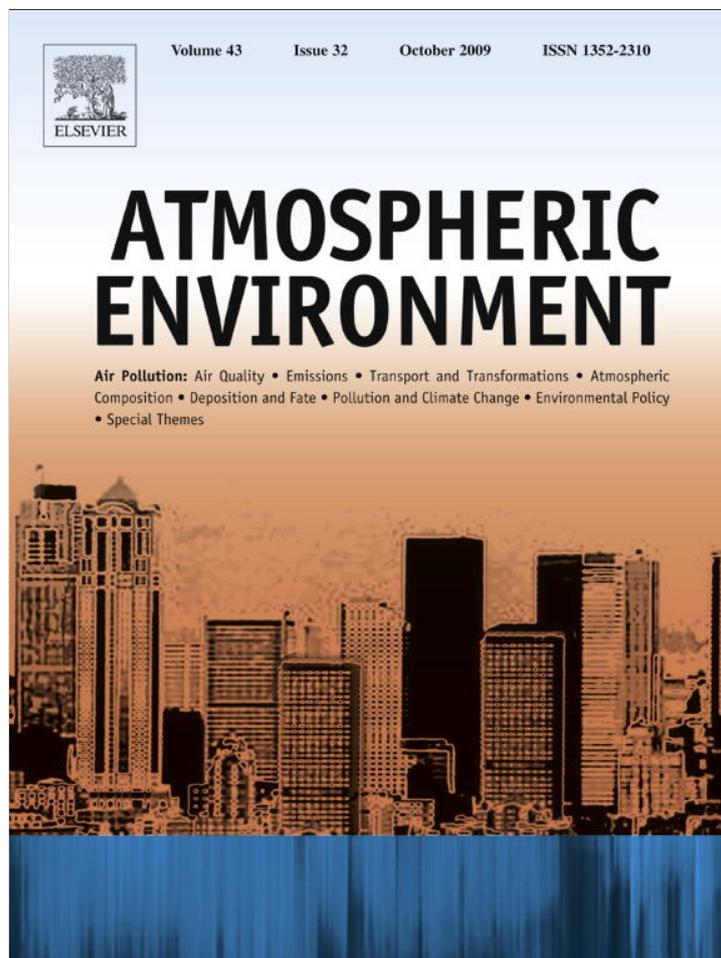


Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

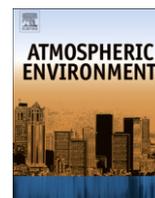
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

## Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

## PM composition and source reconciliation in Mexico City

V. Mugica<sup>a,\*</sup>, E. Ortiz<sup>a</sup>, L. Molina<sup>b</sup>, A. De Vizcaya-Ruiz<sup>c</sup>, A. Nebot<sup>d</sup>, R. Quintana<sup>e</sup>, J. Aguilar<sup>a</sup>, E. Alcántara<sup>a</sup><sup>a</sup> Universidad Autónoma Metropolitana-Azcapotzalco, Mexico D.F., Mexico<sup>b</sup> Molina Center for Energy and Environment, San Diego, USA<sup>c</sup> Centro de Investigación y de Estudios Avanzados-IPN., México D.F., Mexico<sup>d</sup> Universitat Politècnica de Catalunya, Manresa, Spain<sup>e</sup> Instituto Nacional de Cancerología, Mexico

## ARTICLE INFO

## Article history:

Received 12 January 2009

Received in revised form

16 June 2009

Accepted 24 June 2009

## Keywords:

MILAGRO

Mexico City

PM

CMB

Receptor models

DTT

## ABSTRACT

PM<sub>2.5</sub> and PM<sub>10</sub> were collected during 24-h sampling intervals from March 1st to 31st, 2006 during the MILAGRO campaign carried out in Mexico City's northern region, in order to determine their chemical composition, oxidative activity and the estimation of the source contributions during the sampling period by means of the chemical mass balance (CMB) receptor model. PM<sub>2.5</sub> concentrations ranged from 32 to 70  $\mu\text{g m}^{-3}$  while that of PM<sub>10</sub> did so from 51 to 132  $\mu\text{g m}^{-3}$ . The most abundant chemical species for both PM fractions were: OC, EC, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Si, Fe and Ca. The majority of the PM mass was comprised of carbon, up to about 52% and 30% of the PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. PM<sub>2.5</sub> constituted more than 50% of PM<sub>10</sub>. The redox activity, assessed by the dithiothreitol (DTT) assay, was greater for PM<sub>2.5</sub> than for PM<sub>10</sub>, and did not display significant differences during the sampling period. The PM<sub>2.5</sub> source reconciliation showed that in average, vehicle exhaust emissions were its most important source in an urban site with a 42% contribution, followed by re-suspended dust with 26%, secondary inorganic aerosols with 11%, and industrial emissions and food cooking with 10% each. These results had a good agreement with the Emission Inventory. In average, the greater mass concentration occurred during O<sub>3</sub>S that corresponds to a wind shift initially with transport to the South but moving back to the North. Taken together these results show that PM chemical composition, oxidative potential, and source contribution is influenced by the meteorological conditions.

© 2009 Elsevier Ltd. All rights reserved.

## 1. Introduction

Mexico's City Metropolitan Area (MCMA), the world's second largest city, is located in a basin surrounded by mountains on the West, East and South, averaging 2200 m above sea level altitude, bearing an approximate population of 20 million people, with more than 3.6 million circulating vehicles. From 2004 and up to date local regulation authorities have reported that the 15  $\mu\text{g m}^{-3}$  PM<sub>2.5</sub> arithmetic annual standard has been exceeded in all the monitoring stations and that only one out of twenty stations maintained the 50  $\mu\text{g m}^{-3}$  annual PM<sub>10</sub> standard (SIMAT and GDF, 2006). This constitutes a potentially important health risk considering the extensive evidence indicating that exposure to PM is related to cardiorespiratory disease, morbidity and mortality (Nel, 2005; Pope et al., 2002). PM chemical composition can determine the type and intensity of the toxic response, due to the presence of diverse metals and organic compounds, which promote oxidative stress through

generation of reactive oxygen species (Tao et al., 2003; Valavanidis et al., 2008). The latter are generated by redox reactions, where the reactive species are important electron donors; hence, measurements of reactive species may be used as markers for oxidative potential. Free radicals or reactive species are paramagnetic molecules with short time-period, they can be detected by electron paramagnetic resonance spectroscopy (EPR), although free radicals can be stabilized to better measure them, evidence suggests that EPR spectra shows their presence and potentially be an indicator, suggesting that if present could be involved in oxidative stress processes when in contact with biological systems (Kopáni et al., 2006). Furthermore, PM ability to catalyze oxygen reduction using thiol compounds such as dithiothreitol (DTT) by quinone-type compounds has been suggested as an indicator of potential cellular toxicity by oxidative stress induction (Cho et al., 2005).

