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Artigo

INHALABLE PARTICULATE MATTER CHARACTERIZATION IN A MEDIUM-SIZED URBAN REGION IN BRAZIL (SÃO JOSÉ DOS CAMPOS TOWN) — PART I: MORPHOLOGY

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In this study, the concentration and morphological characteristics of inhalable particulate material (PM10) were evaluated and associated with climatic conditions. The mean annual concentration was 11.0 μg m^{-3}, varying between 0,647 μg m^{-3} and 36.8 μg m^{-3}. Wind speed has a higher influence on PM10 dispersion, but direction was associated with particle source. During the wet period, wind speed is the main dispersion factor, while speed and direction both are important during the dry period. Based on the morphological characteristics, it is concluded that biogenic particles prevail during the rainy season and terrigenous particles during the dry period, depending on the wind direction and intensity.

Keywords: inhalable particulate matter (PM10); particle morphology; scanning electron microscopy (SEM-EDS).

INTRODUCTION

Worldwide studies on urban atmosphere composition are being conducted, focusing on source identification and searching for tools to control the amount and quality of airborne material released to mitigate its impacts not only on human health but also on urban ecosystem conservation and transboundary transport of pollutants. Particles dominating the urban atmosphere are derived from natural sources; in addition, particles are released by anthropogenic sources, which contribute significantly to air quality degradation in these regions depending on their geographical extension, inhabitants, degree of industrialization, and transportation matrix there.[1–3] Statistical models applied to data on inhalable particles indicate that the main emission sources in urban areas are vehicles and industries, although crustal elements, solid waste, and biomass burning may also contribute to air pollution.[3–6]

Studies conducted in some Brazilian urban centers have identified a high concentration of inhalable particulate matter (hereinafter referred to as PM10), which surpasses the limits set by the Brazilian national legislation on air quality: a daily mean concentration limit of 150 μg m^{-3} and an annual mean of 50 μg m^{-3}.[3,7,8] As the impacts of PM10 on human health[9] and ecosystems[10] depend strongly on the chemical composition and size distribution of these particles, studies should be conducted to determine the physicochemical characteristics of atmospheric particulate matter in diverse urban environments.

The use of scanning electron microscopy (SEM) for the identification of particulate matter has improved the understanding of the properties and source of PM10; in addition to providing detailed information on particle morphology, this technique also allows the determination of their size, mass, and chemical composition as precise as those by gravimetric methods.[11] SEM, in association with an energy-dispersive X-ray (EDS) system, can identify the source of particles as well as determine their transport through the atmosphere; the characteristics of atmospheric particulate matter are strongly influenced by their origin.[12,13] According to Breed *et al.*,[14] it is possible to correlate the morphological aspects of particles to their chemical composition and distinguish between particles generated from geological materials and those derived from combustion/industrial emission.

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Primary particles are produced from natural sources through mechanical processes such as soil dust resuspension and maritime spray of sea salt.[4,15,16] In general, particles derived from anthropogenic sources, such as industrial emissions, combustion processes, and vehicular emissions, are secondary particles.[14,17,18] These particles are formed by gas–particle transformation through condensation of gaseous precursors and consist primarily of oxides.[19,20]

Considering that most of the studies on atmospheric urban pollution were conducted in large (more than 1 million inhabitants) urban areas where limited action can be implemented to mitigate atmospheric pollution, in some regions conurbation is a fast growing process, and still there is time to take actions to mitigate atmospheric pollution, we choose to study the atmosphere over São José dos Campos, a city with about 630,000 inhabitants, which is a part of an important conurbation area between the two largest urban regions of Brazil.[16,21]

The objective of this research is to study the characteristics of PM10, based on the data from one observation point that was strategically chosen to sample regional air, to identify the potential emission sources and correlating these characteristics to rainfall height, and speed and direction of wind to establish a sensible monitoring network. This study goes beyond the atmospheric monitoring related to respiratory threats, as it investigates the ecological rationales to justify the research effort. Therefore, to achieve our objective, daily PM10 samples were obtained during the year 2010 based on a 24-hour period, which were characterized morphologically, together with the evaluation of the time series concentration by volume for seasonality effects.

EXPERIMENTAL

In this section, we describe the sampling site and collection procedure as well as the methods utilized for the characterization of PM10.

Location

The particulate matter was sampled from the city of São José dos Campos, SP, Brazil, which has a demographic density of 572.8 inhabitants per squared kilometer and a fleet of about 330,000 resident vehicles.[21] Anthropogenic derived particulate matter is produced by a variety of sources, with automotive, chemical-pharmaceutical, petrochemical, and aerospace being the main contributors.

The city municipality is located in the Paraíba do Sul river valley between the Mantiqueira and Serra do Mar rifts, with an average altitude of 600 m above sea level and a territorial area of 1,099.6 km^2 (353.9 km^2 is urban and 745.7 km^2 rural area) with approximately 52% of this area being covered under the environmental protection. In addition, major highways (including the President Dutra Highway (BR-116) that is the main link between Sao Paulo and Rio de Janeiro) with high vehicular flux cross this region, adding to the number of vehicles passing through the region every day . The climate is tropical, with a rainfall season (summer) between October and March, when approximately 70% of the annual rainfall occurs, and a dry season (winter) between June and August; the prevailing winds are from northeast to southeast. The mean annual temperature is about 21.3 °C, with a mean maximum temperature of 30 °C during summer and a mean minimum temperature of around 10 °C during winter.[22]

Sampling procedure

This study period extended from March 2010 until February 2011, covering one full hydrological year. During this period, samples were collected on a daily basis over 24-hour periods for the working days and 48-hour periods for the weekends, using a gent-stacked unit filter (SFU) sampler.[23,24] This sampler was fixed on a 1.5 m high pole and deployed on a fixed point (23° 12' 56" S and 45° 51' 33" W) at a height of approximately 20 m from the ground, on the roof of one of the buildings at the National Institute for Space Research (INPE) (Figure 1). The sampling point was chosen keeping in mind that this height will allow free air masses to move around the collector and the samples can be obtained with minimum interference from tall buildings, trees, or any other barrier;[25] in addition, samples represent the regional air better when the sampler is inside the urban mixing layer, and at the same time free from channelization and stagnation of air masses due to buildings and other urban structures.[6,26] To determine the total amount of collected matter, polycarbonate filter units were equilibrated in the working area for 24 hours and weighed before and after sampling using an analytical scale (Shimadzu-AUW220D) with a sensitivity of 10 µg.[27] The samples were then stored in polycarbonate petri dishes until analysis. Surface meteorological data at 10-minute intervals (precipitation, and wind speed and direction) were obtained for the study period from the *Stradema* website, for a weather station located at INPE.[28]

