CHARACTERIZATION OF ORGANIC CONSTITUENTS IN TROPOSPHERIC AEROSOLS BY NOVEL, RAPID GC/MS TECHNIQUES

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I - INTRODUCTION

Recent studies (Reichhardt 1995) reveal a strong correlation between episodes of high fine particulate matter (FPM) levels in urban air and markedly increased morbidity as well as mortality, especially among population groups with compromised cardiovascular and/or pulmonary function. This has prompted the U.S. Environmental Protection Agency (EPA) to propose stricter standards for airborne particulate matter having the aerodynamic diameter less than 2.5 micrometers (PM 2.5), thought to be more relevant to health concerns than the current PM 10 based standards. Also, the U.S. Congress has mandated additional expenditures for research on the health effects of air particulate matter. Unfortunately, the precise relationships between the chemical composition of fine particulate matter and its observed negative effects on human health are still largely unknown (Abelson 1998). Consequently, the primary incentive for detailed chemical speciation of FPM lies in the need to establish the origin, distribution and fate of fine particulate matter in the environment.

Neither the precise chemical nature and concentration of the dominant air pollutants, nor the relative contributions of the various sources as a function of diurnal and seasonal fluctuations or variations in meteorological conditions, are known in sufficient detail to enable a rational assessment of potential environmental impacts, let alone health related consequences.

Since both inorganic and organic FPM components have been shown to provide important evidence regarding the origin of FPM, the preferred approach to chemical speciation is through combining inorganic [e.g., proton-induced X-ray emission analysis (PIXE), inductively coupled plasma-atomic emission spectrometry (ICP-AES), scanning electron microscopy X-ray emission spectroscopy (SEM-XRES) or X-ray fluorescence (XRF)] and organic [e.g., gas chromatography/mass spectrometry (GC/MS)] based methods. In view of the relative complexity of these methods, most studies reported thus far have only focused on a single analytical method. Although inorganic chemical markers have been shown to provide important information regarding several anthropogenic (e.g., high temperature combustion) as well as terrigenic (e.g., crustal matter) sources, other anthropogenic (e.g., combustion of lead free gasoline or biomass) as well as nonanthropogenic (e.g., plant debris and microorganisms) type sources are much better defined by specific organic chemical markers (Rhamdahl 1983, Simoneit 1989, Voorhees et al. 1991). Extensive source characterization studies of a broad range of organic chemical FPM markers in the Los Angeles air district by means of solvent extraction based GC/MS techniques have been reported by Rogge et al. (1991–1998).

Because the composition and concentration of such components tends to vary widely as a function of location, time of day and weather conditions, there is a need to use field-portable equipment allowing for collection of samples followed by their on-site analysis on an around-the-clock basis. GC/MS based techniques have not only proven to be sensitive and highly specific (Karasek et al. 1985, Simoneit 1984, Zeng and You 1996), but also fast and suitable for use in mobile laboratories and/or roving GC/MS systems, as demonstrated by the authors.
(Meuzelaar et al. 1989; McClennen et al. 1990 & 1997). Therefore, we decided to undertake the development of rapid GC/MS methods for FPM characterization that do not require the use of solvents (which are difficult and time-consuming to use in the field).

Moreover, as shown by Dworzanski et al. (1993) observed variations in FPM composition can be linked to simultaneously measured meteorological parameters and phenomena, as well as to physical FPM properties such as particle count and size distributions. Thus, known diurnal, or rather circadian, variations in anthropogenic activities can help identify the specific source of certain organic FPM compounds or compound classes. In view of the complexity and high apparent dimensionality of the multivariate data obtained, the use of multivariate data analysis methods to filter out noise, reduce overall redundancy, reveal the dominant data patterns in multi-dimensional space and examine the underlying chemical and physical trends is imperative. In our laboratory transparent principal component analysis (PCA) methods (Meuzelaar et al. 1992), rather than "black box" type data manipulation techniques, are generally called upon to help unravel the complex relationships between chemical composition, physical properties and meteorology.

Among the U.S./Mexico border regions receiving attention in recent years because of air pollution problems in general, and high FPM levels in particular, the Lower Rio Grande Valley (LRGV) region has been mentioned only infrequently. Recent reports (Ellenson et al. 1997, Mejia and Meuzelaar 1997, Mejia-Velazquez and Rodriguez-Gallegos 1997) while confirming that current air pollution problems in the LRGV region do not yet appear to be as serious as those observed in some other U.S./Mexico border regions, emphasize the expected worsening of LRGV air quality in view of the unusually rapid growth in the volume of transborder traffic and in the number and size of the "colonias" (unincorporated new settlements). Major primary FPM sources in the region include: road dust from unpaved roads, automotive emissions (particularly at border crossings) (Mejia-Velazquez and Rodriguez-Gallegos 1997, Ellenson et al. 1997); trash burning (e.g., waste dumps); general agricultural practices (specifically sugar cane burning on the U.S. side); the Rio Bravo power plant; the Reynosa oil refinery; industrial activities (e.g., "maquiladoras"); domestic heating, and food preparation (frying, broiling) (Mukerjee et al. 1997). Major sources of secondary particulate matter include combustion sources emitting large quantities of sulfur oxides and/or nitrogen oxides together with conditions leading to high ozone levels and sources of anthropogenic as well as biogenic volatile organic compounds (VOC) and semivolatile organic compounds (SVOC).

Results of exploratory studies of airborne organic pollutants, performed along the U.S./Mexican border, using a field-transportable laboratory equipped with analytical (GC/MS) and weather monitoring instrumentation are reported. These results were obtained by the application of sample collection and analysis techniques developed by the authors for rapid, time-resolved characterization of organic air pollutants. The results of feasibility studies at two LRGV sites, the international bridges at Hidalgo and Brownsville (Texas), known to be threatened by elevated air pollution levels from a variety of different FPM sources will be reported here with occasional references to results obtained earlier at border sites in Nogales (Arizona) and Calexico (California).

II - EXPERIMENTAL

a. Sampler Design and Preparation

PM 10 sampling inlets used for these tests are similar to those used for dichotomous (dichot) sampling. Commercially available dichot samplers separate PM 10 through a size selective inlet head (SSI) that is symmetrically designed and contains circular acceleration nozzles. Because of their larger momentum, particles greater than 10 μm aerodynamic diameter impact onto a greased impaction shim. Particles smaller than 10 μm are carried vertically upward by the
air flow and down vent tubes to a filter where they are collected. In our sampler, aerosol is drawn through an isokinetic sampling inlet with subsequent impactor stage which deposits particles greater than 10 μm on a plate immediately in front of the impactor nozzle, as schematically depicted in Figure 1. The impactor is contained in a stainless steel delivery tube which channels particle ≤10 μm to both a filter holder, and to a climet model CI 208C particle counter which counts particles ≤10 μm in eight separate particle size ranges.

b. Filter Preparation

From among the PM 10 collection methods for MS investigated in our laboratory, quartz fiber filters were selected because of their inherent simplicity, chemical and thermal stability and high collection efficiency. Moreover, quartz fiber filters are extremely efficient particle collectors as well as relatively weak adsorbers of organic vapors (McDow and Huntzicker 1993). For these studies, QM-A type quartz fiber filters (QFFs) from Whatman, (Hillsboro, OR) or QFFs manufactured by Pallflex (2500 QAT-UP grade, Pallflex Products Co., Putman, CO) were used to collect particulate samples. Filter sheets were cut into 19 mm diameter disks which were then cleaned by baking in a covered porcelain crucible at 725 °C for 12-24 hours in air. Clean filters were housed in cylindrical aluminum storage containers which had been thoroughly cleaned prior to filter storage by ultrasonicating in methanol and dichloromethane and subsequently heating to volatilize remaining traces of solvents and other impurities. Each filter holder contained two filters for transportation to and from the field. Filters were protected from contamination by handling only with clean forceps.

