

Novel Analytical Dimensions in Exploratory Field Studies of Air Particulate Matter

Sue Anne N. Sheya, Henk L.C Meuzelaar, Sun Joo Jeon, Jacek P. Dworzanski, Wally Jarman, Christian Kastelar, JoAnn Lighty, Adel Sarofim (University of Utah); Wen Whai Li, Victor Valenzuela (University of Texas El Paso); James Anderson, Soame Banerji (Arizona State University); Gerardo Mejia, Miguel Zavala (Instituto Tecnológico y de Estudios Superiores de Monterrey); and Bernd Simoneit (Oregon State University).

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ABSTRACT

Exploratory ("scoping", "pilot") studies of limited size and duration, but capable of pinpointing the best sampling strategy, as well as helping to select the most informative analytical methods and parameters for subsequent large scale studies, can save time and money. The authors have field-tested several rapid, exploratory PM₁₀/2.5 characterization techniques under the auspices of the EPA-sponsored SCERP (Southwest Center for Environmental Research and Policy) Paso del Norte air quality research program at the USA/Mexico border.

The following combination of methods has proven to be a valuable exploratory tool:

- (1) organic characterization of circadian samples (obtained with a mobile 16.7 lpm sampler at 2-hr intervals) by thermal desorption GC/MS;
- (2) inorganic characterization of circadian samples (obtained with a mobile 16.7 lpm streaker-type sampler at 2-hr intervals) by computer-controlled SEM with energy-dispersive Xray detection (CCSEM-EDAX);
- (3) organic (GC/MS) and inorganic (XRF, PIXE) characterization of 24-hr samples collected from stationary, spatially-distributed hi-vol and dichot sampling stations, respectively;
- (4) on-site, size-distributed particle counting at 1-5 minute intervals by means of a multichannel particle counter; and
- (5) data fusion, reduction and correlation by means of principal component analysis (PCA), cluster analysis and related chemometric methods.

Identification of organic, inorganic and mixed source contributions is performed by PCA of periodic or episodic trends and events in circadian receptor sample profiles, as well as by spatially distributed concentration variations among 24-hr samples. Additional inorganic sources are identifiable by cluster analysis of elemental association patterns among individual particles, as measured by CCSEM-EDAX, as well as by morphological analysis of individual particle images.

Comparison of temporally- and spatially-resolved spectroscopic data, e.g. by multi-way canonical correlation techniques, appears to hold considerable promise for calculation of approximate source locations from receptor data. This is especially valuable for locating sources

under windless or near-windless inversion conditions which prevent source backtracking by means of diagnostic meteorological models. In the absence of quantitative source profiles for the multitude of poorly accessible individual PM sources in the Paso del Norte airshed, preliminary source apportionment is being attempted by using pooled source category and/or source cluster profiles calibrated by means of size-distributed particle counting methods, instead of conventional mass balance techniques.

INTRODUCTION

Currently used characterization methods for PM receptor samples are typically based upon inorganic analysis of 24-hr filter samples by means of x-ray fluorescence (XRF), proton-induced x-ray emission (PIXE), scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDAX), or neutron activation analysis (NAA) methods. Over the past decade organic PM characterization methods involving solvent extraction of 24-hr filter samples followed by combined gas chromatography and mass spectrometry (SX-GC/MS) have demonstrated their power in providing hundreds of potential source marker compounds, particularly for a wide range of petroleum- and biomass-type materials combustion and processing sources which fail to produce characteristic inorganic markers or patterns.¹⁻⁵

Single-particle analysis by automated SEM is well known for its ability to provide source information based on inorganic constituents. In fact, until the relatively recent advent of GC/MS based organic methods, inorganic analysis by PIXE, single-particle analysis by automated SEM and XRF methods was the only way to chemically characterize particulate matter for source identification and apportionment purposes.

The past decade has seen the development of the photoelectric aerosol sensor (PAS) which permits real-time measurements of particle-bound polycyclic aromatic compounds (PAH). PAS instruments have been used in detecting PAH-containing emissions and exhausts from combustors, furnaces, incinerators, and foundries. Although the analyzer response is a measure of total PAHs adsorbed on particles it does not speciate the sample. It can however, be highly sensitive to specific sources.

Over the past few years rapid and reliable methods for organic PM characterization and apportionment were demonstrated by some of the present authors using thermal desorption (TD) GC/MS techniques. Equally fast sampling approaches to inorganic PM characterization by means of SEM-EDAX and PIXE were demonstrated by Anderson et al.⁸.