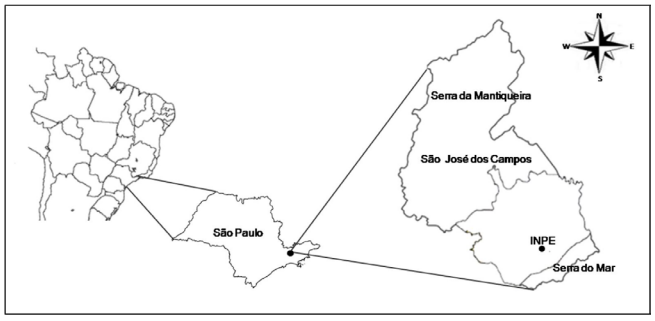

Figure 1. *Sampling site localization*

Particle characterization

To determine the particulate matter morphology, size, and elemental composition a Jeol-JSM-5310 SEM coupled with an EDS detector was employed. From the total 338 samples collected, 17 (eight from the dry and nine from the wet period) were selected for SEM analysis. These samples were chosen based on their observed mass concentration and rainfall amount during the sampling period, that is, for each month of dry and wet periods; one sample was collected after the longest dry period, one sample after the longest rainy period, one sample corresponding to the maximum month concentration value, and another corresponding to the minimum month concentration value, as well as one sample corresponding to the month median value. To evaluate the possible contribution of the filter material to the EDS results, a blank filter was analyzed.

To prepare the sample for analysis, a piece of about 1 cm^2 was cut from the filter and mounted on an aluminum stub fixed with a double-sided carbon tape, whose function was to fix and ground the sample. The sample was then coated with a thin layer of Au (10 nm thick) by spurting it for 2 minutes with a current of 40 mA and at a vacuum pressure of lower than 50 millitorr in a Denton Vacuum Desk II metalizer. The image acquisition parameters were as follows: an energy beam of 15 keV (1 µm depth) and a working distance from the detector of 10 mm. To observe the distribution of particles on the filter, it was scanned at a magnification of 500 times; next, four areas were selected randomly and images were acquired with a 1,000-time magnification. In each of the four areas, three particles were analyzed with a magnification of between 3,500 and 20,000 times; a total of 204 particles were thus examined. An EDS (Thermo Corporation) analysis was carried out for particles with similar morphological aspects, to determine their qualitative and semiquantitative elemental compositions. For these analyses, an electron beam of 15 keV with a working distance of 25 mm was used, which was standardized to 400 counts, these parameters provide the best equipment performance. The equivalent physical diameter of a particle was determined manually from all images using the ImageJ software. Based on the similarities of their morphological characteristics and elemental composition, particles were classified into four groups. The data were analyzed statistically using statigrafics© software.

RESULTS AND DISCUSSION

In this section, we first present the results of particulate matter mass concentration, followed by discussions on its morphology and the effects of wind direction and speed on it.

Atmospheric particulate matter

The PM10 monthly geometric mean concentration values (in µg m^{-3}) and monthly precipitation height (in mm) for the studied period (March 2010–February 2011) are presented in Figure 2. It is well known that particle mass frequency distribution follows a log-normal distribution function instead of a normal one; therefore, geometric mean is the appropriate statistical measure to describe the mean concentration value. Hence, our study is primarily based on the geometric mean values; however, when necessary, e.g. for comparison

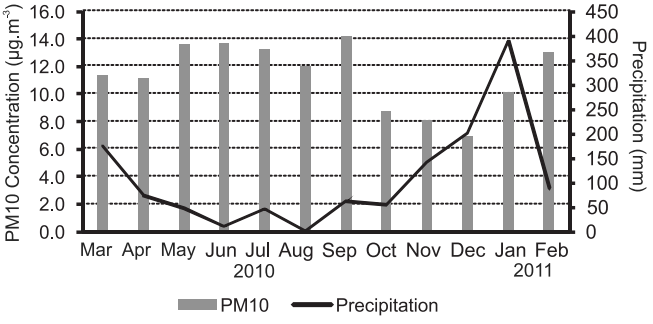

Figure 2. *Monthly PM10 geometric mean concentration values (mg m^{-3}) and monthly precipitation height (mm) for the period March 2010–February 2011*

with the results of other researchers, arithmetic means have also been used.[25] As expected, from Figure 2 it can be observed that the annual concentration of particulate matter has an inverse relationship with the rainfall amount, as the suspended matter is washed out by rain. This process is more pronounced during the rainy season (October–March) than during the dry season (April–September).

The statistics for this data set are presented in Table 1. A comparison between the geometric mean values of particulate matter observed during dry and rainy periods showed a statistically significant difference, with a P-value of 0.0000 and an F-test value of less than 0.05, at the 95.0% confidence level, as can be seen from the box-and-whisker plot (Figure 3). Therefore, it can be inferred that the mean values of particulate matter during these periods are influenced by seasonal factors such as rainfall amount, and wind direction and speed.

Table 1. Statistics for the PM10 sampled between March 2010 and February 2011 for the total, wet, and dry periods

	Total Period	Wet season	Dry season
N	338	163	175
ART(μg m^{-3})	12.9	10.4	15.2
GEOM (μg m^{-3})	11.0	9.22	12.9
STD (μg m^{-3})	7.14	5.00	8.07
MIN (μg m^{-3})	0.647	0.647	2.57
MAX (μg m^{-3})	36.8	27.5	36.8

Concentration is expressed in units of μg m^{-3}. ART = arithmetic mean; GEOM = geometric mean; MAX = maximum value; MIN = minimum value; N = sample number; STD = standard deviation.