c. Sample Collection Procedure

Sample air was delivered to the SSI by use of a small portable air sampling pump with an attached pressure gauge. The air stream, at a flow rate of about 20 l/min, was directed onto 2 stacked (primary and backup) filters which were supported by a stainless steel screen. The flow was monitored with a laboratory-calibrated mass flow controller (model 5850E, Emerson Electric Co., Hatfield, PA) and regulated by a valve. Air was drawn through the sampler for an average of two hours. Sampling was continuous around the clock. A tubular manifold containing a panoramic (360°), isokinetic sampling port was topped with a solvent-rinsed and hot air dried pan as a shield against the rain and sun. The sampling port was raised approximately 5 ft above the roof of a mobile, pick-up truck transportable laboratory module (Figure 2) as described by Meuzelaar et al. (1988).

d. Simultaneous Particle Physics and Meteorology Measurements

In addition to collection of particulate material on filters for chemical analysis, the air stream from the SSI was additionally distributed to a multichannel particle counter. Aerosol concentration and particle size distribution measurements were performed at 1-4 minute intervals over 8 size-resolved channels covering the 0.3-10.0 μm diameter size range, using a multichannel particle counter (model CI-208C, Climet Instruments, Red Lands, CA) with specially designed computer interface for continuous data collection. Simultaneous meteorological parameters of wind speed, wind direction, temperature and barometric pressure were measured with a Davis Weather Monitor II (Davis Instruments, Hayward, CA) interfaced to a PC workstation.

e. Sample Extraction and Introduction Methods

1) Thermal desorption versus solvent extraction

GC/MS techniques are applicable only to those analytes which possess a measurably vapor pressure under the maximum temperature the analyte and/or GC column can be exposed to without chemical deterioration. There are two different types of methods to extract analytes meeting these requirements from complex aerosol particles, namely solvent-based extraction methods (here to be referred to as SX-GC/MS
techniques) and solvent-free methods. The solvent-based approach has several advantages. Many standardized solvent extraction methods are available which use inexpensive equipment, are applicable to many inorganic and organic compounds, have few matrix effects, and are compatible with powerful special techniques, e.g., liquid chromatography (LC), capillary zone electrophoresis (CZE), supercritical fluid chromatography (SFC) coupled directly with MS (LC/MS, CZE/MS, and SFC/MS, respectively). Although these methods have proven their value in the laboratory for a wide range of applications requiring extraction of soluble analytes from a more or less insoluble matrix, there are several conceptual as well as practical problems with the application of solvent-based techniques, particularly for studies requiring rugged, field-portable instrumentation. Solvent-based methods require relatively large sample volumes, typically on the order of 10 m³. In a laboratory setting this method is slow and laborious and the logistics of transferring it to the field are challenging. Extraction of analytes in a field setting is impractical due to the difficulty in automating the procedure and the large quantity of required solvent. Besides potential contamination and dilution of the sample, the eluant has environmental as well as health and safety impacts of its own. Finally, direct coupling of solvent extraction to GC/MS techniques is somewhat hindered by the fact that solubility is not directly correlated with volatility. Solvent extracts will often include large soluble molecules, e.g., synthetic polymers, that are unsuitable for GC/MS analysis and will complicate any attempts to achieve a closed mass balance based on GC/MS analysis data alone. In view of these problems we have investigated the feasibility of solvent-free techniques since 1990. All solvent-free methods require a certain degree of thermal stimulation, whether based on direct desorption of relatively volatile molecules (Dworzanski et al. 1993), pyrolysis of nonvolatile aerosol components (Voorhees et al. 1988, 1991) or on-line chemical derivatization of highly polar components (Dworzanski et al. 1989). An important rationale for using thermal desorption and pyrolysis methods over solvent extraction techniques is that nearly all desorption and/or pyrolysis products evolving from the sample are amenable to GC/MS analysis.

Thermal desorption/pyrolysis of compounds from aerosol particulates is accomplished using a combined sample extraction and injection method. It is a much easier method to adapt to field work because there are fewer procedures to follow, and both method and equipment are suitable for adaptation to rugged environments. There are no solvents involved in the extraction process thereby eliminating chemical exposure risks for personnel and relieving the burden of regulatory compliance for solvent handling and disposal. Because only micrograms of particulate material are needed for complete analysis, this method is quick in comparison (2 hour sampling and a few minutes of sample preparation, versus 24-hour sampling and a few hours of sample preparation prior to GC analysis for the SX-GC/MS method). In addition, the short sampling time allows for time-resolved particulate profiles to be created. These provide the means not only for directly correlating organic particulate behavior with daily human activity patterns, but particulate pollution sources can also be more immediately and easily identified. This allows faster assessment of exposure risks for the sample area population.

2) Thermal desorption/pyrolysis techniques

The technique for this microanalytical method begins with cutting 1.5 x 12 mm strips from the sampled filters which represents approximately 15% of the exposed sample area. As shown in Figure 3, the filter strips are then positioned inside a special glass reaction tube which is lined with a ferromagnetic foil characterized by the Curie-point temperature of 315 °C for desorption, or 650 °C for pyrolysis (Japan Analytical Industry Co., Tokyo, Japan) and placed into a Curie-point desorption/pyrolysis reactor for flash desorption of volatile and semivolatile organic compounds; or pyrolysis of a solid residue remaining after the initial
desorption of volatiles. A more detailed representation of the GC inlet for
desorption/pyrolysis used is shown in Figure 4. Flash desorption or pyrolysis of VOCs and
SVOCs from the airborne particles immobilized
by the quartz fiber filter strips is achieved using a
total heating time of 10 s under a continuous flow of ultrahigh-purity helium. Prior to contact with
the Py-GC/MS system, the helium is additionally
cleaned by flowing through the OMNI-1 Indicating Purifier from Supelco (Bellefonte, PA).
The continuous flow of He transfers the analytes
from the reaction zone into a fused silica capillary
column of a gas chromatograph, coupled to a
mass spectrometer as shown in Figure 5. When
properly performed, TD-GC/MS techniques will
reveal most of the chemical markers observed by
the much less sensitive, more labor-intensive and
more time-consuming SX-GC/MS methods, as
illustrated in Figures 6a and b. This enables us to
use the extensive lists of chemical markers
developed by Rogge et al (1991-98) as a starting
point evaluating TD-GC/MS data obtained on 2-
hour receptor samples of PM 10.

3) On-line derivatization technique

A quite different approach which could
prove helpful in identifying polar and/or some
types of complex polymeric materials, including
biological components in aerosols is the so-called
on-line derivatization (OLD) method. This
method is capable of producing volatile, alkylated
derivatives of polar compounds containing acidic
moieties, e.g., esters of carboxylic acids or ethers
of phenolics without the need for wet chemical
procedures. Such procedures usually involve
separate and time consuming steps of hydrolysis,
derivatization and extraction, characteristic for
conventional methods (Dworzanski et al. 1990).