Since deep knowledge is required on the contribution of each emission source in a receptor site, during IMADA-AVER campaign in 1997, a characterization study was carried out to determine the PM sources in Mexico City (Chow et al., 2002). Furthermore, as part of the MILAGRO campaign, Querol et al. (2008), reported PM source reconciliation through a speciation study. Although this sort of PM

\* Corresponding author.

E-mail address: [vma@correo.azc.uam.mx](mailto:vma@correo.azc.uam.mx) (V. Mugica).

characterization studies can be useful to suggest main sources, the application of receptor models offers a better estimation of source apportionment. 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. Source profiles for fugitive dust from Mexico were published in 2001 (Vega et al., 2001), and recently, PM<sub>2.5</sub> combustion source profiles were developed for Mexico City (Mugica et al., 2008).

Several field studies have been conducted in Mexico City during the last decade, to gain a better understanding of air pollution (Molina and Molina, 2002; Salcedo et al., 2006; Molina et al., 2007). The field campaign named MILAGRO (Megacities Initiative: Local and Global Research Observations), was carried out with the objective to describe Mexico City's pollutant plume evolution. The MILAGRO's campaign included a wide range of meteorological, chemical, gaseous and particulate measurements to investigate the pollutants' chemistry, dispersion and transport processes. Our study was carried out as part of the intensive 4-week MILAGRO campaign held in March 2006. The PM<sub>2.5</sub> and PM<sub>10</sub> collection had four main goals: the characterization of chemical species contained in PM samples, assessment of the reactivity of PM-chemical components and oxidative activity, the application of the CMB model to determine the source contributions to the presence of fine aerosol and the influence of the meteorological conditions on PM characteristics and source contribution in the MCMA.

## 2. Methodology

### 2.1. Sampling site

The Instituto Mexicano del Petróleo (IMP), termed T0 site, was one of the ground sites for the MILAGRO campaign, conveniently chosen for its location in the northern region of Mexico City's basin, at 19°29'23.60 N, 99°08'55.60W, it is surrounded by a mixed industrial and residential and three main heavily used roads, also an important regional bus station is located at approximately 500 m SE, thus, traffic volume is large and some influence of industrial emissions are also present.

PM<sub>2.5</sub> and PM<sub>10</sub> aerosol sampling was carried out daily at T0 site from March 1st to 31th of 2006, on the roof of building 21, two Tisch High Vol Samplers (Model TE-5007) for PM<sub>2.5</sub> and two Tisch High Vol Samplers (Model TE-6070) for PM<sub>10</sub> on 25.4 × 20.3 cm quartz fiber filters and nitrocellulose membranes, over 24 h periods from 08:00 to 08:00 the next day. The total sampling volume was approximately 1450 m<sup>3</sup> each day.

### 2.2. Chemical characterization

Prior to sampling, the quartz filters were baked for 12 h at 500 °C to reduce residual carbon levels associated with new filters. Quartz filters were conditioned 48 h before sampling in a chamber (40 ± 5% humidity and 20 ± 2 °C) and weighed before PM collection in a OHAUS Analytical Plus 250D balance. After sampling, the filters were conditioned in the same chamber during 48 h prior to gravimetric determination of the PM mass.

Quartz filters were split into four sections: the first section was used in the quantification of organic and elemental carbon, the second for the analysis of water-soluble ions, the third for elemental analysis and the fourth for duplicates.

An Atom Advantage Thermo Jarrel Ash Inductively Coupled Plasma-Atomic Emission Spectrometry, ICP-AES, was used to determine the elemental components of the PM collected. For ICP,

the section of each filter was digested with suprapure hydrochloric and nitric acids according to the microwave program established by Method IO 3.1 (USEPA, 1999); analytical details are described in Flores-Rangel et al. (2007). In this study, the reference material used was urban dust SRM 1649a from the National Institute of Standards and Technology (NIST). The elements recovery efficiency was between 98.6 ± 3.9% (Co) to 100.5 ± 2.8% (Cu).

Soluble ions were extracted ultrasonically (Branson bath, 3210) with 20 mL of Milli-Q deionized water during 120 min. After filtration, separation and quantification was performed by ion chromatography (IC), with a Perkin Elmer-Alltech 550 instrument equipped with an LC isocratic pump and a conductivity detector LCD. For anions was used a Hamilton PRPX-100 analytical anion column, the injection volume was 100 µL. Flow rate was 2 ml min<sup>-1</sup>. Ammonium, sodium and potassium were determined by a suppressed chromatography, the analytical conditions were as follows: Hamilton PRPX-200 analytical column, Alltech 335PCS suppressor module (García et al., 2006). The detection limits (3 s) in meq l<sup>-1</sup>, were 1.12, 4.2, 4.5, 2.9, 0.1, and 0.13 Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, respectively.

A Thermal-Optical Carbon Aerosol Analyzer (Sunset Lab, Forest Grove, OR USA), was used to determine organic and elemental carbon (OC and EC), which were determined by automated thermal-optical transmittance (TOT), using the National Institute for Occupational Safety and Health method (NIOSH) 5040 described by Birch and Cary (1996) and Na et al. (2004).

### 2.3. Quality assurance

Quality audits of the sample flow rates were conducted each week of the study period. A 100 mg extraction of a well-characterized urban dust (SRM 1649a standard reference material NIST) and filter blanks were handled and analyzed under the same procedure as filters with air samples. High purity standards were used for each of major ions for calibration. The species values in the actual samples were corrected by subtracting the field blanks and adjusting these values with their respective recoveries of urban dust extracted. For the purposes of calculating weight fractions, elements were normalized for oxygenated species as described by Mc Donald et al. (2000).

### 2.4. Oxidative activity determination using the DTT assay

To account for the PM oxidative activity the DTT assay was used. Redox-active compounds catalyze the oxygen reduction to superoxide by DTT, which is oxidized to disulfide. The remaining thiol is allowed to react with 5,5'-dithiobis-2-nitrobenzoic acid (DTNB), generating the mixed disulfide and 5-mercapto-2-nitrobenzoic acid, which is determined by its absorption at 412 nm, as shown by Kumagai et al. (2002). DTT consumption from PM-contained compounds is measured under linearity rate depletion less than 20%; the catalytic activity is expressed as the DTT consumption rate per minute per microgram of sample less the activity observed in the absence of PM. The redox or electron transfer activity of PM samples in this study was assessed by their ability to catalyze the oxygen reduction by DTT according to Cho et al. (2005). Briefly, samples of PM<sub>10</sub> (40 µg mL<sup>-1</sup>) and PM<sub>2.5</sub> (10 µg mL<sup>-1</sup>) recovered from the nitrocellulose membrane as described above, were incubated at 37 °C with 0.5M PBS, pH 7.4, double deionized water and 1 mM DTT for periods of 0–45 min. An aliquot of the incubation mixture was mixed with 10% trichloroacetic acid to stop the reaction, and a portion of the mixture was dissolved with a Tris buffer at pH 8.9, 20 mM EDTA and 10 mM DTNB solution and was read by its optical density absorption.