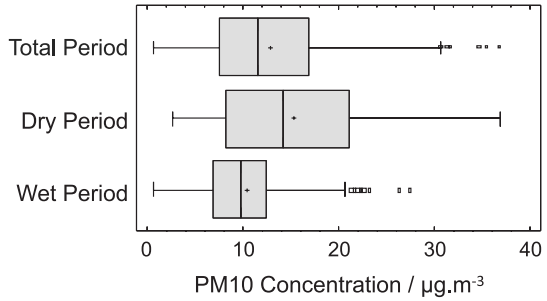

Figure 3. *Box-and-whiskers plot for the PM10 concentration (mg m^{-3}) for the total, wet, and dry periods*

The observed annual geometric mean concentration (11.0 μg m^{-3}) and the maximum daily (24 hours) value (36.8 μg m^{-3}) of particulate matter are within the limits established by the World Health Organization (20 μg m^{-3} per year and 50 μg m^{-3} for 24 hours).[29]

Table 2 presents the data on PM10 concentration for different days of the week, including the P-value and R-ratio of the F-test resulting from the multiple sample comparison analyses applied to the six variables (days of the week). The box-and-whisker plot for PM10 concentration in Figure 4 shows no statistically significant difference between the pairs of these six variables at 95.0% confidence level for the dry and total periods. However, the P-value of the F-test is less than 0.05 for the wet period, indicating a statistically significant difference among the means of the six variables at the 95.0% confidence level. To determine the pairs with statistically significant differences at the 95.0% confidence level, a multiple range test was applied to these data; the results showed that the concentration values differ between Monday and Friday, Tuesday and Friday, and Friday and the weekend days (Saturday + Sunday).

Unlike the results of other studies conducted in São José dos Campos, which pointed out that PM10 concentration was higher during week days than during the weekend due to less vehicular emissions in the latter period, we observed no statistically significant difference between working and weekend days for the whole year, except for during the wet season and on Fridays.[30] We expected to observed lower concentration values during weekends due to less traffic, as pointed out by other investigators. Nevertheless, this hypothesis was not fully confirmed, which allowed us to hypothesize that the atmosphere of this region is largely influenced by the number of vehicles passing the crossroads during specific periods of the year. For example, an increase in vehicular emissions was observed near the main road junction (less than 2 km) with a high traffic toward the coast during the school summer vacation.

Wind characteristics also contribute to the accumulation/dispersion of particulate matter, as pointed out by Liu and Harrison, who observed that wind at an increased speed can disperse the inhalable particles, reducing their local concentration.[31]

To investigate the effect of wind on the particulate matter in São José dos Campos, the wind direction and speed were estimated for the whole sampling period as well as for the wet and dry season separately. Figure 5 shows the distribution of wind speed by source of wind direction for the dry and wet seasons. As can be seen from these graphs, winds are evenly distributed throughout the southeastern hemisphere during the dry season; however, the dominant ones are southeasterly. During the wet season, wind comes from the southwestern quadrant, the prevailing ones being from west.

Therefore, to investigate the effect of wind on PM10 concentrations (expressed by volume), we first performed general variance analyses to examine the components of wind speed and direction. The variance component analysis of PM10 concentration (expressed by volume), considering the abovementioned factors, gave an attributed variance to the wind speed and direction of 81% and 19%,

Table 2. Geometric mean (GM) concentration values and standard deviation (STD) (μg m^{-3}) for the PM10 on working and weekend days for the total, wet, and dry periods and variance analysis result (ANOVA)

	Total period			Rainy period			Dry period		
Week day	Count	GM	STD	Count	GM	STD	Count	GM	STD
Mon	25	13.6	8.0	21	**8.07**	4.32	46	10.7	7.34
Tue	26	12.3	10.1	21	9.06	3.52	47	10.7	8.33
Wed	26	13.6	7.62	20	9.87	4.09	46	11.8	6.71
Thu	26	15.5	8.86	21	10.8	5.29	47	13.2	7.98
Fri	26	15.01	8.34	22	**12.4**	7.32	48	13.7	7.953
Sat + Sun	23	12.6	6.53	21	**8.60**	2.89	44	10.5	5.68
ANOVA									
F-ratio	0.59			3.57			1.97		
P-value	0.7060			0.0048			0.0832		

A bold figure indicates a statistically significant difference.