The profiles of on-line derivatized fatty acids in
the form of methyl esters (OLD-FAME) can
provide information on nearly all biological
matter since fatty acids are present in every living
cell as well as in nonviable cell residues. An
example of OLD profiles of PM-10 sample on a
QFF strip is shown in Figure 7 from the Nogales
site. This profile illustrates the results obtained
by pyrolytic methylation with
tetramethylammonium hydroxide (TMAH) of
organic components associated with PM 10.

f. GC/MS Analysis Techniques

1) Laboratory GC/MS

GC/MS is a proven and reliable analytical
method for microanalysis of organic compounds
in a laboratory setting (Kraske et al. 1985). In
our laboratory this stage of analysis was fully
integrated with the sample extraction and
injection method by replacing a conventional GC
injector with a Curie-point thermal
desorption/pyrolysis module shown schematically
in Figure 4. Subsequent to sample desorption and
introduction of compounds released from
particulates into a fused silica capillary column, a
temperature programmed separation of analytes
coupled with simultaneous MS monitoring of a
column effluent was initialized. Usually, 10-30 m
long 0.20-0.25 mm i.d. fused silica capillary
columns coated with a 0.25-0.4 μm thick film of
a nonpolar liquid phase were used. These phases
included pure poly(dimethylsiloxane) resin (DB-1
from J & W Scientific, Folsom, CA) as well as its
phenyl derivatives of higher stability and/or
polarity (DB-5, DB-5 MS from J & W Scientific
or HP-5 MS from Hewlett-Packard, Avondale,
PA). Highly purified helium was used as a carrier
gas. The capillary GC column was temperature
programmed from 40 to 320 °C at a rate of 8-15
°C/min. The GC column exit was inserted via a
heated transfer line directly to the vacuum of a
model 700 Finnigan MAT Ion Trap Detector
(ITT) mass spectrometer (San Jose, CA) or a
quadrupole type Mass Selective Detector (MSD
5972 from HP). The ITD or MSD were scanned
from m/z 35 up to m/z 450 at the rate of 2-4 scans
per second. The total ion current chromatograms
or selected ion current profiles were used for
quantitation after a calibration curve was
constructed using GC/MS measurements on a
series of known concentrations of reference
compounds in dichloromethane.

2) Field-portable GC/MS

There is currently little understanding of
the extent of temporal and spatial variability,
transport contributions, and meteorological
impacts for PM 10. Assessment of actual ambient aerosol composition and concentration requires the use of field-portable equipment, thereby facilitating on-site collection and analysis of samples on an around-the-clock basis. GC/MS based techniques have not only proven to be sensitive and highly specific (Karasek 1985), but also fast and suitable for use in mobile and/or roving GC/MS laboratories, as demonstrated in our laboratory (Meuzelaar et al. 1988 and 1989, McClennen et al. 1997). Figure 2 shows our mobile, self-contained analytical laboratory at a sampling site on the U.S./Mexican border. This mobile laboratory is designed to be a platform for a range of physical and chemical air pollutant characterization methods, including FPM counting, collection and organic analysis. In particular, by incorporating a field-portable GC/MS system with a thermal desorption/pyrolysis inlet, this laboratory allows the speed and sensitivity of GC/MS techniques to be applied for time-resolved characterization of FPM in near-real time. One version of this fieldable instrument is constructed around the chassis of an ITD-700 Ion Trap Detector, whereas a second configuration incorporates a Hewlett Packard MSD. In both versions, the capillary GC column exit is inserted directly into the electrode region of a ruggedized GC/MS system. Figure 8 compares ambient VOC profiles obtained during the 1991 Nogales field experiment by means of a regular length (15 meter) GC column and a very short (2 m long) capillary column. In spite of the predictable resolution loss, the short capillary column speeds the analysis process up by a factor 10 or so while still permitting identification of individual compound clusters.

g. Standardization, Quantitation and Quality Assurance

1) Data collection and acceptance criteria

The acceptance criteria for data quality indicators included the precision, accuracy, representativeness, completeness and comparability. The precision of data quality was determined through the collection and analysis of duplicate samples, as well as through the addition of target compound spikes to duplicate samples. The accuracy of the methods used was determined through the use of blanks and background samples, artificially prepared samples, and/or through the addition of known amounts of target compounds to site samples. Representativeness was achieved by thorough and repetitive sampling of each sampling area and overlapping samples, however the state of the art in exploratory analysis of VOCs and particulates has not yet resolved the issue of attaining absolute representativeness. Completeness was achieved through collecting extra samples so that any samples which may have inadvertently deteriorated, become contaminated or lost through other means would not reduce the validity of the remaining samples. Comparability for the data obtained was achieved through the proficient use of standard methods of analysis.

2) Survey design and statistical analysis

The field test design incorporated collection of sample aerosols (PM 10) and airborne particles which were collected from the border area. The survey design was systematic in that samples were taken at regular temporal and spatial intervals. However, within these intervals statistical distributions are unknown. In addition, because this was a survey and the above types and quantities of analytes have not been collected for this area, there is no guidance to help in developing a statistical design other than our experience.

3) Sampling, analysis and calibration procedures

Handling of samples was done in ways to minimize sample loss through sorption, contamination, or breakage. Filter samples were placed in separate aluminum storage containers. Samples were labeled according to time of acquisition, location, and sequence number. Sample preservation was effected through freezer storage. To ensure that QFFs and sample containers are free from contamination, a GC/MS system was used to analyze filters kept for a few days at the room temperature in storage containers.
used for transportation to the U.S./Mexican border sampling sites. To assess possible analyte losses during shipping and storage, spiked traveling blanks were analyzed under the same conditions.

Procedures for performance evaluation of sampling methods included periodically checking flows through sample pumps, which were continuously monitored by in-line mass flow controllers. Some samples were analyzed on site with desorption and/or pyrolysis/gas chromatography/mass spectrometry. Duplicate samples were transported back to the laboratory and analyzed using similar instrumentation under similar operating conditions. In addition, dynamic and static system blanks, as well as field blanks were included and analyzed at the sensitivity level that was employed for the sample analysis. A dynamic system blank was collected by passing precleaned air through the sampling system in parallel with the simplified unit composed of an identical filter unit — however, exposed directly to the atmosphere — using the same flow and time conditions as during the actual field sampling.

Calibration procedures for GC/MS included regular tuning of the MS system and calibrating mass axis using perfluorotetrahydroxane (PFTBA) as a calibration standard. Quality Control (QC) procedures included verification of vacuum integrity and set temperatures for all heated zones. In addition to inspection of the mass spectra for PFTBA, mass resolution was always evaluated comparing the degree of separation of the m/z 69/70, m/z 219/220 and m/z 502/503 ions originating from the PFTBA. The procedures described, together with the use of automatic gain control to eliminate space-charge effects in the case of ITD, ensure that mass spectrometers will produce mass spectra consistent with those included in standard data bases used to identify unknown compounds. The stability of instrument response was monitored on a daily basis by analysis of multicomponent standard composed of a subset of the analytes deposited on a QFF.

The compounds identified include two categories: (a) characterized by almost perfect match between mass spectrum and the retention time of unknown analyte in comparison to an available standard; these should be considered as belonging to the category of analytes with confirmed identity (Clement and Koester 1995); and (b) identified by spectra matching with a library standard and/or by manual identification based on detailed interpretation of mass spectra and combined with the most probable retention characteristics for a given compound, however, because authentic standards have not been analyzed under the same conditions, these compounds should be considered as tentatively identified.

4) Data usage and evaluation methods

Chemical nature and concentration, meteorological, diurnal, and seasonal data were used to test and evaluate dispersion models to provide time-resolved analysis for preliminary assessment of the dynamics and sources of regional air pollutants.