**Table 1**  
Meteorology and pollutant concentrations during MILAGRO campaign.

Episode	Label	Characteristics	Days occurred
South-Venting	SV	Northwesterly winds aloft with strong southward surface transport.	1–7, 13
O <sub>3</sub> -South	O <sub>3</sub> S	Winds from the southwest aloft. Northerly surface winds in the morning meet the southeast gap flow in the late afternoon forming an east-west convergence zone that moves northwards into the evening.	8, 12, 15–17
O <sub>3</sub> -North	O <sub>3</sub> N	Stronger southwesterly winds driving surface winds over the basin causing a north-south convergence zone, more stationary than for O <sub>3</sub> S	9–11, 18–20, 22
Cold Surge	CS	Decoupled flow in the vertical with strong, cold and humid surface winds from the Gulf coming over the Sierra Madre Oriental and flushing the basin to the south. Convection takes place when weak westerly winds blow aloft with humid conditions in the basin.	14, 21, 23
Convection-South	CNS	Weak northerly wind component aloft with rain in the southern part of the basin.	24–26, 31
Convection-North	CNN	Weak southerly wind component aloft with a gap flow and rain in the northern part of the basin.	26–30

2.5. Meteorological conditions and selection of the study periods

According to Fast et al. (2007), the overall meteorological conditions during the MILAGRO campaign can be classified in three regimes: the first, previous to March 14 was dry and sunny. The second began with a weak cold surge on March 12 increasing the humidity with light and variable winds. Between March 14 and 18 a series of troughs and ridges propagated from west to east across the U.S., and then the weather became dryer. Finally, the third regime, after March 21, began with a cold surge, precipitation, afternoon convection and strong westerly winds that were present

for the rest of the campaign. De Foy et al. (2008), carried out a cluster analysis in order to identify the dominant wind patterns during the campaign, as well as during the past 10 years of operational data from the warm dry seasons. Their results indicated that March 2006 was representative of typical flow patterns experienced in the MCMA basin during the dry warm season, and six ventilation episodes (that describe transport and basin venting) were recognized in order to relate meteorology and pollutant concentrations, particularly with ozone (Table 1).

2.6. CMB model

The CMB consists of a least squares solution to set linear equations that express the measured receptor concentration of chemical species as a linear sum of products of the source profile fractions for the species and source contributions. In the CMB model the source contributions are calculated by determining the linear combination of source fingerprints that best reconstruct the ambient concentration data set (Watson et al., 1991). The chemical mass balance model can be represented by a set of linear equations as follows (Eq. (1)).

$$C_i = \sum_{j=1}^P F_{ij} \cdot S_j \quad (1)$$

Where C<sub>i</sub> is the ambient concentration of the species “i” measured at the receptor site; P is the number of sources that contribute; (F<sub>ij</sub>) is the fraction of source contribution, given for the source profile; (S<sub>j</sub>) is the calculated contribution of source “j” that reach the receptor. In the present study, the equations system is solved using the CMB8.2 receptor model data processing system (Henry and Willis, 1997). The inputs to the CMB model were the receptor concentrations, obtained in this study, as well as the source profiles developed for Mexico City in other studies. Because most of the source profiles developed in Mexico City are only for the PM<sub>2.5</sub> fraction, and because the PM<sub>2.5</sub> fraction has been shown to be an important health risk factor in terms of inflammatory and toxicological markers in relation to the source contributors (Duvall et al., 2008), the CMB model was applied only for this fraction. The used

**Table 2**  
Average concentrations of PM (µg m<sup>-3</sup>), during the three regimes (Fast et al., 2007). The range of values measured is shown in brackets.

