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$PM_{2.5}$ Source Apportionment Applying Material Balance and Receptor Models in the MAMC

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1. Introduction

The expansion of urban areas and their surroundings suburbs has been increased in the last decades. Many of these cities, particularly in the developing world, experience an uncontrolled growth and face unprecedented severe air quality problems, due to the high demand of energy, industrial activity and transportation (Molina et al., 2010). Policy makers have the challenge to plan and govern, having as one of their priorities the reduction of air pollution with the aim to protect the health's population, providing at the same time infrastructure and services.

Air quality models or source models are important tools in the environmental assessment since they estimate receptor concentrations from source emissions and meteorological measurements. One of the problems when dispersion models application is considered is that they use estimates of pollutant emissions rates and often rely on meteorological measurements from distant airports and emission rate estimates which stand little resemblance to those applicable to the area under study. As a result of this lack of data, dispersion models cannot be applied in many places or their results have large uncertainties.

On the other hand, receptor models include a range of multivariate analysis methods that use ambient air measurements to infer the source types, locations, and contributions that affect ambient pollutant concentrations. Receptor models use the environmental concentration of the studied pollutants, as well as the composition of the chemical compounds emitted by the different sources to determine the source apportionment (Watson et. al., 2002a). These models are used also to evaluate the efficiency of specific control strategies associated with local programs to improve the air quality and also to estimate the emission inventory uncertainty, since they correlate the pollutants with their sources of emission. This article presents the importance to determine the main sources of $PM_{2.5}$ through the use of receptor models. As a case study, the Principal Component Analysis (PCA), the UNMIX and the Chemical Mass Balance (CMB) models were applied for the source reconciliation of $PM_{2.5}$ in the Metropolitan Area of Mexico City (MAMC). The results obtained by the three models are compared and discussed showing the advantages of the different models.

2. Airborne particles

Suspended particles in the atmosphere can be originated from natural sources, such as wind-driven erosion dust, sea spray, and volcanoes, or from anthropogenic activities such as combustion of fuels (by vehicles, food cooking, wood burning or industries). Airborne PM is composed of inorganic salts, organic material, crustal elements and trace metals and possess a range of morphological, physical, chemical and thermodynamic properties. Airborne particles can change in the atmosphere in size and/or composition through condensation of vapor species or by evaporation, by coagulating with other particles, by chemical reaction, or by activation in the presence of supersaturated water vapor to become cloud and fog droplets (Raes et al., 2000). When particles are emitted directly they are known as primary aerosols, but if particles are formed in the atmosphere as a consequence of physical or chemical interactions among gases, particles and/or water vapor they are called secondary aerosols. Many organic secondary aerosols are formed in the atmosphere by incomplete combustion or by photochemical reactions. The most common inorganic secondary aerosols are the ammonium nitrate and sulfate originated by the reactions among dissolved sulfuric and nitric acids (formed also in the atmosphere by the reaction between water and sulfur oxides and nitrogen oxides respectively, with ammonia gas).

An important characteristic of atmospheric particles is their size distribution, as it strongly affects particle behaviour, may determine their fate in atmospheric systems as well as their deposition in the human respiratory tract, and determines the equipment to be used for sampling. As atmospheric particles are not spherical and have a range of densities, the aerodynamic diameter (diameter of a spherical particle with an equal gravitational settling velocity but a material density diameter of 1 gcm^{-3}) is used to define their size (Mugica & Ortiz, 2006). With this in mind, PM_{10}, $PM_{2.5}$ and PM_1 refer to particles with aerodynamic diameter less or equal to 10 μm, 2.5 μm or 1 μm respectively. They are known also as respirable, fine and ultrafine particles, respectively.

Crustal species from mineral dust, such as Si, Fe, Al, Ca, K, and Mg, are often present in large quantities in the coarse fraction of PM (particles with aerodynamic diameter larger than 2.5 μm but smaller than 10μm). Usually organic aerosols can account for 50% or more of the fine PM, and inorganic secondary aerosols are an important fraction of fine particles.

2.1 Health adverse effects of PM

It has been well established that exposure to PM can cause cardiovascular and respiratory problems, and inclusive increase the premature mortality. For that reason the improvement of human health is the priority objective of air quality programs (McKinley, 2003). Fine and ultrafine particles are poorly captured by the lung macrophages and are able to introduce into the epithelia and the interstitial tissue. Then, the possibility of natural cleaning of lungs is diminished, with an increasing of lung toxicity (Schwartz et. al., 1996). It was observed also, than mortality rate is higher in polluted cities, associating the pollution by fine particles with lung cancer (Dockery et. al., 1993; Maynard & Maynard, 2002), as well as with cardiac and respiratory illness (Samet el al., 2000).Pope et al. (2002) reported tan an increase of 10 μgm^{-3} in the average concentrations of $PM_{2.5}$ implicates the increase of lung cancer and cardiorespiratory risk diseases in 8 and 6% respectively.