Qualitative procedures for evaluating project success included getting information about those parameters and sites studied which were previously unavailable for this area. These include information about diurnal and seasonal trends, correlations (weather, traffic, etc.), precursor identification, and characterization and profiles for particulates, and VOCs. The quantitative success of the project is more difficult to assess since minimal data concerning air pollutants has been previously gathered for this area. The multipoint sampling and analysis technique enables mapping of pollutant concentrations thereby integrating the approaches of receptor analysis based and source monitoring based models.

h. Data Processing

1) Compound identification

A group of target compounds were identified by an initial qualitative analysis of representative GC/MS runs from the Nogales site. Compound names, chemical formula, molecular mass, and major positive fragment ions derived from these chemicals and originating from the molecular ion generated under standard electron
impact (EI) ionization (70 ev) conditions are given in Table 1. Selected ion chromatograms (SICs) of indicative m/z ratios from these potential compounds of interest were used to obtain relative retention times and characteristic mass spectra. Retention times were then used to verify the position of the target compound on chromatograms obtained during GC/MS analyses of each two-hour filter sample from all border sampling locations. If an SIC peak from the sample occurred at the corresponding retention time on its chromatogram as the compound of interest, its spectra were matched against library spectra (Registry of Mass Spectral Data, 5th edition, Wiley & Sons, New York and/or Finnigan MAT NBS Library Compilation, 1984) for confirmation of compound identification. Some representative GC/MS total ion and selective ion chromatograms of semivolatile organic compounds obtained by desorption from PM 10 sample collected in Nogales is shown in Figure 9. Compounds representing several chemical classes (e.g., phenols, polynuclear aromatics, terpenes, phthalates) were identified and subsequently quantified through peak area integration.

2) **Multivariate data analysis techniques**

Data were reduced, interpreted and evaluated with the aid of multivariate data analysis (MDA) techniques. MDA techniques used are primarily based on a non-supervised "exploratory" data analysis approach, e.g., principal component analysis (PCA) with subsequent orthogonal rotation of the PCA components using the Varimax technique. PCA is a data analysis tool that is used to reduce the dimensionality of a large number of interrelated variables while retaining as much of the information (variance) as possible. PCA calculates a non-correlated set of variables ("factors" or "components") which are ordered so that the first few retain most of the variance present in the original variables. The first step in PCA is usually to create an autoscaled data matrix, by subtracting the variable mean and dividing by the standard deviation.

New variables are then constructed as weighted averages of the original variables, and are simply linear combinations of those variables. These new variables are called the factors or principal components. Their specific values on a specific row are referred to as the factor scores, and represent the relative contribution of the original value to the factors:

\[ F_j = a_{1j}Z_1 + a_{2j}Z_2 + \ldots + a_{nj}Z_n \]  \( \text{(1)} \)

where \( F_j \) is factor \( j \) and \( a_{nj} \) is the loading (correlation coefficient) of variable \( Z_n \) with \( F_j \) (Windig et al., 1986). The weights, \( a_{nj} \), are constructed so that the variance of \( F_1 \) is maximized, \( F_2 \) explains as much of the remaining variance as possible, and their correlation is zero. The remaining \( F_j \)'s are calculated so that their variances are maximized, subject to the constraint that the covariance between \( F_n \) and \( F_j \) for all \( n \) and \( j \) (\( n \) not equal to \( j \)) is zero; or in other words, that \( F_n \) and \( F_j \) are orthogonal.

Several methods have been proposed for determining the number of factors that should be kept for further analysis. The scree plot, documented by Cattell (1966), is a graphical approach for determining the number of factors. It is a plot of factors versus eigenvalues. Usually factors whose eigenvalues are less than one are discarded. However, important information about possible outliers and linear dependencies may be determined from the factors associated with relatively small eigenvalues, so these may need to be investigated as well. Another method is to preset a certain percentage of the variation that must be accounted for in the factors, and then keep the minimum number of factors which achieves this value. In our data sets, the number of factors which accounted for at least 80% of the original variables' variation were kept.

PCA finds a set of dimensions (or coordinates) in a subspace of the space defined by the set of variables which can be represented as axes which are orthogonal to one another. These axes can be rotated, while keeping the 90-degree angle between them, which improves the ability
to interpret the meaning of each principal component.

In the Varimax rotation technique, the axes are rotated to maximize the sum of the variances of the squared loadings (correlations) within each column of the loadings matrix. Maximizing according to this criterion forces the loadings to be either large or small. By rotation of the factors in this manner, new factors are obtained that are each highly correlated with only a few of the original variables. They reduce the tendency of producing a single dominant general component by making the variances explained by each individual component more equal. This simplifies the interpretation of the factor to a consideration of a few variables which are often more readily identifiable as specific source components. For a more detailed description of exploratory MDA methods such as PCA and subsequent orthogonal rotation methods such as Varimax the reader is referred to standard text books (e.g., Johnson and Wichern 1997).

III - RESULTS AND DISCUSSION
a. Selected Study Sites and Parameters

Of the 6 U.S./Mexico border sites studied for 48 hours or longer since 1991, we will primarily discuss the FPM monitoring and characterization results obtained in 1995 at the Hidalgo and Brownsville sites, with occasional references to the 1991 Nogales and 1993 Calexico sites (Figure 10). All of these sites have in common that measurements were performed in the first half of the month of December, on the U.S. side of the border in close proximity to busy border crossings and just north of a large bustling Mexican cities.

At the two LRGV sites (Hidalgo and Brownsville) the mobile laboratory was set up directly at the foot of the international bridge, just east of the traffic lanes returning to the Mexican side. Consequently, traffic related FPM levels were expected to be highest during the afternoon rush hours, particularly in the absence of significant westerly or northwesterly winds.

Besides multichannel FPM counting every few minutes, QFF sampling at 2-hourly intervals, and continuous monitoring of meteorological parameters (wind speed and direction, ambient temperature and pressure), several VOC samples and microbiological samples were also collected. At the Nogales site temperature and pressure data were lost due to equipment problems (following a lightning-induced, citywide power outage which also destroyed 24 hours worth of chemical and physical particle data), whereas at the Calexico site too much of the particle size data was lost due to equipment malfunction to allow inclusion in the final multivariate data integration step. Fortunately, a directly adjacent county air quality control monitoring station provided a reliable source of PM 10 concentration data (beta attenuation monitor) in addition to ozone data.

We received gracious and generous hospitality and support from city and county air quality and/or health officials as well as from bridge (Hidalgo and Brownsville) and fire station (Calexico) personnel at each of the sites visited. Without their help we could not have performed these field tests.

b. Meteorology and Particle Physics

Meteorological measurement data for the two LRGV sites are shown in Figures 11 and 12. The longest consecutive measurement series (76 hours) was completed at the Brownsville international bridge to Matamoros, Mexico (Figure 12) and the first 30 hours show PM 10 levels in the 40-60 μg/m² range (approximately 1/3 of which due to PM 2.5). Then the weakening North-West wind disappears followed by a steep increase in PM 10 levels to several hundred μg/m², apparently, as a result of bridge traffic related particulate matter generated during the morning rush hour drifting across the monitoring site. The data in Figure 12a show a clear heating trend during the subsequent days while the wind has shifted to the south-east and shows a strengthening diurnal rhythm with maximum wind speeds up to 4 m/sec, coinciding with the temperature maxima (Figure 12b). This is typical of a "sea breeze" mechanism with air from the Gulf of Mexico being drawn landward by rising
hot air above the desert areas. The south-east rather than due east wind direction reflects the local orientation of the Rio Grande valley at the monitoring site. During the diurnal south-east wind speed maxima the largest subfraction of PM 10 particles (i.e., PM 2.5–10) shows strong increases, apparently as a result of re-aerosolization of dust and other terrigenic materials. PM 2.5, however, tends to reach maxima during the morning and evening rush hours with a slight dip between noon and the mid afternoon.