The benefits of combined use of these various PM sampling and analysis methods for source PM_{10/2.5} characterization are amplified by employment of 1- to 2-hr long sampling periods. Because the relative contribution of various source types to receptor samples varies significantly as a function of location as well as time, these shorter sampling times permit creation of time-resolved circadian PM profiles revealing characteristic anthropogenic activity cycles as well as periodic or episodic events. Comparison of these temporally and spatially resolved results with meteorological conditions prevalent during the same time can help establish the approximate source location. Mixed PM characterization techniques used in this receptor scoping study include methods for both organic and inorganic chemical characterization performed on spatially and temporally distributed samples.

EXPERIMENTAL METHODS

Sites to obtain circadian and 24 hour multi-method samples were chosen for spatial location and distribution over both sides of the border. Due to unanticipated and atypical weather (extended periods of high precipitation), only 4 of the planned 6 mobile sites could be operated. In addition, air pollution levels were quite low until well into the third day. A map of site location and distribution is shown in Figure 1. Samples at corresponding US and Mexican mobile sites were coordinated to be taken over the same 2-hour sampling interval for the same duration. After 24 hours, mobile equipment on both sides of the border was relocated to sites spatially separated from the first, and samples were again taken with coordinated sampling intervals. Table I summarizes the types and numbers of samples. Briefly, the sampling included:

- Nine, 24-hour Hi-Vol, quartz fiber filter (QFF) samples for solvent extraction GC/MS (SX-GC/MS) by Jarman and coworkers;
- More than 50, 2-hour (time-resolved) med-vol QFF samples for thermal desorption GC/MS (TD-GC/MS) by Meuzelaar and co-workers;

- Approximately 60, 2-hour low-volume (Lo-Vol) polycarbonate filter (PCF) samples for automated scanning electron microscopy (SEM) and proton-induced x-ray emission (PIXE) analysis by Anderson and co-workers;
- Over 72 hours of photoelectric aerosol sensor (PAS 2000) data by Griffin et al.;
- Approximately 150 hours of multi-channel particle size distribution measurements by Mejia et al., and Meuzelaar et al..

Several (24-hr) Med-Vol Dichot PCB filters obtained for XRF analysis by Li et al. (UTEP) suffered from the low PM₁₀/2.5 level conditions and produced insufficient signal for analysis. Mobile weather data obtained on both sides of the border were lost due to computer malfunctions and had to be replaced by TNRCC data from the Sun Metro and SODAR sites, which were the locations of the two mobile sites on the US side of the border. The Sun Metro data included valuable β -gauge PM₁₀ density readings which were used to calibrate the size-distributed particle count readings obtained, whereas TNRCC's SODAR installation provided us with important inversion layer height data.

Ambient particulate samples for circadian samples to be analyzed by TD-GC/MS were collected on 19 mm diameter quartz fiber (QF) filters in a 16.7 l/min flow of air passing through an isokinetic (dichotomous sampler type) ambient air sampling tower equipped with a 10 micrometer cut-off impactor. QF filters were cleaned by preheating in a high temperature furnace and stored in particle-free containers, as described by Sheya et al.⁹. QF slivers of approximately 2 mm wide were reproducibly cut from the exposed filters and inserted into carefully cleaned borosilicate glass sample tubes and quickly inserted into the hot (250 C) injection port of a GC system (HP 5890A) equipped with a 25 m long, 250 micrometer i.d. GC column coated with a 0.25 micrometer layer of HPMS5 and connected to a desk-top quadrupole mass spectrometer (HP MSD5972). When rapid heating of the QF slivers to higher temperatures is desired, e.g. for pyrolysis studies, the pyrex tubes can be lined with ferromagnetic foils of precisely known inductive heating behavior and a well-defined end point temperature corresponding to the Curie-point temperature of the selected alloy.

GC/MS data were analyzed and identified using the HP ChemStation data analysis program and the Wiley 5th edition mass spectral library. Multivariate statistical analysis of relative peak intensity data, corresponding size-distributed particle count, meteorological data, and inorganic data was performed by means of principal component analysis (PCA) using the NCSS 2000 software package, followed by varimax rotation of the PCA loadings and scores to highlight the most highly orthogonal components in PC space.

The 24-hr Hi-Vol (i.e. 1000 l/min) QFF samples are solvent extracted and concentrated utilizing standard techniques, then analyzed by GC/MS. The SX-GC/MS method is currently the “gold standard” in the analysis of organic PM constituents, thanks to the pioneering work and extensive field studies reported by Simoneit¹ et al. and Rogge²⁻⁴ et al. This method has proven accuracy, but requires milligrams of sample compared to micrograms for the TD-GC/MS technique. There are instances where the large volume of sample might not be feasible or one filter might not yield enough sample to extract. Filters for the high-volume sampler were taken over 9 spatially distributed locations in El Paso/Juarez border region. Two of the sites – Sun Metro on the US side and the Tecnologico institute on the Mexican side – overlapped with the mobile sites giving us a good opportunity to compare the wet and dry chemical extraction methods.