The precise chemical and physical properties and toxicological mechanisms by which PM causes adverse health effects are still uncertain. Significant differences exist in the chemical composition and size distribution of PM based on the wide range of sources, meteorological conditions, atmospheric chemistry, diurnal and seasonal factors. PM aerodynamic size is a relevant element when studying PM toxicity due to its variable ability to penetrate the respiratory system; fine particles can reach the deep regions of the lungs, whereas coarse PM may be deposited early within the nasal-pharyngeal passages of the airways. Fine PM potentially may owe the type and intensity of the toxic response to organic compounds, metals and other reactive chemical compounds, since several of those species can promote oxidative stress through the generation of reactive oxygen species (ROS) (Tao et al, 2003; De Vizcaya et al., 2006). ROS can also damage cellular proteins, lipid, membranes, and DNA and PM exposure is also linked to inflammation through the generation of ROS, particularly those PM derived from combustion of fossil fuels (Nel, 2005).

2.2 Adverse effects of PM in the environment

Fine particles and some pollutant gases scatter and absorb light reducing the visibility and generating a haze that has negative effects on the visibility. Visibility can be defined as the maximum distance at which the outline of the farthest target can be recognized against a horizon background (Horvath, 1981). Although absorbing particles remove light transmitted from the target and make it appear darker, they do not scatter much light into the sight path, and they generally have a lower effect on contrast reduction than light-scattering particles. The particles that are most efficient at scattering light are roughly the same size as the wavelength of visible light (about 0.5 μm) (Horvath, 1981).The correlation between fine and ultrafine particles with the decreasing of visibility has been measured in some studies showing that those PM are responsible of the light scattering. (Watson, 2002b).

Other effects of PM and pollutants have been found in materials, damage forests and crops, ecosystems, due to the abrasion, deposition, direct and indirect chemical attack and electrochemical corrosion (Davis & Cornwell, 1998). In addition, visible haze change the earth's radiation balance

3. Receptor models

Receptor models infer contributions from different source types using multivariate measurements taken at one or more receptor locations. Receptor models use ambient concentrations and the abundances of chemical components in source emissions to quantify source contributions. They are based on the same scientific principles as source models, but they are explanatory rather than predictive of source contributions. (Watson et al, 2002a).While source models need spatial and temporal resolution and accurate emissions rates, receptor models need only a seasonal or annual average, area wide inventory to identify potential source categories. Contributions are quantified from chemically distinct source-types rather than from individual emitters. Sources with similar chemical and physical properties cannot be distinguished from each other (e.g., it is quite difficult to differentiate the diesel exhaust emissions of heavy, cars, trucks, stationary generators and

engines or off-road equipment, thus they can be grouped in one diesel exhaust category). Nevertheless, with appropriate chemical analysis of organic and inorganic compounds of detailed profiles, more chemical markers from sources could be detected and the separation in sub-categories become possible.

Receptor models are based on the chemical mass balance equation and the main assumption is that composition of PM remains constant and chemical species do not react with each other. The source apportionment is accomplished by solving the mass balance equations expressing the measured ambient elemental concentrations as the sum of products between the source contributions and the elemental abundances in the source emissions, e.g. the source profiles. There are different receptor models which differ in the mathematical approaches that they have to solve the mass balance equations, as well as in the different degrees of knowledge about source profiles they need for source apportionment analysis. Receptor models are not statistics methods, and maybe the misunderstanding partially arises to the fact that much of the receptor modeling mathematics is also used to determine and test statistical associations in other scientific fields (Watson & Chow, 2004).

Among the receptor models, Multiple Linear Regression have been widely used from more than three decades due to they have the advantage to be implemented by many statistical packages; identification of markers is required. The application of Enrichment factor is one of the first methods used to identify presence or absence of anthropogenic sources or processes responsible of the different atmospheric chemical species. Sometimes the reference geological material could be different to the sampling site. Multivariate models based in eigenvector analysis but using different normalization and rotation schemes have also been applied the last two decades; the most important are: Principal component analysis (PCA), Empirical orthogonal functions (EOF) and Factor Analysis (FA).The Positive Matrix Factorization (PMF) model was developed by Paatero & Tapper (1993) as a new approach to factor analysis, where the principal components explaining the variance of the speciated data are extracted and then interpreted as possible sources. The CMB model has been widely used to determine source contribution estimates for PM_{10} and $PM_{2.5}$. This model calculates the source contributions by determining the best combination of source profiles needed to simulate the chemical composition of the ambient data. The model is able to estimate the source reconciliation for every day. Table 1 shows most of the common receptor models used in air quality studies to develop pollution control strategies.

Watson and Chow (2004) specify the following qualities which are desirable in any data base of source and receptor measurements: 1) a full range of chemical species in specified size fractions (for solid-phase pollutants); 2) specification of operating parameters (for source measurements), locations and sampling periods (for source and receptor measurements);3) documentation of sampling and analysis methods; 4) results of quality control activities and quality audits; 5) precision and accuracy estimates for each measurement; 6) data validation summaries and flags; and 7) availability in well-documented computerized formats.

Source and receptor models are complementary rather than competitive. Each has strengths and weaknesses that compensate for the other. Both types of models can and should be used in an air quality source assessment on outdoor and indoor air.