	PM10 (1–11 March)		PM10 (12–20 March)		PM10 (21–31 March)		PM2.5 (1–11 March)		PM2.5 (12–20 March)		PM2.5 (21–31 March)	
	Ave	Range	Ave	Range	Ave	Range	Ave	Range	Ave	Range	Ave	Range
Mass	95	(118–79)	94	(132–69)	74	(96–51)	56	(62–50)	47	(70–33)	47	(66–32)
Cl <sup>-</sup>	0.4	(0.6–0.3)	0.2	(0.3–0.1)	0.3	(0.4–0.2)	0.2	(0.4–0.1)	0.2	(0.3–0.1)	0.2	(0.3–0.1)
NO <sub>3</sub> <sup>-</sup>	2.6	(4.3–0.8)	3.9	(6.3–2.2)	2.6	(3.3–1.2)	2.2	(3.1–0.1)	2.3	(3.2–0.1)	1.0	(1.9–0.1)
SO <sub>4</sub> <sup>2-</sup>	6.1	(8.4–3.8)	6.3	(8.3–4.5)	6.7	(8.9–4.4)	4.2	(6.3–1.1)	4.7	(6.8–1.2)	4.3	(5.9–0.9)
NH <sub>4</sub> <sup>+</sup>	1.7	(2.6–1.1)	2.1	(2.9–1.2)	1.9	(2.3–1.4)	1.3	(1.9–0.1)	1.4	(2.0–0.9)	1.5	(2.1–0.9)
Na <sup>+</sup>	0.5	(0.7–0.3)	0.3	(0.5–0.2)	0.3	(0.5–0.2)	0.3	(0.4–0.1)	0.3	(0.4–0.1)	0.2	(0.4–0.1)
K <sup>+</sup>	0.6	(0.8–0.5)	0.4	(0.6–0.3)	0.3	(0.5–0.2)	0.6	(0.7–0.3)	0.4	(0.5–0.1)	0.2	(0.4–0.1)
OC	15	(25–10)	17	(27–9)	14	(22–15)	12	(17–7)	11	(19–6)	12	(21–9)
EC	4.9	(8–2.5)	5.3	(9.2–2.3)	4.4	(8.6–2.3)	3.7	(5.9–1.7)	4.2	(5.9–1.2)	3.3	(5.6–1.3)
Al	2.9	(4–1.7)	2.3	(3.6–1.6)	1.2	(2.9–1.1)	1.3	(2.3–0.6)	0.9	(1.9–0.4)	0.7	(1.8–0.3)
Si	4.9	(6.8–2.2)	4.1	(6.5–1.6)	1.9	(3.2–0.7)	2.7	(4.0–1.6)	2.3	(3.8–1.2)	1.9	(3.2–0.7)
Ca	1.5	(2.8–0.8)	1.3	(1.9–0.5)	0.7	(1.0–0.3)	0.9	(1.9–0.6)	0.8	(1.3–0.5)	0.7	(1.1–0.3)
Mg	0.4	(0.5–0.1)	0.3	(0.4–0.1)	0.3	(0.4–0.1)	0.3	(0.5–0.1)	0.3	(0.4–0.1)	0.3	(0.3–0.1)
Ti	0.3	(0.5–0.24)	0.4	(0.5–0.2)	0.3	(0.5–0.1)	0.2	(0.3–0.2)	0.2	(0.4–0.1)	0.2	(0.4–0.1)
Fe	3.3	(3.8–2.4)	3.6	(5.3–1.6)	2.7	(3.5–1.7)	1.8	(2.7–1.4)	1.7	(3.2–1.1)	1.3	(2.9–0.6)
V	0.03	(0.05–0.01)	0.03	(0.07–0.01)	0.02	(0.03–0.02)	0.02	(0.04–0.01)	0.02	(0.04–0.01)	0.01	(0.03–0.01)
Cr	0.07	(0.08–0.06)	0.07	(0.15–0.04)	0.07	(0.13–0.03)	0.06	(0.09–0.05)	0.05	(0.08–0.03)	0.04	(0.07–0.02)
Mn	0.06	(0.10–0.04)	0.07	(0.16–0.05)	0.05	(0.09–0.02)	0.07	(0.09–0.06)	0.05	(0.08–0.02)	0.04	(0.05–0.02)
Co	0.01	(0.02–0.00)	0.02	(0.03–0.01)	0.02	(0.02–0.01)	0.01	(0.02–0.00)	0.01	(0.02–0.00)	0.01	(0.01–0.01)
Ni	0.05	(0.16–0.03)	0.04	(0.11–0.01)	0.03	(0.10–0.01)	0.03	(0.08–0.01)	0.02	(0.03–0.01)	0.02	(0.04–0.00)
Cu	0.18	(0.24–0.15)	0.14	(0.18–0.09)	0.15	(0.23–0.11)	0.07	(0.15–0.02)	0.06	(0.10–0.01)	0.04	(0.05–0.01)
Zn	0.64	(0.71–0.56)	0.65	(0.82–0.51)	0.60	(1.20–0.17)	0.40	(0.42–0.35)	0.35	(0.43–0.15)	0.30	(0.49–0.04)
Pb	0.33	(1.15–0.13)	0.14	(0.38–0.06)	0.18	(0.37–0.08)	0.26	(0.76–0.13)	0.09	(0.26–0.01)	0.13	(0.19–0.05)

profiles include fugitive dust emitters (Vega et al., 2001), gasoline and diesel vehicle exhaust, food cooking, industrial LP gas steam boilers, wood burning and waste incineration (Mugica et al., 2008). Profiles of gas and diesel combustion boilers from industries were selected from the SPECIATE database (U.S. EPA, 2007). The profiles of ammonium sulfate and nitrate were included also, since secondary inorganic aerosols are important contributors of atmospheric PM<sub>2.5</sub>.

### 3. Results and discussion

#### 3.1. Aerosol mass concentrations

Mass concentrations ranged from 32 to 70  $\mu\text{g m}^{-3}$  and from 51 to 132  $\mu\text{g m}^{-3}$ , for PM<sub>2.5</sub> and PM<sub>10</sub> respectively. Only on March 16 the daily standards were exceeded for PM<sub>2.5</sub> and PM<sub>10</sub> with 70 and 132  $\mu\text{g m}^{-3}$  respectively. With the exception of the holiday weekend in March 18–21, which presented some of the lowest levels of PM<sub>2.5</sub> and PM<sub>10</sub>, the PM<sub>10</sub> levels were relatively high until March 21, when the humidity increased and PM<sub>10</sub> concentrations diminished; this decreasing trend was not so evident in the PM<sub>2.5</sub> levels. The average PM<sub>2.5</sub>/PM<sub>10</sub> ratio was more than 50%. Table 2 summarizes the average and range of PM<sub>2.5</sub> and PM<sub>10</sub> measurements, as well as the concentrations of major and trace species. The OC/TC ratio was in average 0.74 in PM<sub>2.5</sub> and 0.68 in PM<sub>10</sub>, which are in agreement with the results reported by Chow et al. (2002). The SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> accounted in average with 5, 2.6 and 1.6%, respectively in PM<sub>2.5</sub> and 5.2, 3.5 and 1.8  $\mu\text{g m}^{-3}$  respectively in PM<sub>10</sub>. For metal content Fe was the most abundant heavy metal in PM<sub>2.5</sub> and PM<sub>10</sub> (1.61 and 3.13  $\mu\text{g m}^{-3}$  respectively), considering it is an important soil component. High concentrations of heavy metals in particles has been reported previously for the northern region of the City where many industries are located (Mugica et al., 2002; Flores et al., 1999), although in the last decade important reduction of heavy metal concentrations, specially Pb, has been reported. Levels of Pb were below the three month average Mexican standard (1.5  $\mu\text{g m}^{-3}$ ) during all days sampled. Cu, Cr, Fe, Ni, Pb, V and Zn levels in PM<sub>2.5</sub> were relatively high when compared with those of Europe urban sites (Gotschi et al., 2005).

#### 3.2. Aerosol oxidative potential

Fig. 1 shows that the redox activity of organic compounds measured with the DTT assay in PM<sub>10</sub> samples taken during the ventilation episodes (Table 1) comprised within from March 1 to March 21, showed no variability. If some, the highest activity was observed for O<sub>3</sub>S and CS episodes and although the PM<sub>10</sub> pools had some composition differences, the redox activity of PM<sub>10</sub> was similar.

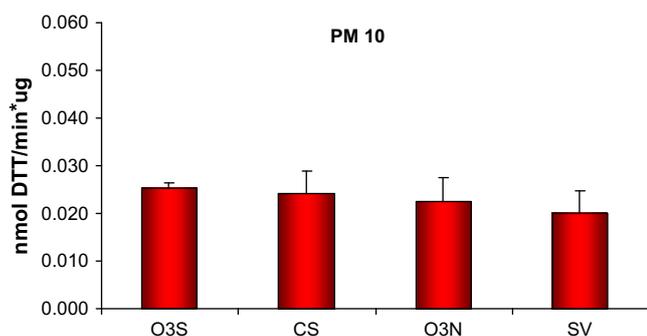


Fig. 1. Redox activity (DTT) during the MILAGRO campaign.

