$PM_{2.5}$ characterisation by scanning electron microscopy (SEM) and its correlation with diverse particle emission sources

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Abstract

In the Valley of Mexico Metropolitan Zone (VMMZ), there are over 20 million people, more than 4.5 million vehicles and about 35,000 industries and services. Daily average fuel consumption has been estimated as 50 million liters which generates thousands of tons of different air pollutants. Among these, an annual average of 5,499 ton of $PM_{2.5}$ which cause health and visibility problems. $PM_{2.5}$ sampling was performed at the Air Quality Sampling Station of UAM-Azcapotzalco, Northwest VMMZ, with a low volume sampler, from Monday to Tuesday and Thursday to Friday, during 24-hour periods for 14 weeks in 2004 (from January to June and September to October). Samples were prepared cutting each filter into three sections which were later observed at the Scanning Electron Microscope (SEM). Several $PM_{2.5}$ were identified. Among these, the chosen ones were those with a good definition of morphology, texture, porosity and size. Once the morphology was described, data were correlated with emission sources considering wind speed direction data as well as particles spatial distribution on the VMMZ maps. In most of the micrographs, observed particles had a spheroidal or ovoidal shape, with smooth or rugged and porous surface depending on their origin. Based on morphology information, it was determined that most of the particles came from combustion processes, both from mobile sources in the downtown area of Mexico City, and from point and area sources Northeast of the VMMZ.

Metals in major proportion were Zn and Pb. Metals in minor proportion were Ti, Mn and Cu.
Keywords: $PM_{2.5}$, scanning electron microscopy.

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1 Introduction

The Metropolitan Zone of the Valley of Mexico is located at 19°20′ North Latitude and 99°05′ West Longitude as a part of the Basin of Mexico which has an average height of 2,240 meters above sea level. This is the reason why oxygen content in the air is 23% less than it is at sea level and combustion processes are less efficient, producing more pollutants. MZMV surface is 9,560 km^2 distributed between part of the states of Mexico, Hidalgo, Tlaxcala and the whole of the Federal District. It is surrounded by the mountains of the Ajusco, Nevada, Chichinautzin, Las Cruces, Guadalupe and Santa Catarina, ranges which are a natural physical barrier against wind circulation and the resulting removal of polluted air towards the exterior. Also, frequent thermal inversions produce pollutants stagnation.

According to the 2010 Census, Mexico had 112 million 322 thousand 757 inhabitants and the MZMV 20 million, which makes it the third urban agglomeration in the world, only after Tokyo and Delhi.

The National Institute of Statistics and Geography (INEGI, in Spanish) reports that there are about 53,500 industries located in the ZMVM, 22,440 in the State of Mexico and 31,100 in the Federal District. About 90% of these facilities are considered as micro industries, 6% as small, 3% as medium and only less than 1% as big. This means that medium and big industries, the ones which are the most important pollutant emitters, represent less than 4%.

Mobile sources produce most of the emissions in the ZMVM. This is due, obviously, to their great number, but also to their poor maintenance, the lack of pollutant control devices in many of them and general bad fuels quality.

2 Methodology

Particle sampling was performed at the UAM-Azcapotzalco Air Quality Monitoring Station, at the VMMZ with a low volume sampler, from Monday to Tuesday and from Thursday to Friday, for a 24 hours period during 14 weeks distributed in January, February, March, May, June, September and October.

Filters were conditioned at constant temperature and humidity, before and after the sampling, at the Environmental Research and Training National Center (CENICA, in Spanish) facilities [1].

A scanning electron microscope (SEM) scans the sample with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface morphology and composition [2].

In order to obtain information on morphology, micrographs were taken from 24 samples selected from a total of 47 collected samples.

For heavy metals characterization, 47 samples were observed in order to obtain information on atoms percent of six metals (Ti, Mn, Fe, Cu, Pb and Zn).

2.1 Sample preparation and observation with the SEM

The filters with sample are cut in circles of about 1 cm. in diameter and put on an inox support (PIN). Then, the filters are placed on the SEM filters stand and introduced in a vacuum container in order to evaporate the carbon in the sample, thus turning it conductive, avoiding electrons accumulation on its surface.

The samples are introduced in the SEM chamber, placing the stand firmly. The samples are observed in order to select several zones, at random, until enough micrographs are obtained to allow the clear observation of the collected particles which are to be later classified [3].

Micrographs are then taken, printed, and visual analysis is performed to determine their shape and size (with a scale). Observed particles morphologies are compared with morphologies reported in literature in order to correlate them with possible emission sources.