At the Hidalgo/Reynosa bridge no clear diurnal wind pattern is observed (in agreement with the much greater distance from the coast). Instead, wind speeds rarely exceed 2 m/sec and wind direction varies between south-east and north-east (Figure 11). Moreover, PM 2.5 levels at the busy bridge crossing never appear to fall below 100 µg/m³ and markedly exceed the remaining PM 10 fraction concentrations. Suddenly, on December 6th at 10 a.m., a pronounced drop in temperature, accompanied by south-west wind gusts, is recorded. Around 4 p.m. the wind dies down and within a few hours extremely high PM 10 and PM 2.5 counts are starting to be recorded (Figure 11c) peaking out at estimated levels in the 1,000 µg/m³ range (precise calibration is not possible due to present lack of information on average particle shape and density). However, the photographs of recovered quartz fiber filters in Figure 13 confirm that very high particulate matter levels were reached indeed. Visual observations during the height of the episode around 8–9 p.m. revealed a strong haze, reducing visibility to less than 200 yds and characterized by a stale, "garbage-like" smell. Clearly, the sudden temperature drop, south-west winds (coming from the Reynosa direction) and subsequent windless condition caused by this cold front conspired to produce smog which was gradually worsened by the evening traffic peak and the low inversion ceiling.

During an aggregate 20 days of field experiments at the U.S./Mexico border over the past seven years PM 10 air pollution episodes exceeding 300 µg/m³ and lasting up to several hours were observed on at least 5 occasions, twice reaching approximately 600 µg/m³ and once exceeding 1,000 µg/m³ on a second occasion. The first two episodes, illustrated in Figure 14, occurred at Calexico (just north of Mexicali and the New River) in December 1992 and at the Brownsville International Bridge in December 1995 (see Figure 12). Whereas the latter episode occurred at the Hidalgo International Bridge (just North of Reynosa and the Rio Grande) in December 1995 (see Figure 11). At Calexico the concentration levels (calculated from multichannel particle size distribution measurements) were confirmed by comparison with an adjacent beta attenuation monitor, while the Hidalgo and Brownsville data were obtained with a factory calibrated instrument using the same average particle volume and density assumptions. Interviews with local fire station personnel (Calexico) and customs officials (Hidalgo) revealed that episodes of severe “haze” were relatively common, particularly between sunset and midnight. Clear evidence of extreme PM 10 air pollution episodes at the U.S./Mexico border has also been presented by Dattner (1994), including a 12 hour average of 621 µg/m³ near Juarez in December 1990.

Recent studies on the potential implications of strongly elevated PM 2.5 levels suggest an imminent threat to life and health, particularly for persons with pre-existing heart and lung conditions (Kaiser 1997). If the occurrence of PM 2.5 levels in the 1 mg/m³ range is indeed a more than sporadic occurrence at the Hidalgo/Reynosa site, then appropriate measures may need to be taken to minimize exposure of bridge personnel. Clearly, establishment of a permanent PM 2.5 monitoring station should be considered here. In order to further evaluate the frequency and cause of such extreme FPM episodes at the Hidalgo Bridge, the University of Utah Center for Micro Analysis and Reaction Chemistry, in collaboration with the Centro de Calidad Ambiental at IITESM, Monterrey, Mexico is currently developing a fully automated FPM monitoring and collection station with the
sponsorship of the Southwest Center for Environmental Research and Policy (SCERP).

c. Comprehensive Multivariate Analysis of Physical and Chemical Data

As demonstrated and discussed under Experimental, direct GC/MS analysis of thermally desorbed particle adsorbrates produces a wealth of information about the origin and nature of fine particulate matter in air. To show all, or even some, of the GC/MS analyses from the more than 60 quartz fiber filters collected in Hidalgo and Brownsville alone is not a practical proposition within the scope of the present report, since every GC/MS run typically consists of several thousand mass spectra. Obviously, a systematic, comprehensive analysis of the many chemical and physical parameters involved requires a multivariate statistical analysis approach, particularly if the data can be shown to possess a significant degree of redundancy.

Table 2 lists 24 different parameters extracted from the measurement data obtained at the two LRGV sites. The chemical parameters in this table represent the most informative peak signals observed in the GC/MS runs, based on earlier analyses (Dworzanski et al. 1993) as well as literature data on solvent extraction experiments (Rogge et al. 1991–1998). Before carrying out a principal component analysis of this data set, it is informative to examine the correlation matrix for the presence of more or less clearly pronounced bivariate correlations. Since the correlation matrix is too large to be printed here in its entirety, let us just mention the fact that approximately 12% of the correlation coefficients in this matrix were found to exceed 0.63, i.e., three times the standard error. A few of the more remarkable correlations are highlighted in the form of bivariate plots (Figure 15). Besides illustrating some of the interesting correlations, e.g., between PM 10 concentration and the intensity of the mass peak at m/z 239 (dehydroabietate), or between m/z 191 (hopanoid) and m/z 202a (fluoranthen), these bivariate plots are also handy for spotting unusual distributions, e.g., dominated by a single measurement with unusually low or high values. Nonetheless, it would be a mistake to think that all informative multivariate correlations can necessarily be found by inspecting all possible bivariate plots. In practice, relatively strong correlations between a given parameter and a hidden, underlying trend might be distributed over multiple weak correlations with the other parameters associated with the trend and can only be found by making linear combinations of these parameters, i.e., by principal component analysis.

Table 3 shows the most prominent principal components (after Varimax rotation) of the 57 x 24 data matrix combining the data from Hidalgo and Brownsville. The first 6 Varimax components explain approximately 80% of the total variance in the data set. A look at the Varimax loadings of these six components in Table 4 reveals some interesting correlations, all of which can be found in both the Hidalgo and Brownsville data sets (verified by analyzing each of the data sets separately as well). More surprising, perhaps, all of the four chemical parameter associations ("urban dust", "automotive emissions", "biomass burning" and "waste burning") are also clearly found in the Nogales and Calexico data (verified by running these data sets separately as well as by combining all four data sets). In addition there are two Varimax components dominated by meteorological parameters which are not found in the Nogales and Calexico data, apparently due to the very different local and regional meteorological conditions and the loss of temperature and pressure data for Nogales. As can be seen from Table 4, the Varimax rotation method succeeds quite well in removing intermediate strength loadings from the five columns, thereby producing prominently visible parameter associations. This result is similar to that reported by Mukerjee et al. (1998) for Varimax-rotated PCA of inorganic particle composition data. Moreover, several of the most prominent particle sources detected by Mukerjee et al. (e.g., biomass burning, automotive emissions) are also clearly visible in our data.
d. Chemical Marker Patterns and Inferred FPM Sources

Automotive emissions are readily identifiable by a characteristic combination of 3 chemical markers: PAH, unresolved hydrocarbon hump, and fossil hopane signatures. Their concentration varies in a predictable manner with the diurnal traffic activity cycles and is moderately affected by meteorological conditions. Typical diurnal variations are at the 2–3 \( \sigma \) level with occasional 4 \( \sigma \) events.

Burning of lignocellulosics and of synthetics appears to produce relatively large particles which are strongly affected by wind direction (south) and speed (moderate speed produces highest levels). At all 4 border sites the pattern divides clearly into 2 subpatterns: syringyl ("hardwood") markers plus retene and diethyl phthalate (DEP) and a guaiaclyc ("softwood") marker accompanied by tributylphosphate (TBPhos) and larger alkyl-substituted phthalates (DBP thru DPP); apparently reflecting a difference between two different activities (e.g., wood stoves versus waste burning). Wood and synthetics burning-derived FPM component concentrations typically vary within the 2–3 \( \sigma \) range with occasional spikes to 3 or 4 \( \sigma \), apparently due to point sources.