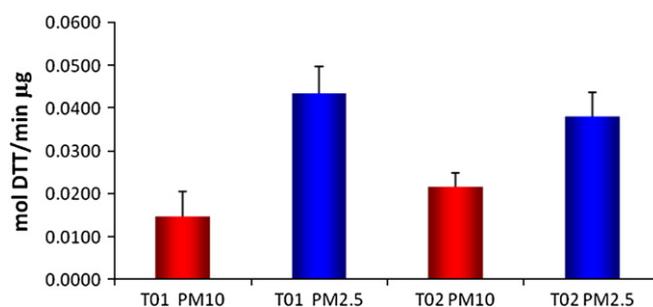


Fig. 2. Comparison of DTT assay for PM<sub>10</sub> and PM<sub>2.5</sub>.

Fig. 2 shows a comparison of the redox activity between PM<sub>2.5</sub> and PM<sub>10</sub> for the two first sampling periods, since the PM<sub>2.5</sub> sample was not sufficient for the other periods, thus: T01 pool: 1–7 March with SV episode, T02 pool: 8–11 March with O<sub>3</sub>S and O<sub>3</sub>N episodes were tested. The redox activity of PM<sub>2.5</sub> is almost two fold greater than the PM<sub>10</sub>, which agrees with our previous results with PM collected in the north of Mexico City in the spring and winter of 2003 (De Vizcaya-Ruiz et al., 2006). Extensive evidence has established the toxic potential of a high redox activity with the induction of oxidative stress and damage (Li et al., 2003; Valavanidis et al., 2008); suggesting that the oxidative activity observed in the PM<sub>2.5</sub> fraction could be an important risk factor for induction of adverse health effects (De Kok et al., 2006). Our results, taken together with other observations that indicate an influence of the meteorological conditions in the generation of oxygenated radical species ( $\cdot\text{OH}$ ) and oxidative DNA damage in PM-exposed alveolar epithelial cells regardless if the metal content or sampled mass (Shi et al., 2003) points out the need for further investigation to establish the

Table 3  
Performance of the CMB model applied to PM<sub>2.5</sub>.

Date	R <sup>2</sup>	Chi <sup>2</sup>	%Mass	Measured. Conc. ( $\mu\text{g m}^{-3}$ )	Calculated. Conc. ( $\mu\text{g m}^{-3}$ )
01/03/2006	0.96	3.3	99	52	52
02/03/2006	1	0.4	101	56	57
03/03/2006	0.98	2.9	110	61	68
04/03/2006	0.99	2.9	104	49	51
05/03/2006	0.98	3.1	102	51	52
06/03/2006	0.95	2.2	101	59	59
07/03/2006	0.98	2.6	110	61	67
08/03/2006	0.94	3.8	106	61	65
09/03/2006	0.98	3.5	100	50	50
10/03/2006	0.95	2.6	105	54	57
11/01/1900	0.95	2.8	105	39	41
12/03/2006	0.97	2.3	109	48	52
13/03/2006	0.98	2.8	107	45	48
14/03/2006	0.97	1.7	108	36	39
15/03/2006	0.96	2.4	97	56	54
16/03/2006	0.97	3.8	102	71	72
17/03/2006	0.99	1.9	102	60	61
18/03/2006	0.95	3.1	101	37	38
19/03/2006	0.95	3.9	109	40	43
20/03/2006	0.94	3.4	101	33	33
21/03/2006	0.99	1.0	107	66	70
22/03/2006	0.99	1.9	103	53	55
23/03/2006	0.98	2.3	100	33	33
24/03/2006	0.99	2.5	98	60	58
25/03/2006	1	1.1	99	32	32
26/03/2006	0.98	2.4	110	40	43
27/03/2006	0.98	2.4	101	37	38
28/03/2006	0.99	0.7	105	56	58
29/03/2006	1	0.4	108	43	47
30/03/2006	0.97	2.5	102	56	57
31/03/2006	0.98	1.5	102	41	42
Average	0.97	2.4	104	50	51

**Table 4**  
Estimated percentage of source contributions.

	1–11 March T01			11–20 March T02			21–31 March T03		
	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
Soil	35	53	20	30	40	19	15	29	4
Vehicles	37	56	26	42	57	28	46	54	31
Industry	11	19	3	6	17	2	13	19	9
Aerosols	8	17	2	14	17	10	13	20	7
Food Cooking	9	15	2	8	15	2	13	21	3

toxicological implications of the influence of meteorological conditions on PM chemical composition and reactivity.

### 3.3. CMB source apportionment model

Table 3 shows the statistical parameters of the model applied to PM<sub>2.5</sub> in T0. In general, it can be observed that the parameters  $R^2$ ,  $\text{Chi}^2$  and mass percentage were within acceptable intervals, suggesting a good performance of the model application. The  $R^2$  values fluctuated from 0.94 to 1, with an average value of 0.97; the  $\text{Chi}^2$  values were smaller than 4 with an average of 2.4. The mass percentages calculated varied from 97 to 111  $\mu\text{g m}^{-3}$ , with an average of 104%. For most of the days, the differences between measured and calculated ambient concentrations in  $\mu\text{g m}^{-3}$  were minimum, although some days there was an overestimation ranging from 5% to 10%.

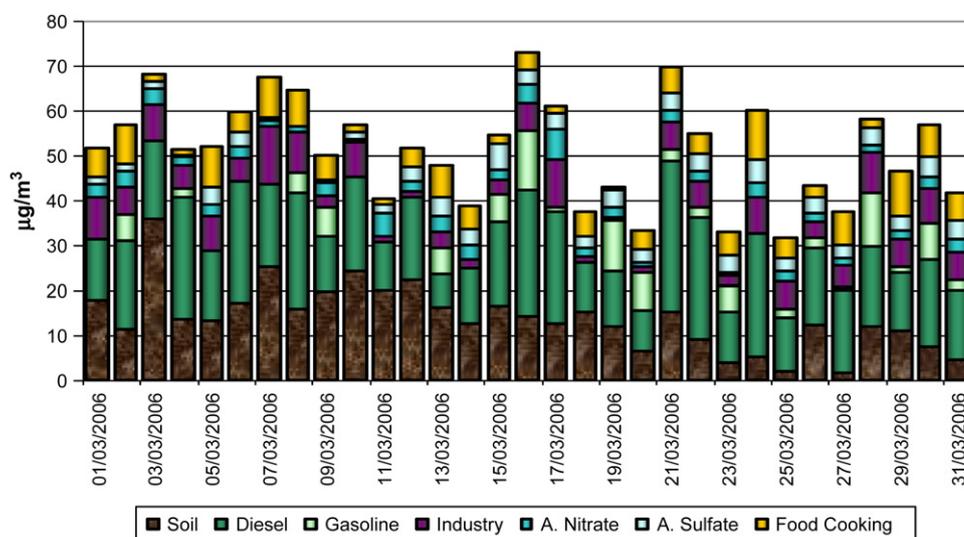
For the whole campaign, the dominant PM<sub>2.5</sub> sources were: motor vehicle exhaust emissions (42%), followed by soil (26%), secondary inorganic aerosols (11%), industry (10%) and food cooking (10%), although the estimated percentage contribution of the PM<sub>2.5</sub> sources was different for each of the three meteorological regimes (Table 4). Vehicle exhaust emissions varied from 25 to 57%, representing the highest concentrations in the last period with a 46% average, since the soil contribution diminished gradually from the first to the third period due to the relative humidity increase and some precipitations. Industry and food cooking had their lower contribution in the second period, where five out of ten days considered were non working days.