Receptor Model	Description
Enrichment Factors (EF)	The ratios of atmospheric concentrations of elements to a reference element are compared to the same ratios in geological or marine material. Differences are explained in terms of anthropogenic sources. It is more useful for identification of anthropogenic processes than for quantification.
Multiple linear regression (MLR)	Mass of chemical compounds is expressed as the linear sum of regression coefficients. The regression coefficients represent the inverse of the chemical abundance of the marker species in the source emissions. They can easy implemented in statistic packages, but limited to sources with marker species. The product of the regression coefficient and the marker concentration for a specific sample is the tracer solution to the mass balance that yields the source apportionment. Requires large data set.
Eigenvector multivariate models: Principal component analysis(PCA), Empirical orthogonal functions (EOF), Factor Analysis (FA)	Temporal correlations are calculated from a time series of chemical concentrations at one or more locations. These are eigenvector analysis multivariate models which can confirm and identify unrecognized source types. Eigenvectors of this correlation matrix are determined and a subset is rotated to maximize and minimize correlations of each factor with each measured species. The factors are interpreted as source profiles by comparison of factor loadings with source measurements. Source profiles from direct measurements are needed to interpret these eigenvectors. Easy implementation in statistic packages, but limited to sources with marker species. Requires large data set.
UNMIX Form of Factor Analysis	The UNMIX model "unmixes" the concentrations of chemical species measured in the ambient air to identify the contributing sources. Chemical profiles of the sources are not required, but instead are generated internally from the ambient data by UNMIX, using a mathematical formulation based on a form of factor analysis. UNMIX uses "edge detection" in a multidimensional space. The edges represent the samples that characterize the source. It can be run feasibly and easily on some statistical software. Requires large data set.
Positive Matrix Factorization [PMF]	The PMF technique is a form of factor analysis where the underlying co-variability of many variables is described by a smaller set of factors (PM sources) to which the original variables are related. The PMF assumption is that the concentration of specie in a site can be explained by the source matrix and contribution matrix. Both matrixes are obtained by an iterative minimization algorithm. A restriction of no-negativity ensures positive abundances and contributions. The main problem with PCA is that it does not provide a unique solution.
ChemicalMass Balance (CMB)	Ambient chemical concentrations are expressed as the sum of products of species abundances and source contributions and the equations are solved for the source contributions. Ambient concentrations and source profiles are supplied as input.The chemical characterization of the possible emission sources together with an estimation of the uncertainties for the species concentrations, are used as input for the CMB model. The main drawback of this model is that the accuracy of the source apportionment depends on the representativeness of the selected sources for the emission types in the area.

Table 1. Most used Receptor Models in Air Quality Studies

4. Sampling and chemical analysis

The Metropolitan Area of Mexico City (MAMC) is located in an elevated basin surrounded by mountains which do not favour the dispersion of air pollutants, especially during the cold season when frequent thermic inversions are present. The MAMC megacity has nearly 20 million inhabitants, more than 4 million of vehicles and around 35,000 industries. A total of 132 aerosol samples were collected from January 2002 to December 2003, every six days, at the Azcapotzalco Campus of the Metropolitan University, located in an industrial-residential area in the Northern. In addition, other three sites studied in previous campaigns (Chow et al, 2002) were sampled in March 2003 during ten days in order to determine the spatial variation. These sites were: 1) La Merced, located in the downtown with high commercial activity and high traffic activity; 2) Xalostoc, located at the Northeast is an industrial district surrounded for very important avenues with heavy traffic, and 3) Pedregal, is a residential neighborhood located at the Southwest.

Samples were collected onto Teflon and quartz 47 mm filters using PM_{10} and $PM_{2.5}$ Minivol samplers (Airmetrics, Eugene, OR). Teflon-membrane filters (Gelman Scientific, Ann Arbor, MI) with 2 mm pore size collected samples for mass and subsequent elemental analysis, whereas precalcinated Quartz fiber filters (Pallflex, Products Corp.,Putnam, CT) collected samples for water-soluble anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, K^+, NH_4^+), organic carbon and elemental carbon analyses. Filters were equilibrated for two weeks in a relative humidity (25–35%) and temperature (20±0.5°C) controlled environment before gravimetric analysis to minimize particle volatilization. Filters were weighed before and after sampling with a Mettler Toledo (MT-5) microbalance. The balance sensitivity is 0.001 mg. Subsequently, the filters were stored in a freezer until aerosol sampling and chemical analyses. Quartz filters were split into two using plastic scissors: the first part was for ion analysis and the second one for the quantification of organic and elemental carbon.

Soluble ions were extracted ultrasonically (Branson bath, USA) with Milli-Q deionized water during 20 min. Sulfate (SO_4^{2-}), water-soluble ammonium (NH_4^+), nitrate (NO_3^-), water-soluble sodium (Na^+), and potassium (K^+), were quantified by ion chromatography, with a Perkin Elmer-Alltech 550 instrument fitted with a conductivity detector), using specific anion and cation Alltech columns. Organic and elemental carbon was determined by an automated thermal-optical transmittance (TOT) carbon analyzer, Sunset Lab, USA, using method 5040 (NIOSH protocol) (Birch and Cary, 1996).