3 Results and discussion

In figure 1 observed metals proportions: Ti, Mn, Fe, Cu, Pb and Zn (as atoms percentages) are presented. On analyzed samples, Fe, Zn and Pb constitute the larger proportions. Ti, Mn and Cu are in minor proportions.

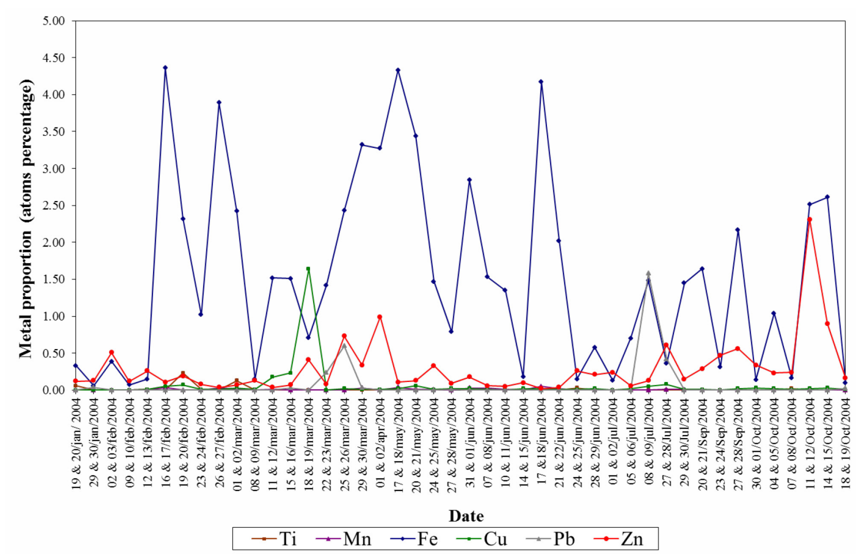

Figure 1: Metals proportion (atoms percentage).

Observed metals variations proportions with wind speed are presented in Figure 2. Fe and Zinc are in major proportion when there is a minor wind speed.

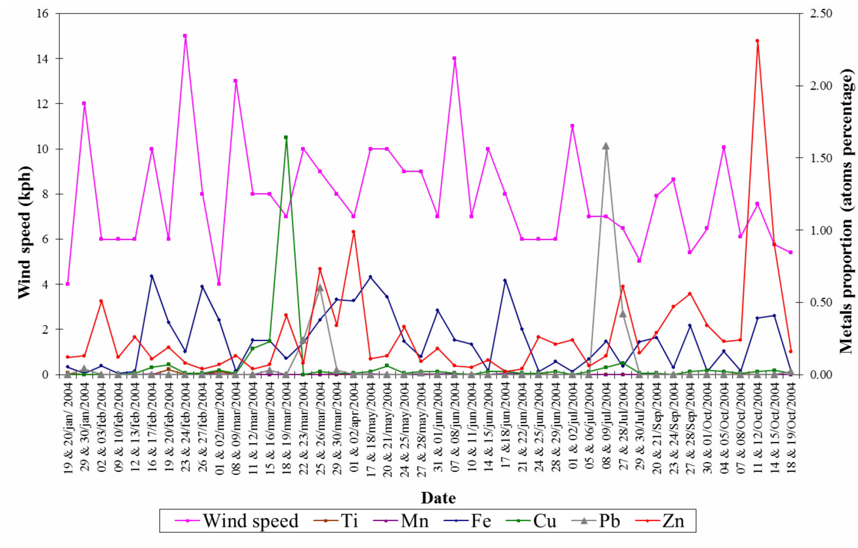

Figure 2: Metals proportion variations with wind speed.

In Figure 3, $PM_{2.5}$, Ti, Mn, Fe, Cu, Pb and Zn concentrations are presented. Metals with highest concentrations were: Zn, with 2.31 atoms percentage and a $PM_{2.5}$ concentration of 36.07 μg/m^3; Pb with 1.58 atoms percentage and a $PM_{2.5}$ concentration of 24.65 μg/m^3 and Cu, with 1.64 atoms percentage and a $PM_{2.5}$ concentration of 40.84 μg/m^3.