The "urban dust" factor is hypothetical at this point, as it is composed of PM 10 and PM 2.5 density variables accompanied by 2 chemical markers: methyl dehydroabietate (assumed to represent car tire abrasion particles) and tetra phenyl (possibly representing some kind of oil used to treat road surfaces). The correlations between these components are strong enough to predict PM 10 and PM 2.5 densities at all 4 U.S./Mexico border sites with reasonable accuracy from these 2 chemical markers alone. The urban dust factor is potentially of great importance as it is involved in two extreme PM 10 episodes encountered in 8 days of circadian monitoring at 4 border sites, reaching >600 \( \mu g/m^3 \) in Calexico (directly North of Mexicali) on December 1992 and >1000 \( \mu g/m^3 \) in Hidalgo (directly North of Reynosa) in December 1995. Generally attributed to waste combustion by local people interviewed during the Hidalgo event (probably because of the characteristic stale, slightly sewer-like smell), multivariate analysis results clearly establish a separate factor strongly affected by meteorological conditions, e.g., moderate south-east or -west wind in the late afternoon accompanied by low temperatures (e.g., due to the passage of a cold front) followed by windless conditions in the late evening, possibly further affected by low inversion layer height and near-dew point temperature and moisture conditions.

Interestingly, episodes characterized by sudden increases in PM 10 and PM 2.5 particle concentrations, whether diurnal or sporadical, appear to be always accompanied by increases in both vapor phase and particle adsorbate phase VOCs such as xylenes/ethylbenzenes. This may reflect the known mechanistic relationship between VOC levels and particle generation rates.
(Meng et al. 1997). GC/MS analyses of quartz fiber filters obtained during (as well as prior to and after) the exceedingly high PM 10 maximum on December 6th revealed an unusually strong unresolved complex mixture (UCM) hydrocarbon pattern. Other particle adsorbed hydrocarbon compound classes which tend to increase with increasing particle concentrations are: n-alkanes —from gasoline engines by mild thermocracking of engine oil (Rogge et al. 1993 a) and fugitive refinery emissions; PAHs (polycyclic aromatic hydrocarbons); and methyl dehydroabietate —thought to be primarily derived from car tire abrasion (Rogge et al. 1993 b, Fraser et al. 1998).

Urban haze formation under rapidly falling ambient temperature conditions during the evening or early hours of the night is a well known phenomenon that is generally blamed on stagnant air masses trapped under low inversion layers. However, our observations suggest that time, place and severity of the PM 10 episodes in Calexico and Hidalgo may also have been affected by a set of parameters characteristic to the border region, namely: (1) the vicinity of huge urban, aerosolizable dust reservoirs; (2) the proximity of a border river; (3) a multitude of strong anthropogenic PM 2.5 sources (idling cars, industrial emissions and open air burning); and (4) peculiar meteorological conditions (e.g., frequent passage of small fronts near the coast).

Although recent emphasis has been on PM 2.5, the "anthropogenic" lobe of the classic bimodal PM 10 distribution, the particle size data shown in Figure 11c clearly illustrate the need to study the entire PM 10 range for understanding the observed severe pollution episodes. Apparently, the mechanisms underlying these events defy easy categorization. A possible explanation for the highly correlated physical behavior and chemical compositions of both small and large particles is rapid particle growth due to nucleation phenomena near the dew point, as the relatively humid air cools during the evening hours.

Especially for persons with compromised cardiovascular and pulmonary functions these types of extreme PM 10 episodes, which tend to be short enough to be only detectable by time-resolved measurements, could pose a health risk. Potential remedial and/or preventative measures include spraying or paving of unpaved streets and filtering of indoor air.

V - CONCLUSIONS

- Curie-point desorption GC/MS of PM 10 samples collected on quartz fiber filters is a promising, fast alternative approach to solvent extraction based field screening methods for FPM-type air pollutants which requires only microgram amounts of organic particulate matter, usually equivalent to less than 1 m³ of ambient air.

- Curie-point Py-GC/MS analysis of PM 10 samples collected at 2 hourly intervals and of the corresponding meteorological information and particle concentration followed by multivariate data analysis provides a non-supervised, exploratory method for preliminary source detection and apportionment.

- Time resolved analysis makes it possible to distinguish car emission sources from other combustion sources such as wood burning or food preparation. It also can separate and elucidate source rhythms as diurnal circadian (car traffic, food preparation), irregular (wood burning) or incidental (urban dust).

- The multipoint sampling and analysis technique enables mapping of pollutant concentrations thereby integrating receptor based and source monitoring models.

- Combining organic FPM analysis with meteorological measurements and particle concentration using PCA provides essential information regarding the origin and behavior of FPM type air pollutants.

- The main three sources of organic FPM components at the Hidalgo and Brownsville international bridges are: (1) automotive emissions ("mobile sources");
(2) burning of lignocellulosics ("wood") and synthetics; and (3) urban dust.

Health threats may be posed by recurrent high urban dust episodes and by the presence of high levels of alkyl phthalates and tributyl phosphate in wood smoke particles.

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The research reported here was supported by the Southwest Center for Environmental Research and Policy (SCERP; Project No.: AQ95-10).