Data for PIXE and SEM analysis were collected on 2- hour filters which were obtained using mobile 1 lpm streaker- type samplers on each side of the border.

On the American side, size-distributed particle measurements were taken with a Climet Model CI 208C particle analyzer with specially built computer interface. Measurements were taken at 4 min intervals over 8-channels in the 0.3 - 10 μm diameter size range. The PAS 2000 was used at the Sun Metro site in conjunction with the previously described data. On the Mexican side, a similar set-up was used but without a PAS 2000 instrument and using a 5-channel, instead of 8-channel, particle counter.

RESULTS AND DISCUSSION

Meteorological data during the study period is summarized as 2- hour average time profiles as shown in Figure 2. Note the near-windless and cool weather conditions, along with a low inversion layer, during the late evening of Dec. 4. Hourly diagnostic wind direction models were constructed for the period of the study using data obtained from the eight meteorology stations in the Paso del Norte region shown in Figure 3a. The coarse and fine grid patterns shown on the map correspond to the area occupied by each of the calculated wind direction vectors from the model, which are illustrated in Figure 3b.

Volumetric particle time profiles from the Sun Metro and SODAR sites are shown in Figure 4. They were calculated from the measured 8-channel, particle-size distribution profiles and the corresponding calculated PM₁₀, PM_{2.5}, and dPM (which represents the difference between PM₁₀ and PM_{2.5}). Calculations were based assuming spherical particles of unit density and an average radius between the low and high cut-off diameter of each particle size “bin” counted by the particle analyzer. Relatively low PM levels were measured directly following the extended rainy weather (which lasted into the late night on Wednesday, December 2nd), followed by an episode of a moderate ‘urban dust’ event in the evening of December 4th. Unfortunately, the low wind velocities (which are difficult to measure) prevailing at the time of this large dust cloud prevents reliable meteorology station readings and thus the certainty of the diagnostic model is also relatively low. Meteorological based backtracking can help in determination of source originations in situations where measurable wind conditions exist. However, the lack of measurable wind speeds during the worst PM 10/2.5 conditions, together with the loss of the mobile site weather data and the lack of sufficient published data from meteorology monitoring sites in Juarez and El Paso (which are necessary for reliable interpolation to the receptor and source sites of most interest) made our attempts at model-based backtracking fail. Nonetheless, visual observations of the urban dust cloud movements on the evening of Friday, December 4th were quite helpful in interpreting the measurement data.

Calibrated PM mass measurements were taken throughout the study’s duration by means of a β -gauge which was also located at the Sun Metro site and which is operated by TNRCC. Thus,

direct comparisons can be made for particle counts measured with our 8-channel Climet and particle mass obtained with the β -gauge. Correlating our volumetric particle data with the calibrated readings meant that corresponding gravimetric time profiles could be calculated by means of a correction factor for average particle shape and density. The correlation results are shown in Figure 5. Correlating the two results enables direct weight/density calibration of particle data. The resulting particle density curves for PM 10 and PM 2.5 are shown in Figure 6 along with real-time PAS 2000 data. There are several peaks and spikes of increased PAH response indicating transient sources of PAH; possibly mobile sources such as diesel engines. These spikes do not correlate strongly with the PM data, but this is most likely due to the character of the PM, rather than its density.

The gradually worsening PM air quality situation, interspersed by rush hour traffic peaks as shown in Figures 4 and 6, culminates in the severe transient PM episode in the late evening of Dec 4 when PM10 concentration reach values in the several hundred $\mu\text{g}/\text{m}^3$ range. Much remains to be learned about these types of late night PM episodes, in this case apparently representing transport of massive dust clouds accumulated over the city of Juarez to the American side by little or no wind, cooling temperatures and low inversion ceilings. However, such episodes appear to be relatively frequent at the USA/Mexico border, particularly in the vicinity of the largest Mexican border cities. Over a total of 10 - 12 winter period monitoring days from 1992 to 1998 several intensive late evening PM events at various US border sites have been observed and are summarized in Figure 7. These episodes occurred at Calexico in 1992 (vicinity of Mexicali; $> 600 \mu\text{g}/\text{m}^3$), Hidalgo in 1995 (vicinity of Reynoso; $> 1,000 \mu\text{g}/\text{m}^3$), Brownsville in 1995 (vicinity of Matamoros; $> 200 \mu\text{g}/\text{m}^3$) and the above mentioned Sodar site (vicinity of Juarez; $> 250 \mu\text{g}/\text{m}^3$).