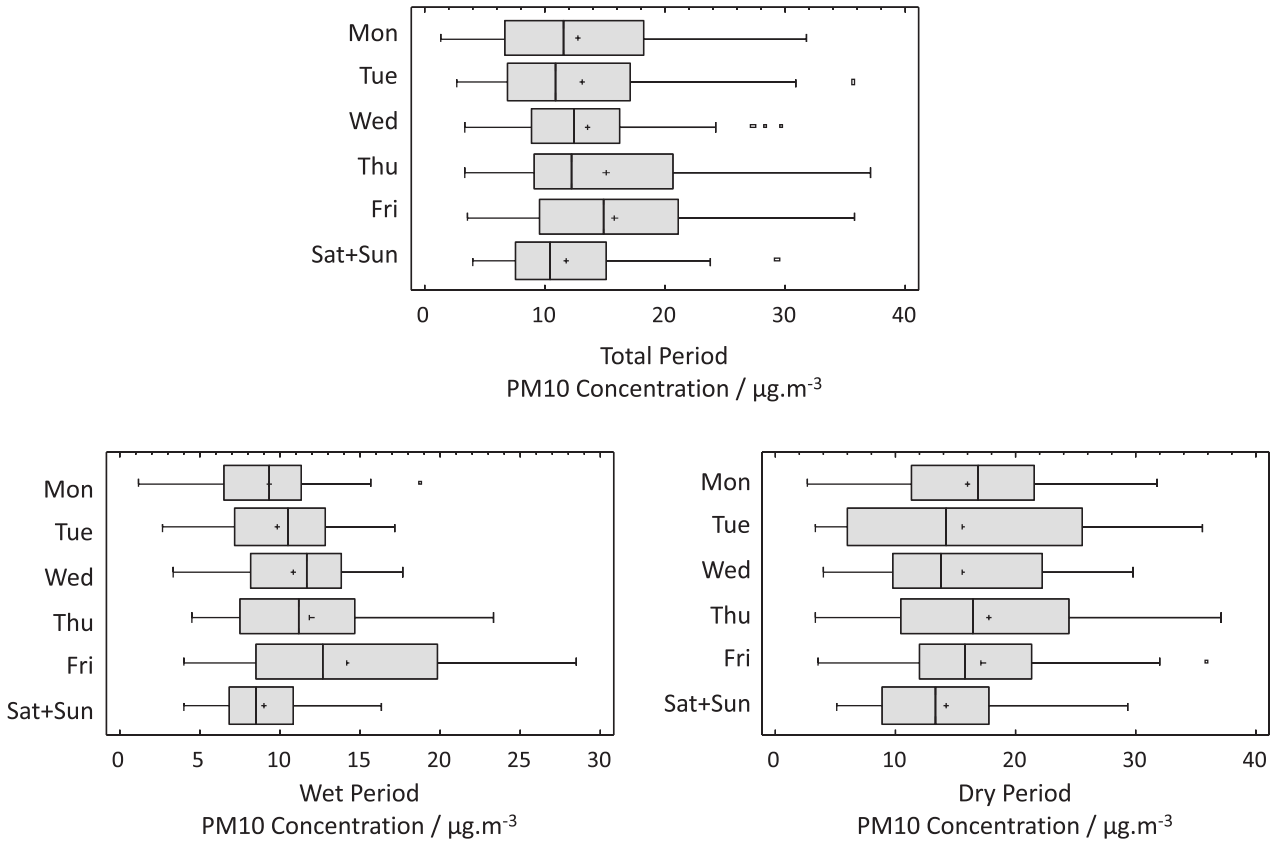

Figure 4. *Box-and-whiskers plot for the PM10 concentration (mg m^{-3}) for each working day of the week and for the weekend (Sunday + Saturday) for the total, wet, and dry periods*

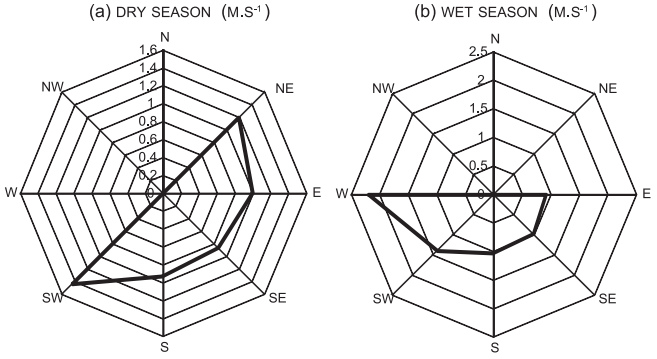

Figure 5. *Distribution of wind speed (m s^{-1}) by the source of wind direction for (a) dry and (b) wet seasons*

respectively, for the wet season and of 89% and 11% for the dry season. Therefore, wind speed has a higher influence on PM10 dispersion than its direction, although direction can be associated with some specific particle characteristics such as its source.

Hence, assuming that wind speed is the main determinant of PM10 dispersion, a multifactor analysis of variance (ANOVA) was carried out to determine the factors that have statistically significant effect on PM10 concentration during the wet and dry seasons. For this analysis, wind direction was divided into eight components (N, NE, E, SE, S, SW, W, and NW) and wind speed into components with 0.5 m s^{-1} intervals. The analysis for the wet season gave P values of 0.0748 for the wind direction and 0.0366 for wind speed; as the value for wind speed is less than 0.05, only this factor has a statistically significant effect on PM10 concentration at the 95.0% confidence level. For the dry season, the P values were 0.0003 and 0.0240 for the wind direction and speed, respectively; since both P values are less than 0.05, both the factors have a statistically significant effect on PM10 concentration at the 95.0% confidence level.

To complement the previous analysis, a multicomparison procedure was applied to the diverse wind components, and the results are presented in Figure 6a as a scatterplot by level code and in Figure 6b as mean values of PM10 concentration at 95% confidence interval (Tukey HSD) associated with both wind direction and speed components for each seasonal period.

These figures show that only three wind direction components for both seasons affect PM10 concentration in the study significantly, as have been shown in the wind speed distribution diagrams of Figure 5. Similarly, only three values of speed components are dominant, which are between 1 and 3 m s^{-1}. No statistically significant differences were observed between any pair of PM10 mean concentrations (distributed according to the wind components) at the 95.0% confidence level associated with wind direction and speed factors for the wet season. However, statistically significant differences were observed between the PM10 mean concentrations pairs (E–SW), (S–SW), and (SE–SW) at the 95.0% confidence level associated with wind directions as well as with wind speed components within the 1–2 m s^{-1} interval.

These results indicate that for the considered sampling site, the wind directions associated with the PM10 source are SE and SW for the dry and wet season, respectively, and that the wind speed components associated with the full range concentrations are between 1 and 3 m s^{-1} for both seasons.

Like other studies in São José dos Campos, this one was also based on single-site sampling point, and our results indicate an improved atmospheric condition as the observed particulate matter concentration (expressed by volume) was lower than the observed values for the year 2004.[30] However, it is necessary to emphasize that the observed lower values can also be a result of diverse climatological