Fig. 3 shows the daily variation of the source apportionment during the whole campaign. Just as the PM<sub>2.5</sub> concentrations diminished at the end of the campaign, due to the presence of

humidity and rainfall, the concentration of particles from soil re-suspension also decreased two to three fold compared to the first and second periods. The greatest contribution from soil during the field campaign was on March 3 with 53% of the total mass ( $36 \mu\text{g m}^{-3}$ ). Large concentrations of re-suspended soil were also measured from March 9th to 12th as a consequence of the high wind speed, namely up to  $15 \text{ m s}^{-1}$ , showing once again the influence of weather conditions over this specific source. The estimated average contribution to PM<sub>2.5</sub> of re-suspended soil (26%) was within the 15–28% range of crustal material estimated by Querol et al. (2008).

As mentioned above, vehicle emissions were the greatest contributors to the total mass of PM<sub>2.5</sub> throughout the whole field campaign. It was not possible to separate the gasoline and diesel vehicle emission contributions every day due to the existence of colinearity, but in the 20 days that this discrimination was achievable, diesel vehicle emissions contributed with 35% and gasoline vehicle emissions with 7% in average. This source was the main contributor of carbonaceous material contained in PM<sub>2.5</sub>. The contribution of vehicle emissions did not show a particular trend during the sampling campaign, however, on Saturdays, Sundays and the long holiday (March 18–21), the contribution of vehicles to the total mass was around 13% less than during the week days. Wood burning source was included in all runs but it displayed colinearity in all cases with the diesel vehicle emissions and industrial, which made it impossible to know if the emissions due to fires are included in the above mentioned sources.

The largest contribution of secondary aerosols estimated by the CMB model was during the second period (14%), which increased with the humidity raise, thus reaffirming the importance of this meteorological parameter during aerosol formation. Ammonium sulfate accounted in average a 55% of secondary aerosols with up 12% of total PM<sub>2.5</sub> mass. The CMB calculated contribution to secondary inorganic aerosols was lower than the estimated contribution given by Querol et al. (2008), from their results on chemical composition. This difference is due to the fact that not all ammonium nitrate and sulfate are a product of secondary aerosol formation in the atmosphere (as is considered in Querol's apportionment), since some of these salts are contained in the emissions of other sources. The source contribution to  $\text{NH}_4^+$  in PM<sub>2.5</sub> was quantified from the CMB model, thus  $82.4 \pm 8.6\%$  is due to secondary aerosols, whereas



**Fig. 3.** Source apportionment during MILAGRO campaign.

**Table 5**  
Comparison of mass contribution in working and no working days.

	Working days ( $\mu\text{g m}^{-3}$ )	No working days ( $\mu\text{g m}^{-3}$ )	Difference (%)
Total Mass	52.4 ± 9.6	43.2 ± 9.7	17%
Vehicles	22.5 ± 7.2	19.5 ± 7.7	13%
Diesel	18.8 ± 6.1	16.7 ± 7.5	11%
Soil	14.1 ± 7.8	13.3 ± 5.5	6%
Aerosols	5.6 ± 2.2	5.2 ± 1.3	7%
Gasoline	5.5 ± 3.7	4.7 ± 3.7	14%
Food Cooking	5.9 ± 2.7	3.9 ± 2.4	33%
Industry	6.5 ± 2.8	3.5 ± 2.5	46%

13.3 ± 3.7% is due to mobile sources, 2.52 ± 0.8% to food cooking and from 0.5 to 5.3% to re-suspended dust.

The contribution to particles due to industrial emissions displayed a 2–19% variation with concentrations of 0.7 and 12.9  $\mu\text{g m}^{-3}$ . Except for the first weekend of the campaign (March 4–5), the lowest industrial  $\text{PM}_{2.5}$  emissions were for the long weekend (March 18–21), that exhibited the minimum contributions for this source. At the beginning of the campaign, large contributions of industrial emissions (more than 12%) occurred on March 1, 7, 8 and 10, though except in March 10, during these days the wind directions were from the NW and N, coincidentally, where the industrial zones are located. The latter days from March 23 to the end of the campaign, industry emissions were in average 13%, suggesting that industrial facilities close to the sampling site had a high influence.

Finally, the contribution of food cooking emissions had values from 2 to 21%. The large contributions can be explained partly because the samplers received the emissions of the IMP refectory (with no chimney) at about 100 m from the samplers: this situation may induce to overestimate the emissions due to this source, and as a consequence, other sources could be underestimated.

Table 5 displays the source contribution considering working and nonworking days, such as weekends and holidays. It is possible to observe that the  $\text{PM}_{2.5}$  mass has a 17% increase for working days. The mass difference in the case of soil (6%) is quite similar to the standard deviation of the contribution of that source, which means that such increment could be due to the variability due to meteorological conditions over that source, on the opposite, the increased contribution to mass percentage for the other sources is clearly much larger than the respective standard deviations; then it is possible to affirm that the increment resulted from anthropogenic activities.

Finally, the six meteorological episodes identified by De Foy et al. (2008) were associated with the source apportionment as presented in Fig. 4. Not only the largest  $\text{PM}_{2.5}$  mass measured on March 16th corresponded to the  $\text{O}_3\text{S}$  episode, but also, in average, the greater mass concentration occurred during  $\text{O}_3\text{S}$ , that correspond to a wind shift initially with transport to the South but moving back to the North, as confirmed by the ozone peaks located

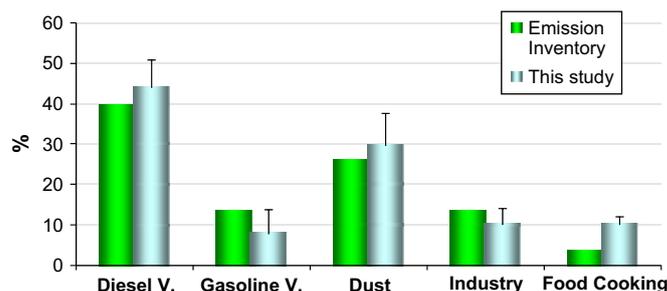


Fig. 5. Comparison with the emission inventory.

in the south of the city on those days (De Foy et al., 2008). In contrast, the lower concentrations are associated with episode  $\text{O}_3\text{N}$  where the Northeast flow yields pollutant accumulation in the morning, which is transported to the North of the basin. In general, the behavior of  $\text{PM}_{2.5}$  mass concentration is similar to vehicle emissions, showing once again the importance of this source. The South-venting, SV, episodes characterized for straightforward uniform transport from the Northwest to the South, showed the highest contribution of soil and the second of the total  $\text{PM}_{2.5}$  mass.