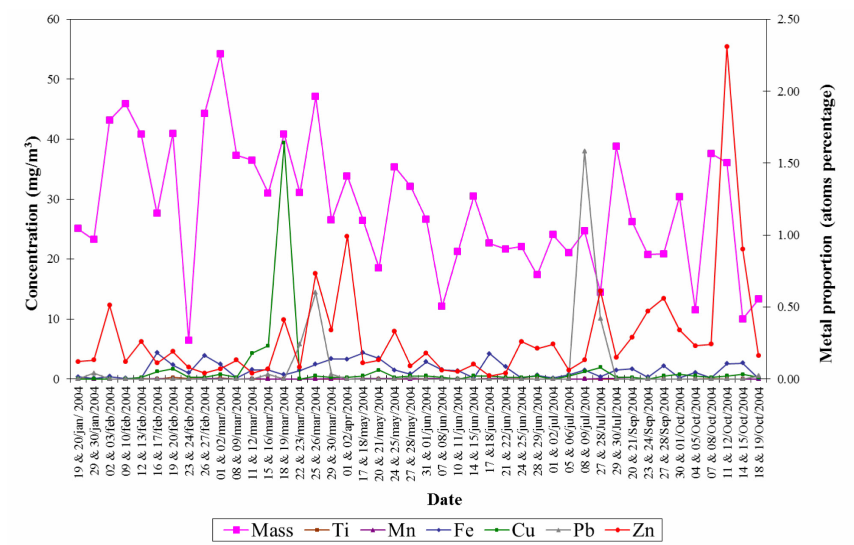

Figure 3: Concentration of $PM_{2.5}$ and metals.

In table 1 there is information (morphology and origin) on observed micrographs. $PM_{2.5}$ show spheroidal shape. Some others present undetermined shape with a rough surface. Some of these particles are resuspended dust and others come from stationary and from mobile sources [4].

Table 1: Micrographs observed at the SEM.

Micrograph	Morphology	Origin
1b (Filter 01, zone 2)	Ovoid shape, smooth surface.	Mobile sources, mainly from Venustiano Carranza and Cuauhtemoc districts.
2b (Filter 01, zone 2)	Undetermined shape, rough surface.	Mobile sources, mainly from Venustiano Carranza and Cuauhtemoc districts.
5b (Filter 05, zone 2)	Spheroidal shape, Smooth, depressed surface.	Mobile sources, mainly from Venustiano Carranza, Cuauhtemoc and Benito Juarez districts.
5b (Filter 05, zone 3)	Ovoid shape, smooth surface.	Mobile sources.
7b (Filter 07, zone2) D1	Spheroidal shape, slightly rough surface.	Mobile sources.
7b (Filter 07, zone2) D2	Spheroidal shape, smooth surface.	Mobile sources.
7b (Filter 07, zone3)	Undetermined shape, rough surface.	Mobile sources.
7b (Filter 07, zone3)	Undetermined shape, porous surface.	Resuspended dust.
8b (Filter 08, zone2)	Undetermined shape, porous surface.	Resuspended dust.
8b (Filter 08, zone3)	Undetermined shape, porous surface.	Mobile sources.
10b (Filter 10, zone2)	Undetermined shape, porous surface.	Mobile sources.
11b (Filter 11, zone3)	Spheroid shape, rough and porous surface.	Mobile sources.
13b (Filter 13, zone2)	Ovoid shape, smooth surface.	Mobile sources.
19b (Filter 19, zone3)	Particles agglomerate, rough surface.	Mobile sources.
23b (Filter 23, zone3)	Spheroid shape, rough and porous surface.	Mobile sources.
25b (Filter 25, zone3)	Undetermined shape, rough and porous surface.	Stationary sources, mainly in the Naucalpan zone.
27b (Filter 27, zone3)	Undetermined shape, rough and porous surface.	Mobile sources.
29b (Filter 29, zone3)	Undetermined shape, rough and porous surface.	Mobile sources.

$PM_{2.5}$ characteristics have been obtained from literature [5–7]. In 2008, $PM_{2.5}$ emissions in the ZMVM were estimated as 5499 ton/year. Main generators of these emissions (36%) were heavy duty vehicles and buses because of the use of bad quality fuel. Light duty vehicles emissions represent 9% of the total because of their large number. Among area sources, unpaved roads contribute with a 21% and, finally, point sources, generate 16% of the total. Here, non metallic minerals and energy production sectors are the major emitters, as well as industries such as cement and flour plants [8].

The State of Mexico concentrates 50% of the industry of the ZMVM. It is the entity that contributes with most of the point sources $PM_{2.5}$ emissions to the total [9].