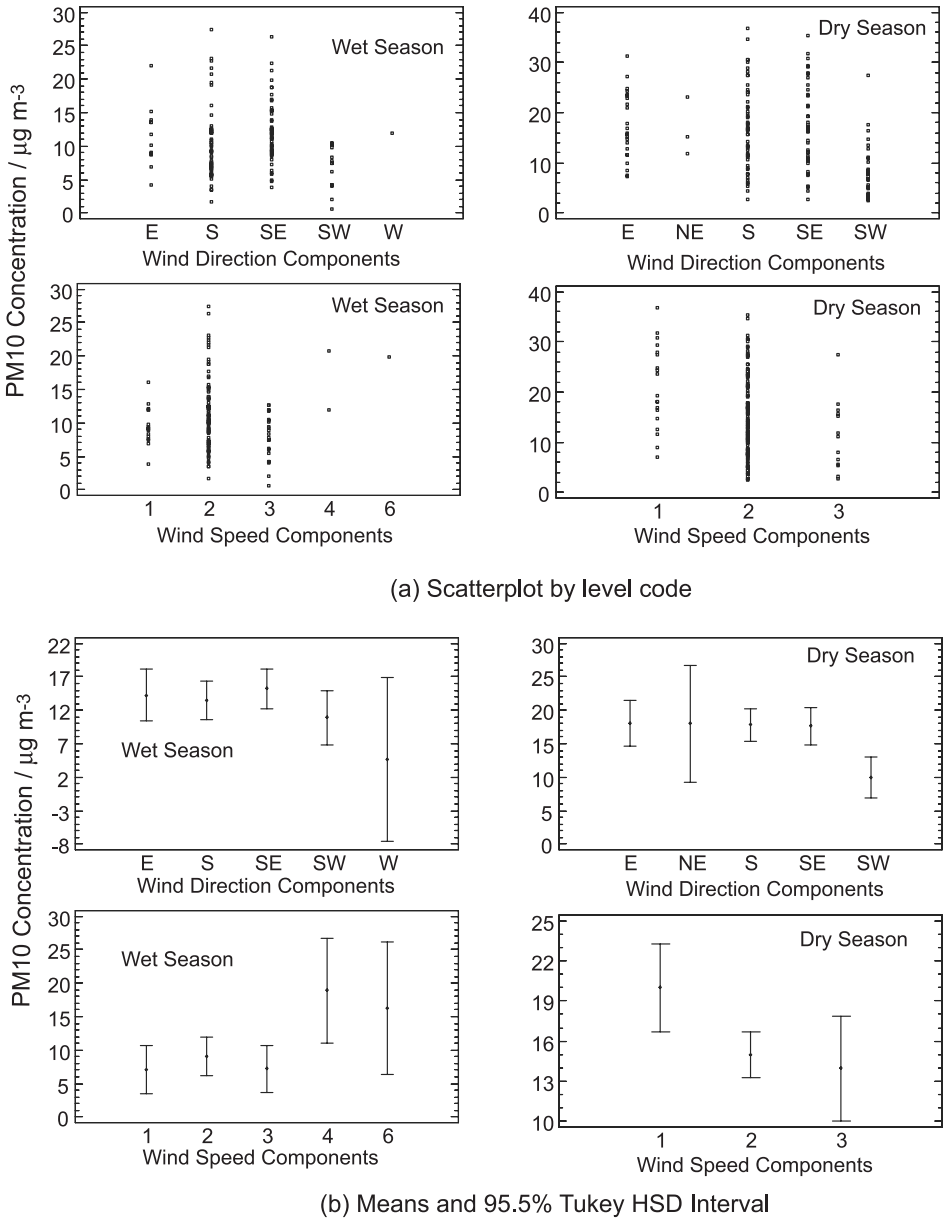

Figure 6. *(a) Scatterplot by level code and (b) means and 95.5% Tukey HSD interval for the wind direction and speed (m s^{-1}) during wet and dry seasons*

conditions, as the total rainfall height during this work (1,650 mm) was 30% higher than that for the year 2004 (1,126 mm). Another factor is the height of the sample collector: our collector was placed approximately 20 m above ground, as reported in other works,[6] where in the previous work at the same area the collector was installed not more than 1.5 m above ground; this difference in height can account for a difference in concentration of up to 30% due to the effect of surface roughness on atmospheric mixing at the ground level.[30,32]

Research studies concerning atmospheric pollution and monitoring network for PM10 in Brazil were conducted mainly at large urban center such as São Paulo city, Rio de Janeiro, Porto Alegre, Curitiba, and Belo Horizonte.[4,6,16] The environmental agency responsible for atmospheric monitoring and air quality for São Paulo state (Companhia Ambiental do Estado de São Paulo—CETESB) has a monitoring network for atmospheric pollution control in São Paulo city. However, in less populated urban centers, such as São José dos Campos, generally only one monitoring point exists for determination of particulate mass and soot concentration. Therefore, medium--size urban centers lack proper measurement strategies; hence, the physicochemical characteristics and the main dispersion factors of PM10 at these centers are not yet clearly understood.

Particle morphology

In general, large urban centers host many industries and have high vehicular traffic, and according to the morphological characterization based on these sources, the particles are round shaped, with high density, and frequently consisting of carbon and various metals.[13]

In the present study, morphological characterization results allowed us to classify the observed particles into four groups whose morphology and elemental composition were associated with the origin of these particles: (a) terrigenous, (b) biogenic, (c) soot, and (d) crystalline (Figure 7). Due to the presence of carbon in the collected sample, the elemental composition spectra were only qualitative and semiquantitative. The analysis of carbon-rich particles was possible due to its strong signal and characteristics specific to organic and soot particles. Gold (Au) peaks found in the spectrum must be ignored, as they come from the metallization process. Seasonal differences