Figure 8 shows the close agreement between TD-GC/MS and SX-GC/MS analysis profiles of PM samples obtained from the same Hi-Vol quartz fiber filter. Nearly 100 compound peaks have been identified in our GC/MS profiles and are used as a standard identification database, and approximately 90 % of these are present in both profiles, with the intensities of most of these showing strong correlations. Clear differences are seen in the broad multimodal "humps"

underlying both profiles. These humps, generally referred to as the unresolved complex matter (UCM), are highly characteristic of the GC/MS profiles of both solvent and thermal extracts from PM receptor samples and are also seen in most combustion source samples. Apparently, the physicochemical differences between both extraction methods result in somewhat different relative UCM fraction yields. Presumably, for the SX-GC/MS method these relative UCM fraction yields will also be affected by the choice of the solvent whereas the relative UCM yields of the TD-GC/MS technique may well vary as a function of desorption conditions. Thus far, the observed differences appear to be quantitative rather than qualitative and, thus, should be amenable to routine standardization and calibration procedures.

The type of information obtainable from time-resolved circadian TD-GC/MS profiles is illustrated by the skyline plots shown in Figure 9. Each m/z value is indicative of a particular organic compound and acts as a marker for the presence of that compound in each PM filter. The 2-hour time profiles of these selected markers indicate relative quantities and trends of particular PM chemical events. Comparing these profiles with inorganic elemental data profiles obtained through the PIXE technique (Figure 10), confirms the possibility of the high PM_{10/2.5} episode in the evening of December 4th resulting from a broad, re-aerosolized dust. Both these figures suggest that the high PM episode of Friday evening consists of several, somewhat sequential, chemical events.

Each skyline plot in Figure 11 shows a linear combination ("factor") of highly correlated compound profiles, thought to represent a particular PM₁₀ source or combination of related sources which were obtained by performing PCA on combined data sets (see Table III). Figure 11 shows the 6 most significant components and their tentatively identified sources of variance. The episodes include biomass (firewood, yard waste, agricultural residues), or biomass-rich waste (e.g. dump site) combustion. One of these coincided with a weak north-easterly wind just prior to the main dust episode. This wind apparently brought hardwood fireplace emissions from a US residential area directly bordering the site (see Figure 11, factor 5). A second biomass combustion event mixed with some synthetic burning products (e.g. plasticizers), coincides with the tail of the dust cloud rolling across the site and, therefore, possibly represents wood-burning

emissions from the main cluster of brick kiln emissions surrounding the Advanced Transformer site (Figure 11, Factor 6).

CONCLUSIONS

Direct TD-GC/MS analysis of 1- to 2-hr QF filter samples containing microgram quantities of particulate matter provides a rapid approach to characterization and identification of organic PM components in receptor as well as source samples. A 2- hour time interval is sufficient to obtain circadian PM profiles allowing for the deconvolution of overlapping events, trends and gradients.

Inorganic particle compositions obtained by time-resolved single-particle analysis using automated SEM and PIXE techniques clearly complements the organic data.

The use of a diagnostic meteorological model to backtrack receptor measurements to specific source areas was generally unsuccessful because of very low wind velocities during the most severe PM 10/2.5 episodes, the loss of mobile site weather data and the lack of sufficient meteorological monitor locations to allow reliable interpolation of measurements to predict conditions at specific receptor or source locations.

Principal component analysis and associated chemometric techniques of combined spectroscopic data from temporal sample series resulted in data reduction, fusion and correlation. Numerically extracted patterns from PCA analysis often resulted in the presence of specific organic marker compounds, which may be interpreted in terms of potential origins and types of sources.

Organic PM compound profiles and PCA patterns are dominated by suites of compounds which appear to be characteristic of automotive emissions, re-suspended urban dust, and biomass combustion/waste burning/plant debris. Furthermore, these categories are very heterogeneous and need to be subdivided. Automotive source types appear to include diesel engines and possibly idling engines. Open combustion sources include hardwood burning, vegetation/waste burning, and possibly food preparation.

Urban dust, presumably continuously re-aerosolized by traffic, and containing a complex mixture of automotive emissions, unpaved road dust – and many other combustion and non-combustion sources – tends to achieve high concentrations under near-windless conditions; particularly during the late evening and early night hours, when temperatures are falling and in the presence of low inversion layer altitudes. Movement of these dense dust clouds by drainage flows and/or slow convective gradient flows can lead to severe transient PM 10/2.5 episodes in receptor areas at considerable distance from the specific source.

The occurrence of a 4-6 hr long PM episode reaching several hundred $\mu\text{g}/\text{m}^3$ occurred on the last night of the study. Similar episodes have been observed along the USA/Mexican border in several other locations during winter months. All appear to represent slow, late evening drainage flows of massive dust clouds accumulated over the sprawling border towns on the Mexican side of the border under meteorological conditions characterized by little or no wind, cooling temperatures and low inversion ceilings.

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