VI - REFERENCES


Table 1. Major components of semivolatile organic compounds desorbed from particulates collected along the U.S./Mexican border and identified using GC/MS.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Formula</th>
<th>M.W.</th>
<th>Major Ions (Intensity, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Acetyl-2,6-dimethoxyphenol</td>
<td>C_{10}H_{12}O_{4}</td>
<td>196</td>
<td>181(100); 196(42); 43(28); 153(15)</td>
</tr>
<tr>
<td>4-Acetyl-2-methoxyphenol</td>
<td>C_{9}H_{10}O_{3}</td>
<td>166</td>
<td>151(100); 166(46); 123(22); 43(16)</td>
</tr>
<tr>
<td>Alkanes</td>
<td>C_{n}H_{2n+2}</td>
<td>14n+2</td>
<td>43, 57, 71, 85, ...</td>
</tr>
<tr>
<td>Alkenes</td>
<td>C_{n}H_{2n}</td>
<td>14n</td>
<td>41, 55, 69, 83, ...</td>
</tr>
<tr>
<td>Benz(a)anthracene</td>
<td>C_{16}H_{12}</td>
<td>228</td>
<td>228(100); 226(20); 229(20); 43(18)</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>C_{20}H_{12}</td>
<td>252</td>
<td>252(100); 126(23); 253(21); 250(16)</td>
</tr>
<tr>
<td>Benzo(ghi)perylene</td>
<td>C_{22}H_{12}</td>
<td>276</td>
<td>276(100); 138(37); 137(28); 277(25)</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>C_{20}H_{12}</td>
<td>252</td>
<td>252(100); 253(23); 126(22); 250(21)</td>
</tr>
<tr>
<td>Chrysene</td>
<td>C_{18}H_{12}</td>
<td>228</td>
<td>228(100); 226(21); 229(20); 114(15)</td>
</tr>
<tr>
<td>Dibutyl phthalate (DBP)</td>
<td>C_{16}H_{22}O_{4}</td>
<td>278</td>
<td>149(100); 57(18); 86(18); 223(17)</td>
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<tr>
<td>Diethyl phthalate (DEP)</td>
<td>C_{12}H_{14}O_{4}</td>
<td>222</td>
<td>149(100); 177(28); 150(13); 176(9)</td>
</tr>
<tr>
<td>Dipentyl phthalate (DPP)</td>
<td>C_{18}H_{22}O_{4}</td>
<td>306</td>
<td>149(100); 150(10); 237(6); 219(3)</td>
</tr>
<tr>
<td>Di-(2-ethylhexyl) phthalate (DEHP)</td>
<td>C_{20}H_{38}O_{4}</td>
<td>390</td>
<td>149(100); 57(32); 167(29); 279(7)</td>
</tr>
<tr>
<td>Fluoranthenic</td>
<td>C_{18}H_{10}</td>
<td>202</td>
<td>202(100); 203(19); 200(17); 101(14)</td>
</tr>
<tr>
<td>17α(H),21β(H)-Hopane</td>
<td>C_{26}H_{50}</td>
<td>398</td>
<td>191(100); 81(45); 95(44); 177(41)</td>
</tr>
<tr>
<td>17α(H),21β(H)-Hopane</td>
<td>C_{26}H_{52}</td>
<td>412</td>
<td>191(100); 95(42); 81(38); 69(33)</td>
</tr>
<tr>
<td>4-Hydroxy-3,5-dimethoxybenzaldehyde</td>
<td>C_{9}H_{10}O_{4}</td>
<td>182</td>
<td>182(100); 181(46); 39(23); 167(15)</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>C_{29}H_{12}</td>
<td>276</td>
<td>276(100); 138(28); 274(19); 137(18)</td>
</tr>
<tr>
<td>Methyl dehydroabietate</td>
<td>C_{29}H_{30}O_{2}</td>
<td>314</td>
<td>239(100); 240(22); 289(19); 314(14)</td>
</tr>
<tr>
<td>Pyrene</td>
<td>C_{16}H_{10}</td>
<td>202</td>
<td>202(100); 203(26); 200(21); 101(21)</td>
</tr>
<tr>
<td>Quinoline</td>
<td>C_{9}H_{7}N</td>
<td>129</td>
<td>129(100); 102(21); 51(17); 128(16)</td>
</tr>
<tr>
<td>Retene</td>
<td>C_{15}H_{18}</td>
<td>234</td>
<td>219(100); 234(83); 205(23); 189(19)</td>
</tr>
<tr>
<td>Tetrphenylene</td>
<td>C_{28}H_{18}</td>
<td>390</td>
<td>306(100); 307(25); 229(23); 228(20)</td>
</tr>
<tr>
<td>Tributyl phosphate (TBPhos)</td>
<td>C_{15}H_{27}O_{4}P</td>
<td>286</td>
<td>99(100); 155(32); 211(30); 57(15)</td>
</tr>
<tr>
<td>4-Vinyl-2,6-dimethoxyphenol</td>
<td>C_{10}H_{12}O_{3}</td>
<td>180</td>
<td>165(100); 180(70);</td>
</tr>
</tbody>
</table>
Table 2. List of variables used for combined Hidalgo and Brownsville data matrix. For identity of chemical markers: see Table 1.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ambient temperature (°C)</td>
<td>13</td>
<td>m/z 149, DPP</td>
</tr>
<tr>
<td>2</td>
<td>ambient pressure (mfar)</td>
<td>14</td>
<td>m/z 149, DEP</td>
</tr>
<tr>
<td>3</td>
<td>total wind speed (m/s)</td>
<td>15</td>
<td>m/z 151, 4-acetyl-2-methoxyphenol</td>
</tr>
<tr>
<td>4</td>
<td>N/S wind vector (m/s)</td>
<td>16</td>
<td>m/z 153, 4-acetyl-2,6-dimethoxyphenol</td>
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<tr>
<td>5</td>
<td>E/W wind vector (m/s)</td>
<td>17</td>
<td>m/z 165, 4-vinyl-2,6-dimethoxyphenol</td>
</tr>
<tr>
<td>6</td>
<td>total PM 10 (µg/m³)</td>
<td>18</td>
<td>m/z 191a, hopane [C₉H₅₀]</td>
</tr>
<tr>
<td>7</td>
<td>PM 2.5 (µg/m³)</td>
<td>19</td>
<td>m/z 191b, hopane [C₉H₅₂]</td>
</tr>
<tr>
<td>8</td>
<td>PM 2.5 - PM 10 (µg/m³)</td>
<td>20</td>
<td>m/z 202a, fluoranthene</td>
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<tr>
<td>9</td>
<td>Σ m/z 83 -85, alkanes/alkenes</td>
<td>21</td>
<td>m/z 202b, pyrene</td>
</tr>
<tr>
<td>10</td>
<td>m/z 99, tributylphosphate</td>
<td>22</td>
<td>m/z 219, retene</td>
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<td>11</td>
<td>m/z 129, quinoline</td>
<td>23</td>
<td>m/z 239, methyl dehydroabietate</td>
</tr>
<tr>
<td>12</td>
<td>m/z 149, DBP</td>
<td>24</td>
<td>m/z 306, tetraphenylene</td>
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Table 3. Eigenvalues of principal components (after Varimax-rotation) for combined Brownsville and Hidalgo data set.

<table>
<thead>
<tr>
<th>Factor Number</th>
<th>Eigenvalue</th>
<th>Individual Percent</th>
<th>Cumulative Percent</th>
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<tr>
<td>1</td>
<td>4.567</td>
<td>18.27</td>
<td>18.27</td>
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<tr>
<td>2</td>
<td>3.271</td>
<td>13.08</td>
<td>31.35</td>
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<tr>
<td>3</td>
<td>3.243</td>
<td>12.97</td>
<td>44.32</td>
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<tr>
<td>4</td>
<td>2.485</td>
<td>9.94</td>
<td>54.26</td>
</tr>
<tr>
<td>5</td>
<td>3.852</td>
<td>15.41</td>
<td>69.67</td>
</tr>
<tr>
<td>6</td>
<td>2.162</td>
<td>8.65</td>
<td>78.32</td>
</tr>
<tr>
<td>7</td>
<td>1.033</td>
<td>4.13</td>
<td>82.45</td>
</tr>
<tr>
<td>8</td>
<td>1.719</td>
<td>6.88</td>
<td>89.33</td>
</tr>
<tr>
<td>9</td>
<td>0.711</td>
<td>2.84</td>
<td>92.17</td>
</tr>
<tr>
<td>10</td>
<td>0.578</td>
<td>2.31</td>
<td>94.48</td>
</tr>
<tr>
<td>11</td>
<td>0.381</td>
<td>1.52</td>
<td>96.01</td>
</tr>
<tr>
<td>12</td>
<td>0.274</td>
<td>1.09</td>
<td>97.10</td>
</tr>
<tr>
<td>13</td>
<td>0.175</td>
<td>0.70</td>
<td>97.80</td>
</tr>
<tr>
<td>14</td>
<td>0.152</td>
<td>0.61</td>
<td>98.41</td>
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<tr>
<td>15</td>
<td>0.138</td>
<td>0.55</td>
<td>98.96</td>
</tr>
<tr>
<td>16</td>
<td>0.073</td>
<td>0.29</td>
<td>99.26</td>
</tr>
<tr>
<td>17</td>
<td>0.052</td>
<td>0.21</td>
<td>99.46</td>
</tr>
<tr>
<td>18</td>
<td>0.043</td>
<td>0.17</td>
<td>99.64</td>
</tr>
<tr>
<td>19</td>
<td>0.037</td>
<td>0.15</td>
<td>99.79</td>
</tr>
<tr>
<td>20</td>
<td>0.016</td>
<td>0.06</td>
<td>99.85</td>
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<tr>
<td>21</td>
<td>0.014</td>
<td>0.06</td>
<td>99.91</td>
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<tr>
<td>22</td>
<td>0.011</td>
<td>0.05</td>
<td>99.95</td>
</tr>
<tr>
<td>23</td>
<td>0.007</td>
<td>0.03</td>
<td>99.98</td>
</tr>
<tr>
<td>24</td>
<td>0.005</td>
<td>0.02</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Table 4. Varimax-rotated principal component (PC) loadings for combined Brownsville and Hidalgo data set

