significant amounts in comparison with their local or regional average values in soil and geological rocks, or clarks (Dobrovolsky, 1994). Accordingly, the annual HM deposition rates were compared with both values of HM content in upper humus layer and clarks. The average depth of heavy metal accumulation layer is assumed to be 20 cm.

Calculations have shown that even in the case of maximum area of impacted zone, 12321 km², the annual deposition rates of some heavy metals (As, Ni, Cs, La, V) are equal to 0.2 – 0.5 % of their clarks and achieve 13.5 % for Barium for the area of the most polluted LoLa grid cell of 18°N – 100°E. Nevertheless, many of these metals are biogeochemically active elements and their accumulation is much greater in the upper humus layer. The relative increase in this layer is significantly less and ranges between 0.005 – 0.05 % from corresponding values. Thus, the danger might be connected with As, which could accumulate in soils with annual rate of 0.5 % to the clark value and which is ecologically considered to be one of the most important pollutants.

A much more dangerous scenario can be calculated for the minimum impacted area, 159 km². In this case, even in humus layer the annual increase for biogeochemically active elements achieves 6.43 % for Ba being in range of 0.16 – 3.12 % for other HMs from their content in humus layer. Since the clark values are significantly less than those characterizing an accumulation in humus layer, the relative annual enrichments of HM content in soils are estimated to be between 3.48 % (for Rb) and 103.0 % (for As). These values are undoubtedly dangerous.

The situation is made worse by the synergistic influence of acidification loading from sulfur compounds, which is also dramatic in the region of interest. The increase in acidity of soils and surface waters is known to be accompanied by increasing the mobility of most heavy metals. It leads to possible accumulation of HM in food chains of both terrestrial and aquatic ecosystems.

Table 2 represents the accumulated amounts of HM in soil-biogeochemical fluxes in Tropical Wet Forest ecosystems surrounding the Mae Moh Fuel-Power Complex. The assumption was made that all amount of deposited HM might be accumulated in upper soil layers and could migrate with soil-biogeochemical fluxes of these trace elements. This is reasonable, taking into account high content of Ca and Mg in fly ash of Mae Moh Power Plant. One can see that in case of almost all trace metals (the exception is Sr), the 20 year exploitation of Power plant has led to significant accumulation of HM in the upper soil layers. The values of accumulation might vary from 1.8 ppm for U till 488.0 ppm for Ba. These values have to be added to the natural content of heavy metals in soils. The resulting values are higher than existing environmental quality criteria (limits) for HM contents in soils concerned As, Ba, Cr, Ni, and V (Radojevic and Bashkin,

Table 2. Accumulation of Some HM in Soils over the Minimum Impacted Area (159 km²) (during the period of 1981 – 1999)

Element	Natural content, ppm		Accumulation due to HM emission, ppm
	Upper humus layer	Clark	
As	-	5.0	62.0
Ba	432	0.6	488.0
Cr	197	5.8	19.4
Ni	84	3.2	15.5
Sb	-	1.0	2.51
Cs	20	1.8	7.6
La	80	2.0	9.5
U	-	1	1.8
Rb	-	100	41.9
Sr	-	300	203.5
V	212	3.2	38.1

1999). Furthermore, in many cases the content of HM is higher than the requirements for the remediation, even for commercial or industrial land use.

CONCLUSIONS

1. The emissions and environmental effects of heavy metals from the lignite-burned Mae Moh Power Plant (Northern Thailand) were estimated for the 30-years period from early 80's to year 2010. With increase in power production late in 90's and early in the next century, the major values of emissions were found for Barium and Strontium (more than 650 tons per year). The emissions of Vanadium, Rubidium, and Arsenic ranged between 120 and 220 tons per year. Relatively small emissions were calculated for Cesium, Chromium, Nickel, Cerium and Lanthanum (26 - 70 ton/year). The minimum values were shown for Uranium, Thorium and Antimony, ranging from 5 to 9 tons/year.
2. If the impacted area were considered as minimum one (159 km²), the values of HM deposition rates might be varied in the range from 0.04 (for U) to 4.1 (for Sr) ton/km²/year. The deposition rates, ton/km²/year, of the most dangerous elements were roughly estimated be 1.2 for As, 0.4 for Cr and 0.3 for Ni. If the impacted area were treated as 12321 km², the deposition rates of heavy metals for the most polluted 1°x1° Lola grid cells (100°E - 18°N) in 1995 would have varied from 0.174 (for U) up to 19.7 kg/km²/year (for Sr). The intermediate values were found for As (6.0 kg/km²/year), Cr (1.9 kg/km²/year) and Ni (1.5 kg/km²/year).
3. The 20-years period of exploitation of the Mae Moh Power Plant has led to significant accumulation of HM in the upper soil layer and their migration with soil-biogeochemical fluxes in the Tropical Wet Forest ecosystems surrounding the plant. The values of HM accumulation were estimated to vary from 1.8 ppm (for U) to 488.0 ppm (for Ba). Being added to the natural content of heavy metals in soils, the resulting values for As, Ba, Cr, Ni, and V are higher than the environmental quality criteria (limits) for HM contents in soils. In many cases, the contents of HM exceed the respective requirements for the remediation, even for commercial or industrial land use.

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