Inductively Coupled Plasma-Atomic Emission Spectrometry, ICP-AES, from Atom Advantage Thermo Jarrel Ash, was used to analyze the elemental components of the PM collected on the teflon filters. Filters were digested in a microwave oven (OI-Analytical, USA) using high-pressure Teflon digestion vessels with 2 ml of HF, 1 ml HCl and 2 ml HNO_3 (67%). The average filter blank value was used as a background subtraction for each sampled filter. 20 mg extractions of a well-characterized urban dust (SRM 1649a standard reference material NIST), field samples and filter blanks were handled and analyzed under the same procedure as filters with air samples. Quality audits of the sample flow rates were conducted each week of the study period. Data were submitted to three levels of data validation (Watson et al., 2002a.), so intercomparison and performance tests were carried out between CICATA-Altamira and UAM-Azcapotzalco. For the purposes of calculating weight fractions, elements were normalized for oxygenated species as described by Mc Donald (2000).

5. Mass of $PM_{2.5}$

Table 2 shows the basic statistic of the total mass of $PM_{2.5}$ in the four sampling sites. Traditionally (GDF, 2008), Xalostoc is the most polluted site due to the high industrial and vehicular activities. Winds use to blow from Northeast to Southwest, and although Pedregal is the less polluted place by PM, usually exceed the ozone standard.

Site	N	Mean	Max	Min
Azcapotzalco (N)	132 Two whole years 2002-2003	56.9±13.9	93.1	34.5
Merced (Center)	10 March 2003	58.1±19.3	74.2	39.6
Pedregal (Southwest)	10 March 2003	26.8±11.7	47.2	21.6
Xalostoc (Northeast)	10 March 2003	69.2±23.4	105.7	47.2

Table 2. Levels of $PM_{2.5}$ in the MAMC

For CMB model application is necessary to select fitting species, as well as the adequate sources profiles, thus, in this study the strategy was to use the Factor Analysis Models (PCA) and UNMIX to identify the main emission sources and marker elements, and subsequently apply the CMB model with speciated source profiles for a more robust source apportionment.

6. Factor analysis: principal component analysis

PCA model belongs to the category of factor analysis (FA) techniques, i.e. it is a multivariate method used to study the correlations among the measured elemental concentrations at the receptor. With this method, the principal components explaining the variance of the chemical species data, and then they interpreted as possible sources. Assuming a linear relationship between the total mass concentration and the contributions of each specie, PCA factors the data in several steps. First, the chemical composition data are transformed into a dimensionless standardized form

$$Zij = \frac{Cij - Cj}{\sigma j} \tag{1}$$

where i=1, …, n samples; j=1, …, m elements; Cij is the concentration of element j in sample i; and Cj and σj are the arithmetic mean concentration and the standard deviation for element j, respectively. The PCA model is expressed as:

$$Zij = \sum_{k=1}^{p} gik\ hkj \tag{2}$$

where k=1,p sources, and gik and hkj are the factor loadings and the factor scores, respectively. This equation is solved by eigenvector decomposition. Varimax rotation is

often used to redistribute the variance and provide a more interpretable structure to the factors. PCA not provide a unique solution mainly because of its simple approach to factor analysis. Despite this drawback, known as rotational ambiguity, PCA has been applied as a tool for source apportionment in many air quality studies (Karar and Gupta, 2007).

With the chemical data obtained from the chemical analysis of samples, a data base was prepared for the PCA. The ambient data were normalized with media=0 and standard deviation = 1, to reduce the excessive influence of the species with mass. The statistic software SPSS v.12 for windows was used to obtain the number of factors, the mass matrix and the Varimax Rotation. The selection of chemical species was performed to get the better fittings. Maatlab 6.5 package was used to execute the matrix operations. Matlab estimated the not scaled contributions for further lineal regression to convert them in mass unities. Finally the mass balance matrix was cleared to determine the profiles. Model performance was evaluated with the mass percentage and the linear regression coefficient R^2.

PCA resulted to be very useful to determine the potentially contribution of source types, including those with small data set (as was de case of Merced, Pedregal and Xalostoc with only ten samples). The fitting species were: sulfate, ammonium, organic carbon, elemental carbon, aluminum, silicon, sulfur, calcium, and iron. Table 3 shows the factor loadings normalized with the VARIMAX rotation, which maximizes the variances of the squared normalized factor loadings across variables for each factor, thus making the interpretation easier. The final solution of PCA reported three values higher than 1, suggesting three main factors (sources) in the four sites: Vehicular, soil and secondary aerosols. These three sources accumulated more than the 90% of the system variance.

The markers related to the first factor associated with "soil" that explained 34% of variance were Al, Si, Ca, and Fe, which are crustal elements. The markers associated to the second factor "secondary aerosols" are SO_4^{2-} and NH_4^+ related with ammonium sulfate, a secondary aerosol which can be formed in the atmosphere. The third factor "vehicular", is mainly represented by organic and elemental carbon.