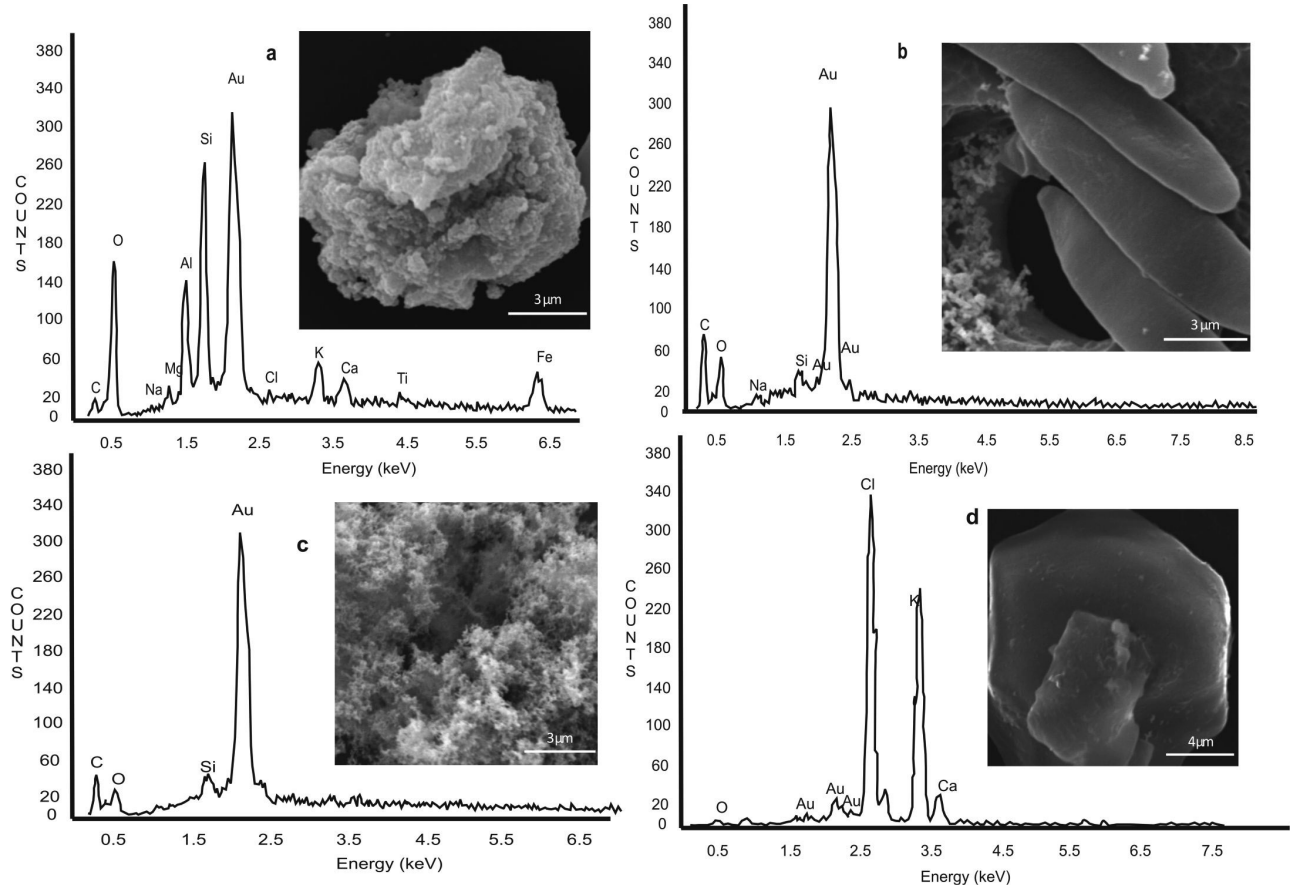

Figure 7. *Examples of SEM images and spectrum for the four identified particle groups: (a) terrigenous, (b) biogenic, (c) soot, and (d) crystalline*

between particle groups were statistically evaluated only for terrigenous and biogenic groups, because they were the ones with enough observations.

Terrigenous particles: This particle group is the prevailing one in the analyzed set; these particles have irregular shapes, some of them are rough and others are smooth with sleek laminar shapes resembling a schistous structure. The EDS spectrum identified the existence of several elements such as C, O, Si, Mg, Ca, Fe, Ti, Al, K, Ba, and Na with fairly varied composition in this group. Oxygen (O), iron (Fe), silicon (Si), and aluminum (Al) were the dominant elements for both rough and schistous particles (Figure 7a). These elements reflect the soil mineralogy, indicating that their main source can be natural and derived from soil. No seasonality was observed for these particles and their average diameter was around 10 µm. No statistically significant difference was observed between the means of the two samples at the 95.0% confidence level. The terrigenous particles comprise the main particle group in the studied samples; most of them were found as individual particles and some appeared as nucleation of small particles atop the large ones, which is an attribute of coarse particulate. These particles are in general found in natural or slightly polluted environments. According to Srivastava *et al.*,[13] the particles in natural areas are flat like a blade as a result of rocky erosions, and their composition reflects the soil chemical elements known as mineral dust. Among these particles, diverse mineral fragments with irregular crystallization, such as quartz (Si, O), calcite (C, O, Ca) and dolomite (C, O, Ca, Mg); those with better crystallization such as feldspars (Si, Al, Na, K); and phyllosilicates (Si, Al, K, Fe) that are schist like in shape are also observed.[1]

Biogenic Particles: The second identified group on the examined samples consisted of biogenic particles rich in carbon, as indicated by its strong signal on the EDS spectrum.[33] These particles are rounded and cylindrical in shape and have regular borders; many of them presented a wilt aspect, and their average diameter was about 7 µm for both analyzed periods. The obtained EDS spectrum showed carbon (C) and oxygen (O) as the main elements, which are characteristic of organic biogenic particles that can be identified easily (Figure 7b). These particles were observed mainly in the rainy season samples, indicating a seasonal pattern for this particle class. No statistically significant difference was observed between the mean values of the two samples at the 95.0% confidence level.

Soot particles: These particles have a spongy aspect and are formed by well-defined small spheres with size in the order of nanometers; they are united in chains, forming a mass of amorphous agglomerates, which give rise to larger particles. Due to the structural complexity of these particles and their composition being dominated by carbon (C) and oxygen (O), it was not possible to determine their equivalent diameter (Figure 7c). The soot particles appeared as large clusters of small spheres united by chains. Bourotte *et al.*[34] found similar results in their studies of the São Paulo city atmosphere, where soot particles were identified as very small particle clusters with spongy aspects that were rich in carbon. Such particles are known to be produced by anthropogenic sources such as vehicular and industrial emissions. According to Murr and Bang,[35] burning of fossil fuels emits ultrafine (of the order of nanometers), carbon-rich particles into the atmosphere, which can evolve as aggregates forming larger particles, called carbonaceous particles. Because these particles are rich in elemental carbon or black carbon, they can absorb solar radiation effectively and, therefore, may impact the radiation balance on earth's surface. Studies by Yue *et al.*,[36] in Shanghai (China), have shown that metallurgical industries, vehicular emission, and coal burning were the main sources of fine particulate matter, with soot and ash being the prevailing type of particles. These authors

Table 3. Particle's group, main wind direction, relative percentage (%), mean speed, maximum speed direction, and maximum speed intensity (m s^{-1}) for selected days of the analyzed particles