### 3.4. Emission inventory comparison

The CMB model is useful 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 it correlates the pollutants with their sources. A comparison of the results obtained in this study with those provided by the Emission Inventory is not an easy one to do due to several limitations. Notwithstanding, this research provides the source apportionment only for one month, whereas the Inventory reports the average emissions during one year. Also, the CMB model estimates all industrial emissions together, since profiles have been obtained directly from the sources, however, the theoretical calculation of emissions in the Inventory allows the separation of different emissions from one source, i.e. industrial combustion emission and processes emissions. Fig. 5 shows the comparison of the last Emission Inventory of MCMA with the results of this study, where the contribution of secondary inorganic aerosols was subtracted from the results of this study, since these contributors to  $\text{PM}_{2.5}$  are formed in the atmosphere. In general, considering the limitations mentioned above and with the exception of food cooking, there is a relative good agreement with the Emission Inventory; the differences remain within the standard deviation of the sources estimated in this study. In the case of food cooking, this source could be underestimated by the Emission Inventory, because only the particles emitted by the LP gas combustion are

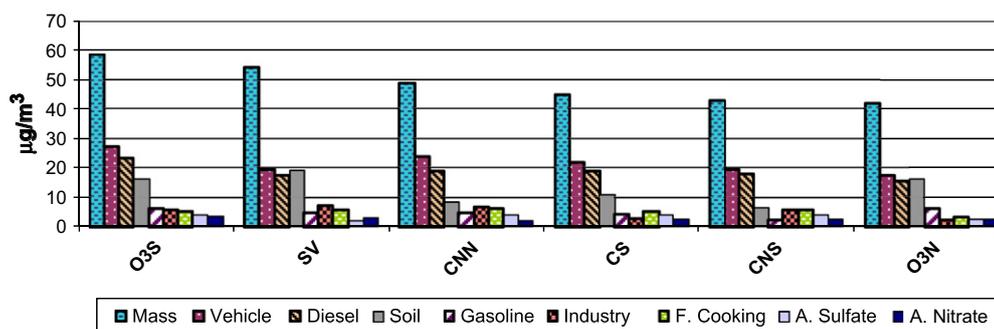


Fig. 4. Relationship among source apportionment and meteorological episodes.

considered but not the particles emitted during the food cooking process.

#### 4. Conclusions

The results obtained in this study, strongly suggest that meteorological conditions and the climate, greatly influence atmospheric particle concentration. The lowest concentrations appeared on Saturdays and Sundays, and particularly the holiday weekend, which is in accordance with a decrease in anthropogenic activities, mainly industrial and heavy transport and brings about an associated reduction of suspended particles. On the other hand, DTT results show that suspended particulate matter, especially PM<sub>2.5</sub> have an important redox activity which could contribute to oxidative stress induction and consequently impose relevant health implications. In general, vehicle exhaust emissions are the highest contributors of PM<sub>2.5</sub> followed by soil, secondary organic aerosols, industry and food cooking. Our findings suggest that PM size fractions and sources are influenced by the meteorological conditions as well as anthropogenic activities, and should be considered for regulatory strategies.

#### Acknowledgements

The authors want to thank the CAM, México and the Molina Center for the support to this study, as well to Mario Romero for the final revision of this paper.