	Rotated Component Matrix*		
	Component		
	Soil	**Sec Aerosols**	**Vehicle**
SO4	0.005	0.994	0.042
NH4	-0.123	0.963	0.190
OC	0.412	0.197	0.830
EC	-0.004	0.067	0.964
AL	0.982	-0.094	0.065
SI	0.988	-0.048	0.101
SU	0.000	0.990	0.055
CA	0.984	0.008	0.089
FE	0.964	-0.012	0.173
% Total Variance	34.210	28.541	27.453
% AccumulatedVariance	34.210	62.750	90.204
Extraction Method: Principal Component Analysis.			
Rotation Method: Varimax with Kaiser Normalization.			
* Rotation converged in 4 iterations.			

Table 3. PCA final solution in Azcapotzalco site

Figure 1 shows graphically the apportionment of $PM_{2.5}$ considering the three sources mentioned above, obtained with PCA for the different sites. In all cases the most important contributor to $PM_{2.5}$ was the mobile sources with more than 45% of the total mass, followed by secondary aerosols. Pedregal had the lowest contribution of soil. It is important to highlight that the results from Merced, Pedregal and Xalostoc represent only the apportionment of PM measured in March 2003 that is part of the warm dry season in the MAMC, whereas the measurements in Azcapotzalco were carried out during two years, so these results are the average of measurements done in the dry and rainy seasons.

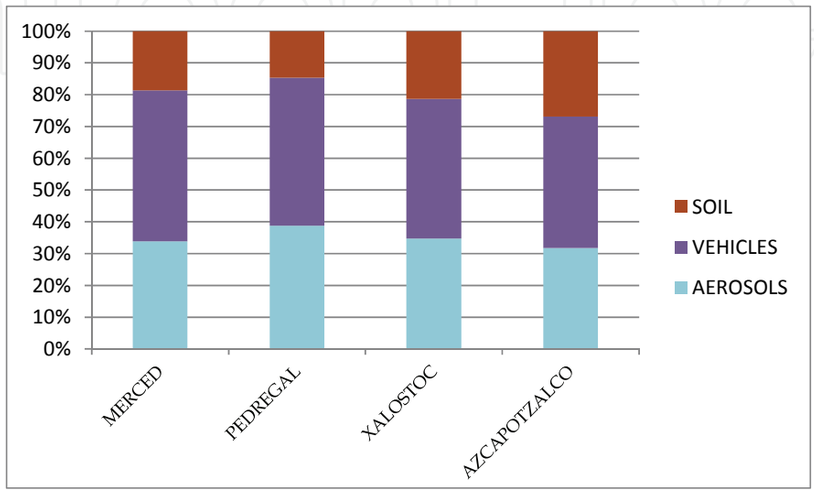

Fig. 1. Source apportionment results from PCA at the four sites

7. UNMIX model

The UNMIX model is a refined multivariate receptor model that uses a new transformation method based on the self-modeling curve resolution technique toderive meaningful factors. UNMIX incorporates user-specified non-negativity constraints and edge-finding algorithms to derive a physically reasonable apportionment of source contributions (Henry, 2001; Poirot et al., 2001). The edges are constant ratios among chemical components that are detected in multi-dimensional space. The edges detected by this model are translated into source profile abundances.This model does not require a previous knowledge about emission sources, although it is necessary a big number of measurements to estimate the different factors, as well as the magnitude of their contributions (Chen et al., 2002; Hellén et al. 2003). UNMIX try to solve the problem of the chemical species mixture with the assumption that the data of each sample has a lineal combination of an unknown number of sources which contributes with an unknown mass concentration to the total mass. Another assumption is that all values are positive (> 0).

UNMIX uses the singular value decomposition (SVD) method to estimate the source number by reducing the dimensionality of data space m to p (Henry, 2001). The UNMIX model can be expressed as

$$Cij = \sum_{i=1}^{p} \left(\sum_{k=1}^{p} Uik\ Dkl \right) Vlj + \varepsilon ij \tag{3}$$

Where *U*, *D*, and *V* are n×p, p×pdiagonal, and p×mmatrices, respectively; and *εij* is the error term consisting of all the variability in *Cij* not accounted for by the first *p* principal components.

Geometrical concepts of self-modeling curve resolution are used to ensure that the results obey (to within error) the nonnegative constraints on source compositions and contributions.The data are then projected to a plane perpendicular to the first axis of p-dimensional space. The edges represent the samples that characterize the source. Such edges in point sets are then used to calculate the vertices, which are used with the matrices decomposed by SVD to obtain the source profiles and contributions. The stand-alone EPA UNMIX version 5.0 was used in this study. For a given selection of species, UNMIX estimates the number of sources, the source compositions, and source contributions to each sample.

UNMIX has been applied to several studies for source apportionment of particulate matter (Chen et al., 2002; Song et al. 2006). One of the first applications was performed by Lewis et al. (2003) in a three years data set in Phoenix, Arizona. The model estimated the source profiles for five source categories (gasoline-vehicles, diesel-vehicles, secondary sulfates, soil and wood burning), and the results were consistent with other study that applied the PMF model. Maykut et al. (2003) compared CMB, PMF and UNMIX in Seattle to determine the $PM_{2.5}$ sources with the coincidence of three sources: wood burning, mobile sources and secondary aerosols. Larsen y Baker (2003) applied UNMIX and PMF models to determine the origin of polycyclic aromatic hydrocarbons in Baltimore.