<table>
<thead>
<tr>
<th>Variables</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp, °C</td>
<td>-0.047</td>
<td>-0.320</td>
<td>0.193</td>
<td>-0.852</td>
<td>0.074</td>
</tr>
<tr>
<td>Press, mbar</td>
<td>0.181</td>
<td>-0.071</td>
<td>-0.238</td>
<td>0.920</td>
<td>-0.022</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>0.183</td>
<td>-0.096</td>
<td>-0.063</td>
<td>-0.097</td>
<td>-0.083</td>
</tr>
<tr>
<td>N/S wind vector</td>
<td>0.007</td>
<td>0.091</td>
<td>0.087</td>
<td>0.548</td>
<td>0.086</td>
</tr>
<tr>
<td>E/W wind vector</td>
<td>0.069</td>
<td>-0.062</td>
<td>0.118</td>
<td>-0.559</td>
<td>0.127</td>
</tr>
<tr>
<td>PM 10, :g/m3</td>
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<td>-0.028</td>
<td>0.086</td>
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<tr>
<td>PM 2.5, :g/m3</td>
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<td>0.159</td>
<td>-0.156</td>
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<tr>
<td>dPM, :g/m3</td>
<td>-0.354</td>
<td>-0.162</td>
<td>-0.090</td>
<td>0.115</td>
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<tr>
<td>m/z 83 - 85</td>
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<td>0.067</td>
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</tr>
<tr>
<td>m/z 99</td>
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<td>0.088</td>
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<tr>
<td>m/z 129</td>
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<tr>
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<td>0.106</td>
<td>-0.899</td>
<td>0.265</td>
<td>-0.171</td>
</tr>
<tr>
<td>m/z 149 (C4)</td>
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<tr>
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<tr>
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</table>
Figure 1. PM 10 inlet type used: (a) schematic cross section; and (b) photograph of a stand-alone version (used with highly mobile, van-based monitoring station). For mobile laboratory use, see Figure 2.
Figure 2. The mobile laboratory module on a pick-up truck at the Hidalgo/Reynosa International Bridge site. Note the PM 10 sampling inlet on the roof.
Figure 3. Depiction of PM 10 sampling on quartz fiber filter and subsequent sample preparation steps. Note special procedure for on-line methylation with TMAH (steps 2a and 2b).
Figure 4. Detailed configuration of special, Curie-point type thermal desorption unit used for flash desorption of (semi)volatile organic compounds into the GC/MS system. The same unit can be used to pyrolyze nonvolatile particle constituents by employing Pyrofoils with higher Curie-point temperatures.
Figure 5. Schematic overview of entire TD-GC/MS system and the type of data produced.
Figure 6. Comparison of chemical marker profiles obtained by (a) SX-GC/MS and (b) TD-GC/MS of the same sample of particulates collected on a quartz fiber filter. Note semiquantitative correspondence between both profiles (each of which is composed of a collage of several selected ion chromatograms).
Figure 7. Typical fatty acid methyl ester (FAME) profile obtained by the on-line, pyrolytic methylation technique illustrated in Figure 4. Note presence of long-chain fatty acids, characteristic of certain types of microorganisms. Peak designation: number before the colon refers to the number of carbon atoms of fatty acids and the number after the colon to the number of double bonds.
Figure 8. Comparison of VOC profiles obtained by Curie-point desorption of miniature, active charcoal traps using: (a) a regular length (15 m) capillary GC column; and (b) a short (2 m) column. Note approx. 10 times faster elution of homologous (alkyl) naphthalene series which can still be readily quantitated thanks to combined use of GC and MS.
Figure 9. Example of total ion chromatogram (TIC) and selected ion chromatograms (SICs) obtained from a typical PM 10 sample obtained in Nogales and showing several chemical marker compounds, e.g., associated with various combustion sources. Also note characteristic hump of unresolved hydrocarbons, known as UCM (unresolved complex matter) in TIC and m/z 83-85 profiles.
Study (1696/1861) is being performed in Juarez/El Paso. This city has one of the largest populations in its U.S. metropolitan area. The characteristic occurrence of twin cities with the Mexican border area is illustrated in this map. Note the sampling sites where PM10 sampling has been performed for TD.
Physical characterization data recorded at the international bridge in Hidalgo, Texas during a 48 hour monitoring period in December 1995: (a) ambient pressure and temperature profiles; (b) wind speed and direction data (N/S and E/W vectors, plus total speed); and (c) PM 10 and PM 2.5 density profiles (calculated from 8-channel particle size distribution data). Note also the dPM trace showing the difference between the PM 10 and PM 2.5 traces, i.e., the contributions from larger particles. Note extremely high PM 10 and PM 2.5 levels (> 1000 µg/m³) observed in the evening of December 6, 1995.
Figure 12. Same as Figure 11 but recorded at the International Bridge in Brownsville, Texas.
Figure 13. Quartz-fiber filter halves representing the twelve hour period between noon and midnight on December 6th 1995 at the Hidalgo site. Note the dramatically increased particle concentrations after 8 pm.
Figure 14. Use of beta attenuation monitor particle density measurements to calibrate particle density values calculated from multichannel particle count data at the Calexico site in December 1992. The December 1995 Hidalgo data of the extreme PM 10 episode shown in Figure 11 used the same calibration parameters.
Figure 15. Examples of several bivariate correlation trends between selected chemical and physical parameters. Note the apparent split in the PM 2.5/PM 10 correlation apparently indicating the presence of multiple particle sources.
Figure 16. Time-resolved plot of four Varimax-rotated factor scores for the Hidalgo data set, corresponding to the factor loadings listed in Table 4. This "skyline" plot format is helpful in correlating the chemical and physical properties of air particulate matter with specific anthropogenic sources and/or activities as well as with meteorological parameters (compare with Figure 11). All interpretations (between quotation marks) are tentative until confirmed by area-specific source sampling. Since factor scores are standardized a score of "3" can be regarded as a "3 σ event" in statistical terms, and so on. Note the characteristic traffic peak pattern of F5 events, the transient event character of major F1 and F2 events and the broader nature of the main F2 event. Further compare with Figures 18 and 19.
Figure 17. As Figure 16, but for Brownsville data set. Compare with Figures 12, 18 and 19 and with Table 4.
Figure 18. Two-dimensional projection of loadings and scores for the combined (Hidalgo and Brownsville) data set in principal component space onto a plane defined by Varimax-rotated components 1 and 5, as described in Table 4 (loadings) and Figures 16-17 skyline plots (scores). Only loadings >0.2 shown. Individual variables identified in Table 2. Scores of Brownsville filter samples 1-33 (black squares) and Hidalgo filter samples 34-58 (black triangles) shown if >1.0. Large circle corresponds to hypothetical loading values of 1.0 and standardized score values of 5.0. Grey disk in the center covers all loadings ≤0.2 and scores ≤1.0 (too closely clustered to show individually). Note that both Hidalgo and Brownsville filter samples participate in defining the "urban dust" and "automotive emissions" sources. Further note that m/z 83-85 loadings (representing the characteristic UCM hump shown in Figure 9) fall between the "urban dust" and "automotive emissions" source components, apparently since the UCM participates in both events.
Figure 19. Combined two-dimensional loading and score plot for Varimax-rotated factors 2 (F2 “waste burning”) and 3 (F3 “biomass burning”). See general explanations in the caption of Figure 18.