#### References

- Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology* 25 (3), 221–241.
- Cho, A.K., Sioutas, C., Miguel, A.H., Kumagai, Y., Schmitz, D.A., Misra, C., Singh, M., Eiguren-Fernandez, A., Froines, J.R., 2005. Redox activity of airborne particulate matter (PM) at different sites in the Los Angeles basin. *Environmental Research* 99, 40–47.
- Chow, J.C., Watson, J.G., Edgerton, S.A., Vega, E., 2002. Chemical composition of PM<sub>10</sub> and PM<sub>2.5</sub> in Mexico City during winter 1997. *Science of the Total Environment* 287, 177–201.
- Chow, J.C., Watson, J.G., 2002. Review of PM<sub>2.5</sub> and PM<sub>10</sub> apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model. *Energy & Fuels* 16, 222–260.
- De Foy, B., Fast, J.D., Paech, S.J., Phillips, D., Walters, J.T., Coulter, R.L., Martin, T.J., Pekour, M.S., Shaw, W.J., Kastendeuch, P.P., Marley, N.A., Retama, A., Molina, L.T., 2008. Basin-scale wind transport during the MILAGRO field campaign and comparison to climatology using cluster analysis. *Atmospheric Chemistry and Physics* 8, 1209–1224.
- De Kok, T.M., Driee, H.A., Hogervorst, J.G., Briedé, J.J., 2006. Toxicological assessment of ambient and traffic-related particulate matter: a review of recent studies. *Mutation Research – Reviews in Mutation Research*, 103–122.
- De Vizcaya-Ruiz, A., Gutiérrez-Castillo, M.E., Uribe-Ramírez, M., Cebrián, M.E., Mugica-Alvarez, V., Sepúlveda, J., Rosas, I., Salinas, E., García-Cuellar, C.M., Martínez, F., Alfaro-Moreno, E., Torres-Flores, V., Osornio-Vargas, A., Sioutas, C., Fine, P.M., Singh, M., Geller, M.D., Kuhn, T., Eiguren-Fernandez, A., Miguel, A., Schiestl, R., Reliene, R., Froines, J., 2006. Characterization and in vitro biological effects of concentrated particulate matter from Mexico City. *Atmospheric Environment* 40 (Suppl. 2), 583–592.
- Duvall, R.M., Norris, G.A., Dailey, L.A., Burke, J.M., McGee, J.K., Gilmour, M.I., Gordon, T., Devlin, R.B., 2008. Source apportionment of particulate matter in the U.S. and associations with lung inflammatory markers. *Inhalation Toxicology* 20, 671–683.
- Fast, J.D., de Foy, B., Acevedo Rosas, F., Caetano, E., Carmichael, G., Emmons, L., McKenna, D., Mena, M., Skamarock, W., Tie, X., Coulter, R.L., Barnard, J.C., Wiedinmyer, C., Madronich, S., 2007. A meteorological overview of the MILAGRO field campaigns. *Atmospheric Chemistry and Physics* 7, 2233–2257.
- Flores, J., Aldape, F., Diaz, R.V., Hernandez-Mendez, B., Garcia, R., 1999. PIXE analysis of airborne particulate matter from Xalostoc, Mexico: winter to summer comparison. *Nuclear Instruments and Methods in Physics Research* 150, 445–449.
- Flores-Rangel, R.M., Rodríguez-Espinosa, P.F., Montes de Oca-Valero, J.A., Mugica-Alvarez, V., Ortiz-Romero-Vargas, M.E., Navarrete-López, M., Dorantes-Rosales, H.J., 2007. Metal content in air Simple collected in an urban zone in Tampico, Mexico. A first survey. *Human and Ecological Risk Assessment*, 1359–1372.
- García, R., Del Torres Ma, C., Padilla, H., Belmont, R., Azpra, E., Arcega-Cabrera, F., Báez, A., 2006. Measurement of chemical elements in rain from Rancho Viejo, a rural wooded area in the State of Mexico, Mexico. *Atmospheric Environment* 40, 6088–6100.
- Gotschi, T., Hazenkamp-von Arx, M., Heinrich, J., Bono, R., Burney, P., Forsberg, B., Jarvis, D., Maldonado, J., Norback, D., Stern, W., Sunyer, J., Toren, K., Verlató, G., Villani, S., Kunzli, N., 2005. Elemental composition and reflectance of ambient fine particles at 21 European locations. *Atmospheric Environment* 39, 5947–5958.
- Henry, R.C., Willis, R.D., 1997. *Chemical Mass Balance Receptor Model Version 8 (CMB8) User's Manual Prepared for US Environmental Protection Agency*, Research Triangle Park, NC, by Desert Research Institute, Reno, NV.
- Kopáni, M., Celec, P., Danixovi, L., Michalka, P., Biró, 2006. Oxidative stress and electron spin resonance. *Clinica Chimica Acta* 364, 61–66.
- Kumagai, Y., Koide, S., Taguchi, K., Endo, A., Nakai, Y., Yoshikawa, T., Shimojo, N., 2002. Oxidation of proximal protein sulfhydryls by phenanthraquinone, a component of diesel exhaust particles. *Chemical Research in Toxicology* 15 (4), 483–489.
- Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J., Wang, M., Oberly, T., Froines, J., Nel, A., 2003. Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environmental Health Perspectives* 111, 455–460.
- Mc Donald, J., Zielinska, B., Fujita, E., Sagebiel, J., Chow, J., Watson, J., 2000. Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science & Technology* 34, 2080–2091.
- Molina, L.T., Kolb, C.E., de Foy, B., Lamb, B.K., Brune, W.H., Jimenez, J.L., Molina, M.J., 2007. Air quality in North America's most populous city – overview of MCMA-2003 Campaign. *Atmospheric Chemistry and Physics* 7, 3133–3177.
- Molina, M.J., Molina, L.T., 2002. *Air Quality in the Mexico Megacity: an Integrated Assessment*. Kluwer Academic.
- Mugica, V., Mugica, F., Torres, M., Figueroa, J., 2008. PM<sub>2.5</sub> emission elemental composition in the metropolitan area of Mexico city from diverse combustion sources in the metropolitan area of Mexico city. *The Scientific World* 8, 275–286.
- Mugica, V., Maubert, M., Torres, M., Muñoz, J., Rico, E., 2002. Temporal and spatial variations of metal content in TSP and PM<sub>10</sub> in Mexico City during 1996–1998. *Journal of Aerosol Science* 33, 91–102.
- Na, K., Sawant, A.A., Cocker III, D.R., 2004. Primary and secondary carbonaceous species in the atmosphere of western Riverside County, California. *Atmospheric Environment* 38, 1345–1355.
- Nel, A., 2005. Atmosphere. Air pollution-related illness: effects of particles. *Science* 308 (5723), 804–806.
- Pope III, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thurston, G.D., 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Journal Air & Waste Management Association* 287, 1132–1141.
- Querol, X., Pey, J., Minguillón, M.C., Pérez, N., Alastuey, A., Viana, M., Moreno, T., Bernabé, R.M., Blanco, S., Cárdenas, B., Vega, E., Sosa, G., Escalona, S., Ruiz, H., Artiñano, B., 2008. PM speciation and sources in Mexico during the MILAGRO-2006 campaign. *Atmospheric Chemistry and Physics* 8, 111–128.
- Salcedo, D., Onasch, T.B., Dzepina, K., Canagaratna, M.R., Zhang, Q., Huffman, J.A., DeCarlo, P.F., Jayne, J., Mortimer, P., Worsnop, D.R., Kolb, C., Johnson, K., Zuberi, B., Marr, L., Volkamer, R., Molina, L.T., Molina, M., Cardenas, B., Bernabe, R., Márquez, C., Gaffney, J., Marley, N., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Leshner, R., Shirley, T., Jimenez, J., 2006. Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass spectrometry: results from the CENICA Supersite. *Atmospheric Chemistry and Physics* 6, 925–946.
- Shi, T., Knaapen, A.M., Begerow, J., Birmili, W., Borm, P.J., Schins, R.P., 2003. Temporal variation of hydroxyl radical generation and 8-hydroxy-2'-deoxyguanosine formation by coarse and fine particulate matter. *Occupational and Environmental Medicine* 60, 315–321.
- Simat, Gdf, 2006. Informe de la Calidad del Aire en la Zona Metropolitana de la Ciudad de México.
- Tao, F., Gonzalez-Flecha, B., Kobzik, L., 2003. Reactive oxygen species in pulmonary inflammation by ambient particulates. *Free Radical Biology and Medicine* 35, 327–340.
- U.S.EPA. U.S. Environmental Protection Agency, 1999. Method IO-2.1. Compendium of Methods for Inorganic Air Pollutants. Office of Research and Development, United States Environmental Protection Agency, OHIO.
- U.S. Environmental Protection Agency, 2007. *Air Emission Species Manual: SPECIATE Data Base*.
- Valavanidis, A., Fiotakis, K., Thomais, V., 2008. Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. *Journal of Environmental Science and Health, Part C* 26, 339–362.
- Vega, E., Mugica, V., Reyes, E., Sánchez, G., Chow, J.C., Watson, J.G., 2001. Chemical composition of fugitive dust emitters in Mexico City. *Atmospheric Environment* 35, 4033–4039.
- Watson, J.G., Chow, J., Pace, T.G., 1991. Chemical mass balance. In: Hopke, P.K. (Ed.), *Receptor Modeling for Air Quality Management, Data Handling in Science and Technology*. Elsevier Science.