When UNMIX model was applied to the MAMC samples, the same three sources obtained in the PCA were clearly identified. Table 4 shows the output of the model for Azcapotzalco site, where not only the total mass contributions are displayed, but also the contribution of the most abundant species to the total mass of $PM_{2.5}$.

Calculated Composition (µg·m^{-3}) - Azcapotzalco			
	Soil	**Vehicle**	**Sec. Aerosol**
Total	13.5358 ± 3.3193	21.0042 ± 4.4152	18.8298 ± 3.2149
SO4	0.0014 ± 0.0386	0.0754 ± 0.0186	0.3383 ± 0.0367
NH4	−0.0202 ± 0.0227	0.0555 ± 0.0093	0.1457 ± 0.0136
OC	0.2382 ± 0.0345	0.3856 ± 0.0279	0.2075 ± 0.0271
EC	0.0704 ± 0.0229	0.2492 ± 0.0118	0.0861 ± 0.0130
Si	0.1110 ± 0.0229	0.0087 ± 0.0049	0.0072 ± 0.0049
S	0.0006 ± 0.0149	0.0314 ± 0.0071	0.1296 ± 0.0140
Ca	0.0495 ± 0.0106	0.0014 ± 0.0022	0.0033 ± 0.0020
Fe	0.0354 ± 0.0065	0.0062 ± 0.0018	0.0044 ± 0.0019
Br	0.0001 ± 0.0001	0.0007 ± 0.0001	0.0003 ± 0.0001

Table 4. Output of UNMIX model for Azcapotzalco site.

Figure 2 shows the contribution of the three mentioned sources to the total mass of $PM_{2.5}$ at the three sites. It is possible to appreciate some difference of the apportionment yield by PCA. UNMIX apportioned a higher quantity due to mobile sources than PCA.

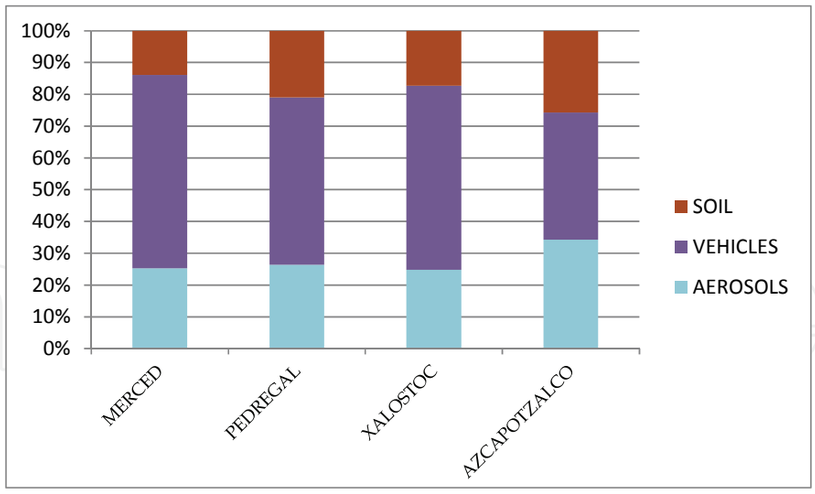

Fig. 2. Source apportionment results from UNMIX at the four sites

8. Chemical Mass Balance receptor model (CMB)

The CMB model is similar to a tracer model, in which a specific compound, that is associated with a particular type of source, is used to identify and quantify the contributions of each source. The model uses the complete model of chemical emissions of a category of specific source to determine its contribution. For the application of the CMB model is necessary to have the databases of the ambient and the source emission profiles. The first one is obtained by collecting samples of ambient air at different locations with the purpose of obtaining information of the population that is investigated. When taking the samples it is expected that they are representative and reflect the properties of the site. On the other hand, source profiles are obtained directly inside the source or as near as possible. The quality of the data will depend on the number of taken samples, used devices, the place and time of the sampling. Equation 4 is the fundamental base of the receptor model, this expresses the relationship between the concentrations of the chemical species measured in the receptor with those emitted in the source.

$$Ci = \sum_{j=1}^{p} Fij \cdot Sj \tag{4}$$

Where
Ci = Ambient concentration of the species "i" measured in the receptor site
p = Number of sources that contribute j = 1, 2,...j
Fij = Fraction of the emissions of the species "i" starting from the source "j"
Sj = Impact to the receptor (calculated contribution) of the source "j"
These equations are solved for the source contributions. Several different solution methods have been applied, but the effective variance least squares estimation method is most commonly used because it incorporates precision estimates for all of the input data into the solution and propagates these errors to the model outputs
The CMB model provided values for several performance measures to evaluate the solution. These measured values included chi-square, the weighted sum of the squared differences between calculated and measured fitting species concentrations divided by the effective

variance and degrees of freedom (ideally chi-square would be zero, but values up to 4 are acceptable). R^2 is the fraction of the variance in the receptor concentrations. R^2 ranges from 0 to 1, when R^2 is less than 0.8 the source contribution estimated did not explain the observations clearly with the fitting source profiles. The calculated mass should be in the range of 100 ± 20 (Watson et al., 1991).