Date	Particle group	Wind main direction	Relative percentage (%)	Wind mean speed (m s^{-1})	Maximum wind speed direction (m s^{-1})	Maximum wind speed intensity (m s^{-1})
Wet period Mar/10/2010	TER	NE	45	0.510	W–NW	1.86
Mar/12/2010	BIO/TER	W	20	1.45	W–NW	1.37
Mar/15/2010	BIO/TER	SW	32	0.510	W–NW	1.06
Mar/20/2010	BIO/TER	NE	26	2.81	W–NW	1.36
Mar/25/2010	BIO/TER	SW	38	0.900	N–NW	1.05
Jan/5/2011	BIO	NE	38	0.930	N–NW	0.988
Jan/14/2011	BIO/TER/soot	SW	22	0.512	W	0.791
Jan/26/2011	TER/soot	W	19	0.695	NW	1.27
Jan/31/2011	BIO/TER	NE	32	0.756	NW	1.12
Dry period Jul/8/2010	TER	SW	46	0.658	NW	1.55
Jul/9/2010	TER	SW	23	0.776	NE	1.11
Jul/15/2010	BIO	SW	41	0.753	NW	1.02
Jul/27/2010	TER/soot	SE	31	1.08	N	1.16
Aug/13/2010	TER	SW	46	1.46	NW	2.12
Aug/16/2010	TER/soot	E	21	1.41	SE	1.897
Aug/24/2010	TER	SW	21	0.541	NE	1.31
Aug/20/2010	TER	SW	50	1.50	NW	1.801

BIO = biogenic; TER = terrigenous.

associated coal burning and metallurgical industries with ash particles that are spherical in shape and have Si, Al, Mn, Fe, K, Ca, and S as the main constituents.

Crystalline particles: Considering the whole selected data set for morphological study, this class contained the smaller number of observed particles. They present particles of cubic and octahedron-like crystal shapes with well-defined faces and diameter of 2 μm; chloride (Cl) and potassium (K) are the main chemical elements (Figure 7d). Probably they originate from sea salt crystals such as halite (Cl, In) and silvite (Cl, K), which are cubic in shape, as pointed out by other authors.[1,12]

These results showed that, in general, organic and inorganic particles were present in all analyzed samples. However, organic particles were the dominant ones during the rainy season, whereas the inorganic ones dominate during the dry season. In Table 3, the main wind direction and speed as well as the maximum speed and direction for typical days are presented, for each predominant particle group associated with the wind in the selected days. From that table it is observed that, during the dry, the prevailing wind directions were northeast, southeast, and southwest, with speed being around 1 m s^{-1}, while for the rainy season the prevailing wind direction was south–southwest, with a higher mean speed from west. The prevailing winds for the dry period were from southwest–southeastern direction, with higher mean speeds from southwest and northwest directions; the latter was less frequent but more intense. For the analyzed samples, the wind with higher speed was from west–northwest–north directions.

From the relationship between the particle group and wind characteristics (direction and speed) for each sample, we observed that organic or biogenic particles were found mainly on days with winds flowing from northwest toward the sampling site. This direction is associated with the Mantiqueira ridge, a natural area of Atlantic forest, which may explain the predominance of organic particles. The particulate matter with more inorganic components was found when the prevailing winds blew from southwest and southeast regions, which are associated with the urban region.

In the present study, seasonality pattern is observed for the particle group distribution along the year: the biogenic particles prevail during the rainy season and terrigenous particles during the dry period, which can be related to the wind direction and intensity for each period. During the dry period, the prevailing winds have a speed of approximately 1 m s^{-1} and are from S, SE, and E, blowing from the urban region toward the sampling site. On the other hand, during the rainy period, although the prevailing winds were from SW, we observed more intense winds from SW and W, with a speed of around 1.5 m s^{-1}. For this sector, the winds blow from the Mantiqueira ridge that is largely occupied by a natural forested area, which may explain the larger amount of organic particles coming from this region.

CONCLUSIONS

This study indicates that the PM10 mean values obtained for the analyzed periods are influenced by seasonal factors such as rainfall amount and wind direction and speed. A comparison among the week and weekend days indicates that there is no statistical difference between these days for the whole year, except for during the wet season and on Fridays. Although this region's atmosphere can be influenced largely by the passing of traffic, our results indicate that this happens in specific periods of the year, such as during the school summer vacation. These results also point out that wind speed has a higher influence on the PM10 dispersion than the direction, although the direction can be associated with some specific particle characteristics such as its source. However, the seasonal pattern shows that during the wet period the speed is the main dispersion factor, while speed and direction both are important during the dry period. For this site, the components of wind direction related to the PM10 sources are SE and SW for the dry and wet seasons, respectively, and the components of wind speed related to the full range concentrations are between 1 and 3 m s^{-1} for both seasons. Morphological characterization allowed us to identify four main particle groups (terrigenous, biogenic, soot, and crystalline), whose morphology and composition were associated with the source of the particles. The group of terrigenous particles is the prevailing one in the analyzed set. Biogenic particles were observed mainly in the rainy season, indicating a seasonal pattern for this particle class; therefore, organic particles dominated during the rainy season, whereas inorganic particles dominated during the dry season. The relationship between the particle group and wind

characteristics (direction and speed) points out that particles derived from biogenic sources were found mainly on days with wind flowing from northwest toward the sampling site and therefore are associated with the Mantiqueira ridge. The particulate matter associated with inorganic component dominates when the prevailing winds blow from southwest and southeast regions, which are associated with the urban region. From the present study, it can be concluded that the biogenic particles prevail during the rainy season and terrigenous ones during the dry period, depending on the wind direction and intensity for each period.

Based on the results of this study, one can infer that PM10 concentration is below the maximum values recommended by WHO and that the air quality in São José dos Campos has improved. However, as our results demonstrate that wind speed and direction are important factors controlling the aerosol characteristics, there is a need for a more detailed study associating the transport processes within a larger geographical region with diverse climatic situations and examining the particle morphology more closely to allow a better understanding of the transformation processes to define the particle sources more accurately.

Therefore, to account for the large observed variations resulting from diverse studies and to be able to make early intervention regarding atmospheric quality, it would be of significant importance to implement a monitoring network in the urban areas that are under conurbation, to be able to estimate the regional atmospheric quality more accurately as well as to identify the areas more prone to atmospheric pollution, thereby preventing atmospheric degradation.