On Figure 4, $PM_{2.5}$ concentration variation with wind speed and relative humidity is presented.

Lowest $PM_{2.5}$ concentration (6.44 μg/m^3) may be due to non collected particles because of their coagulation, caused by meteorological conditions, and later deposition outside the sampling device.

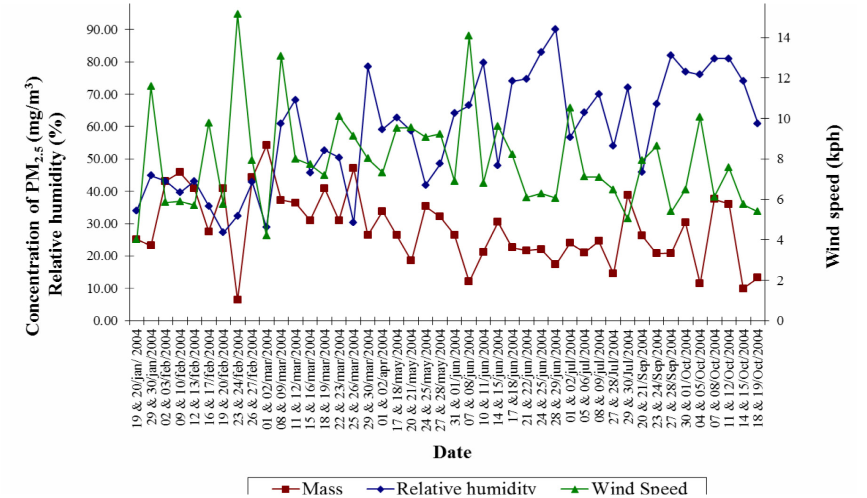

Figure 4: Concentration of $PM_{2.5}$ with wind speed and relative humidity.

4 Conclusions

$PM_{2.5}$ concentration is affected by meteorological conditions. Lowest $PM_{2.5}$ concentration is reported when there are high humidity and wind speed conditions because particles are wind dragged, coagulated with humidity and deposited outside the sampling device.

Therefore, high $PM_{2.5}$ concentrations are observed with relatively low wind speed and low humidity. On the other hand, $PM_{2.5}$ morphology is relatively uniform (spheroid or ovoid shape) since most of these particles have been produced in combustion processes.

Among observed metals, those which present the major proportions (as atoms percentages) are Fe, Zn and Pb, all of them likely coming from metal and metallurgical processes stationary sources.

References

[1] Minivol PM10 and PM2.5 Sampler, Model No. G10557PM10, Serial No. P5018, Calibrated with Rootsmeter S/N 9323995, Thermo Andersen 2003.
[2] M. Grágeda and S. Montesinos, Aplicaciones de Microscopía Electrónica de Barrido, Universidad de Chile.
[3] H. Rehme; H. Oppoizer; H. Fuchs; (1990) Particle Beam Microanalysis, 3a ed., VCH, Weinheim, Estados Unidos de América.
[4] McDonald Rafael, Patrim Biswas, (2004) “A Methodology to Establish the Morphology of Ambient Aerosols”, Journal of the Air and Waste Management Association, volume 54, p. 1069.
[5] Chow, J.C.; Watson, J.G.; Edgerton, S.A. and Vega, E.; (2002) “Chemical composition of $PM_{2.5}$ and PM_{10} in Mexico City during winter 1997”, Science of The Total Environment, volume 287, p. 177.
[6] Vega, E.; Reyes, E.; Ruiz, H.; García, J.; Sánchez, G.; Martínez-Villa, G.; Gónzalez, U.; Chow, J.C. and Watson, J.G.; (2004) “Analysis of $PM_{2.5}$ and PM_{10} in the atmosphere of Mexico City during 2002”, Journal of the Air and Waste Management Association, volume 54, p. 786.
[7] Weber R., (2003) “Short-Term Temporal Variation in $PM_{2.5}$ Mass and Chemical Composition during the Atlanta Supersite Experiment, 1999”. Journal of the Air and Waste Management Association, volume 53, p. 347.
[8] Dirección de Programas de Calidad del Aire e Inventario de Emisiones, Secretaria del Medio Ambiente, Gobierno del Distrito Federal, México Inventario de emisiones de contaminantes criterio de la ZMVM 2008.
[9] Sistema de Monitoreo Atmosférico, Instituto Nacional de Ecología y Cambio Climático, Secretaría del Medio Ambiente y Recursos Naturales, Red Manual de Monitoreo Atmosférico, México 2004.