The chemical mass balance model, CMB, which is based upon regression analysis of PM chemical composition, is the fundamental receptor model to find the most appropriate combination of source apportionment. This model has been used in other countries (Chow and Watson, 2002) with the aim to establish control measurements for the main PM contributors.

In this study, each of the daily ambient concentrations of $PM_{2.5}$ and elemental components were submitted as input to the CMB model (Henry, 1997). The source profiles for fugitive dust (Vega et al., 2001), food cooking (Mugica et al., 2001) and combustion source profiles developed for Mexico City (Mugica et al., 2008) were used also as input. The most common inorganic components were included as fitting species in the CMB model as well as organic and elemental carbon (OC and EC). In order to account for secondary aerosol contributions to $PM_{2.5}$, ammonium sulfate, and ammonium nitrate profiles were introduced in the analysis. Each result was evaluated by using the regression statistical parameters available for each CMB output.

CMB model could identify six different sources: soil, gasoline vehicles exhaust, diesel vehicles exhaust, food cooking, ammonium sulfate and ammonium nitrate. This means that CMB could separate two different types of vehicles (e.g. those which use gasoline and those that use diesel), as well as the two types of inorganic secondary aerosols. Table 5 displays the average of the statistical parameters of the model in the $PM_{2.5}$ source reconciliation in the four sites. In general, the parameters of R^2, Chi^2 and percentage of mass were in the acceptable interval. The values of R^2 fluctuated between 0.92 and 0.96. Likewise, the values of Chi^2 were smaller than 4. The percentages of mass calculated when applying the model varied from 88.1 to 104.5, with an average of 93.5%.

Site	R^2	CHi^2	%Mass	Meas. Conc. [µgm-3]	Calc. Conc. [µgm-3]
Azcapotzalco	0.95	0.95	95.7	56.92	54.17
Merced	0.96	2.34	94.3	51.25	48.04
Pedregal	0.96	3.49	94.6	26.32	25.74
Xalostoc	0.97	2.86	91.6	68.32	70.74

Table 5. Average statistical parameters of the CMB model applied to $PM_{2.5}$

The estimated contributions in μgm^{-3} by CMB model vary considerably from one day to another in every site, although in all the cases the major emission sources were the vehicles (sum of diesel plus gasoline exhaust) with contributions between 50 and 66%, followed by aerosols (ammonium sulfate plus ammonium nitrate) and soil (Figure 3).

Figure 4 shows the source contribution of the six sources separated by CMB model in some selected samples of the Azcapotzalco site. In this graphic the separation between gasoline exhaust (with around 28% of the total of $PM_{2.5}$) and diesel exhaust (with 26%) is visible. The new source due to food cooking was also identified with contributions up to 10%, and it was possible to detect that ammonium sulfate concentration is more than four times greater than ammonium nitrate.

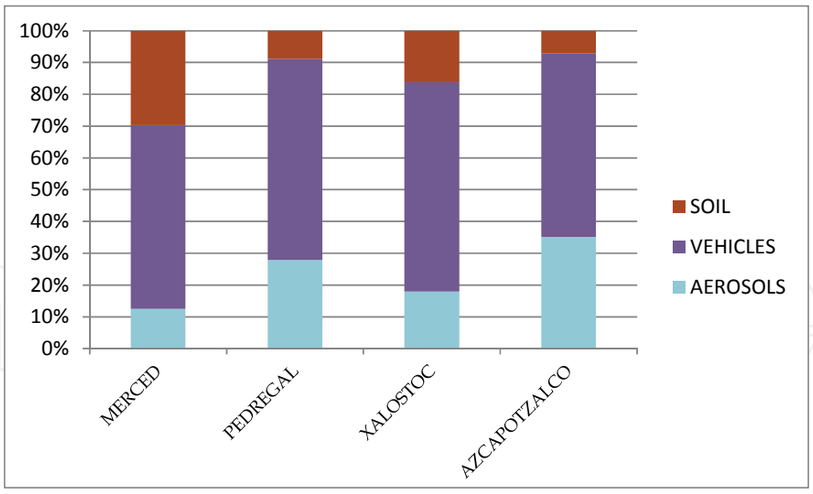

Fig. 3. Source apportionment from CMB at the four sites.