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REFERENCES

1. Bernabé, J.M.; Carretero, M.I.; Galán, E.; *Atmos. Environ*. **2005**, *39*, 6777.
2. Slezakova, K.; Pereira, M.C.; Reis, M.A.; Alvim-Ferraz, M.C.; *J. Atmos. Chem.* **2007**, *58*, 55.
3. Toledo, V.E.; Almeida Júnior, P.B.; Quiterio, S.L.; Arbilla, G.; Moreira, A.; Escaleira, V.; Moreira, J.C.; *Environ. Monit. Assess.* **2008**, *139*, 49.
4. Godoy, M.L.D.P.; Godoy, J.M.; Roldão, L.A.; Soluri, D.S.; Donagemma, R.A.; *Atmos. Environ.* **2009**, *43*, 2366.
5. Srivastava, A.; Jain, V.K.; *J. Hazard. Mat.* **2007**, *144*, 283.
6. Vasconcellos, P.C.; Balasubramanian, R.; Bruns, R.E.; Sanchez-Ccoyllo, O.; Andrade, M.F.; Flues, M.; *Water, Air & Soil Pollution* **2007**, *186*, 63.
7. CONAMA Conselho Nacional do Meio Ambiente, Resolução/conama/N.º 003 de 28 de junho de 1990. *http://www.mma.gov.br/port/conama/res/res90/res0390.html*, accessed date August 2010.
8. Queiroz, P.G.M.; Jacomino, V.M.F.; Menezes, M.A.B.C.; *Quim. Nova* **2007**, *30*, 1233.
9. Cao, J.; Xu, H.; Xu, Q.; Chen, B.; Kan, H.; *Environ. Health Perspect*. **2012**, *120*, 373.
10. Klumpp, A.; Hintemann, T.; Lima, J.S.; Kandeler, E.; *Environ. Pollut.* **2003**, *126*, 313.
11. Lorenzo, R.; Kaegi, R.; Gehrig, R.; Grobéty, B.; *Atmos. Environ.* **2006**, *40*, 7831.
12. Moreno, T.; Jones, T.P.; Richards, R.J.; *Sci. Tot. Environ.* **2004**, 334.
13. Srivastava, A.; Jain, V.K.; Srivastava, A.; *Environ. Monit. Assess.* **2009**, *150*, 405.
14. Breed, C.A.; Arocena, J.M.; Sutherland, D.; *Atmos. Environ.* **2002**, *36*, 1721.
15. Miranda, R.; Tomaz, E.; *Atmos. Res.* **2008**, *87*, 147.
16. Andrade, M.F.; Miranda, R.M.; Fornaro, A.; Kerr, A.; Oyama, B.; Andre, P.A.; Saldiva, P.; *Air Qual. Atmos. Health* **2012**, *5*, 79.
17. Perrino, C.; Canepari, S.; Cardarelli, E.; Catrambone, M.; Sargolini, T.; *Environ. Monit. Assess.* **2008**, *136*, 69.
18. Slezakova, K.; Pires, J.C.M.; Pereira, M.C.; Martins, F.G; Alvim-Ferraz, M.C.; *J. Atmos. Chem.* **2008**, *60*, 221.
19. Freitas, A.M.; Solci, M.C.; *Quim. Nova* **2009**, *32*, 1750.
20. Miranda, R.M.; Andrade, M.F.; *Atmos. Environ*. **2005**, *39*, 6188.
21. IBGE Instituto Brasileiro de Geografia e Estatística. *http://www.ibge.gov.br/cidadesat/topwindow.htm?1*, accessed date February 2011.
22. CEPAGRI Centro de Pesquisas Meteorológicas e Climáticas Aplicadas à agricultura, 2012. Clima dos Municípios Paulistas. *http://www.cpa.unicamp.br/outras-informacoes/clima_muni_560.html*, accessed date May 2012.
23. Hopke, P.K.; Xie, Y.; Raunemaa, T.; Biegalski, S.; Landsberger, S.; Maenhaut, W.; Artaxo, P.; Cohen, D.; *Aerosol Sci. Technol.* **1997**, *27*, 726
24. Bourotte, C.; Curi-Amarante, A.P.; Forti, M.C.; Luiz Pereira; L.A.A.; Braga A.L.; Lotufo, P.A.; *Atmos. Environ*. **2007**, *41*, 2036.
25. Vincent, J. H.; *Aerosol Sampling – Science, Standards, Instrumentation and Applications*. John Wiley and Sons: Chichester, 2007.
26. Gál, T.; Unger, J.; *Build. Environ*. **2009**, *44*, 198.
27. U.S.E.P.A. United States Environmental Protection Agency; *Compendium of Methods for Determination of Inorganic Compounds: Selection, Preparation and Extraction of Filter Material (Method IO-3.1).* In: *Ambient Air - Compendium.* Center for Environmental Research Information, Office of Research and Development, Cincinnat, OH, 1999, (EPA/625/R-96/010a). *http://www.epa.gov/ttnamti1/files/ambient/inorganic/mthd-3-1.pdf*, Accessed date April 2010.
28. FUNCATE Fundação de Ciência, Aplicações e Tecnologias Espaciais, *http://strademaweb.funcate.org.br/STRADEMAWEB*, Accessed date April 2011.
29. WHO World Meteorological Organization; *Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide: Summary of risk assessment, 2006. http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf*, Accessed date May 2012.
30. Souza, P.A.; Mello, W.Z.; Mariani, R.L.; Sella, S.M.; *Rev. Bras. Geof.* **2011**, *29*, 71.
31. Liu, Y.; Harrison, R.M.; *Atmos. Environ*. **2011**, *45*, 3267.
32. Alcaide, R. L. M., *Personal communication*.
33. Mogo, S.; Cachorro, V.E.; Frutos, A.M.; *Atmos. Chem. Phys.* **2005**, *5*, 2739.
34. Bourotte, C.; Forti, M.C.; Melfi, A.J.; Lucas, Y.; *Water, Air & Soil Pollution* **2006**, *170*, 301.
35. Murr, L.E.; Bang, J.J.; *Atmos. Environ.* **2003**, *37*, 4795.
36. Yue, W.; Li, X.; Liu, J.; Yan, L.; Yu, X.; Deng, B.; Wan, T.; Zhang, G.; Huang, Y.; He, W.; Hua, W.; Shao, L.; Li, W.; Yang, S.; *Sci. Tot. Environ.* **2006**, *368*, 916.