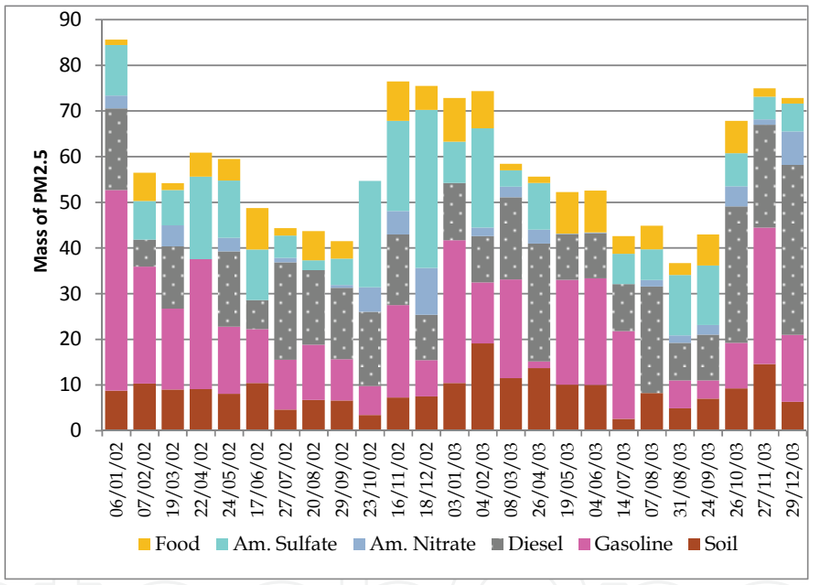

Fig. 4. Source apportionment of $PM_{2.5}$ (μgm^{-3}) in Azcapotzalco

Mann-Whitney U test was used to determine differences among the results obtained for the three models. The findings showed that the contributions of soil, vehicles and secondary aerosols estimated by the three models are statistically equivalent, with ($p > 0.05$). CMB fully apportions receptor concentrations to chemically distinct source-types depending upon the source profile database, while UNMIX and PMF internally generate source profiles from the ambient data.

9. Conclusion

In this paper, the principles of different receptor models were revised and the performances of CMB, PMF and PCA were evaluated in their application to $PM_{2.5}$ samples from different sites of the MAMC. The use of several types of models helps to identify and quantify model

inaccuracies and focus further investigation on the areas of greatest uncertainty. PCA and UNMIX apportioned one single source of mobile sources, but the CMB model was able to distinguish between the two main sources of mobile sources (gasoline and diesel exhaust) in the four sites. In addition CMB could separate the two different types of secondary aerosols. Thus, in this study was demonstrated the capability of CMB model to better apportion on PM mass. Nevertheless the use of PCA and UNMIX was fundamental to identify the main sources as well as the marker elements which were further used during the CMB application as fitting species. The use of three models improve the source reconciliation and allows a better knowledge of the suspended $PM_{2.5}$ in the MAMC.

10. Acknowledgements

The authors wish to express their thanks for the chemical analysis to the Applied Chemistry laboratories at the Metropolitan University-Azcapotzalco, and CICATA/IPN. V. Mugica and J. Aguilar gratefully acknowledge the SNI for the distinction of her membership and the stipend received.

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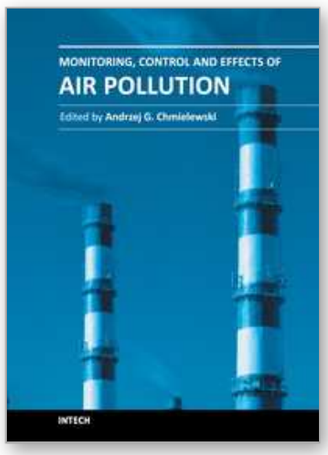

Monitoring, Control and Effects of Air Pollution

Edited by Prof. Andrzej G. Chmielewski

ISBN 978-953-307-526-6
Hard cover, 254 pages
Publisher InTech
Published online 23, August, 2011
Published in print edition August, 2011

The book addresses the subjects related to the selected aspects of pollutants emission, monitoring and their effects. The most of recent publications concentrated on the review of the pollutants emissions from industry, especially power sector. In this one emissions from opencast mining and transport are addressed as well. Beside of SOx and NOx emissions, small particles and other pollutants (e.g. VOC, ammonia) have adverse effect on environment and human being. The natural emissions (e.g. from volcanoes) has contribution to the pollutants concentration and atmospheric chemistry governs speciation of pollutants, as in the case of secondary acidification. The methods of ambient air pollution monitoring based on modern instrumentation allow the verification of dispersion models and balancing of mass emissions. The comfort of everyday humanâ€™s activity is influenced by indoor and public transport vehicles interior air contamination, which is effected even by the professional appliances operation. The outdoor pollution leads to cultural heritage objects deterioration, the mechanism are studied and the methods of rehabilitation developed. However to prevent emissions the new technologies are being developed, the new class of these technologies are plasma processes, which are briefly reviewed at the final part of the book.

How to reference

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V. Mugica, R. Vallesa, J. Aguilar, J. Figueroa and F. Mugica (2011). PM2.5 Source Apportionment Applying Material Balance and Receptor Models in the MAMC, Monitoring, Control and Effects of Air Pollution, Prof. Andrzej G. Chmielewski (Ed.), ISBN: 978-953-307-526-6, InTech, Available from: http://www.intechopen.com/books/monitoring-control-and-effects-of-air-pollution/pm2-5-source-apportionment-applying-material-balance-and-receptor-models-in-the-mamc

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