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Study of atmospheric particulate matter in Buenos Aires city

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Abstract

The data reported here constitute the results of the first long-term monitoring campaign of daily PM10 and PM2.5 concentration levels in Buenos Aires city. Twenty-four hour averages atmospheric concentrations of PM10 and PM2.5 were measured (not simultaneously) at a site near downtown Buenos Aires, since December 1998–September 1999. The values of PM2.5 concentrations correlate well with the concentrations of carbon monoxide (CO) during the winter period, indicating that direct traffic emissions have an important contribution to PM2.5. The data are less correlated for the case of PM10, indicating that the sources of the coarse fraction are not only traffic emissions, with an important contribution of other sources, for example re-suspended material.

Scanning electron microscopy and atomic force microscopy images of atmospheric particles on nucleopore filters are shown. Information about the ion and metal content of these particles is reported.

Keywords: Urban air pollution; Atmospheric particles; Carbon monoxide; Atomic force microscopy; PIXE

1. Introduction

Buenos Aires city and surroundings is one of the three largest megalopolises of Latin America. The population of the federal district is about 3 million inhabitants and the population of the whole urban area is about 14 million. The geographic and topologic characteristics are very different to that of Latin American cities which are considered as paradigms for urban air pollution studies, like Santiago de Chile, Mexico city and São Paulo. In contrast to these cities, which are surrounded by hills or high mountains, Buenos Aires and surroundings lie on a vast plain area, within La Plata River, (which is here around 50 km wide) and a flat sea level region, the Pampa (Fig. 1).

Considering that the atmosphere of Buenos Aires city has not been characterized yet, and that there are no systematic controls of air quality in the city by local authorities, we have started few years ago a research project toward exploring its main characteristics. These series of studies are oriented to investigate some relevant aspects, such as the levels of atmospheric pollutants and its sources, on the basis of systematic measurements. The first systematic studies of gas pollutants performed in the city using continuous measurements with fully automated equipments were reported in a first work (Bogo et al., 1999). The results of modeling the dispersion of primary gas pollutants were reported in a second article (Bogo et al., 2001).

On the basis of these works, some very well-defined facts were established, that can be used as a reference frame valid for the densely populated area. The first conclusion of relevance for the present work is that vehicle emissions are undoubtedly the main source of

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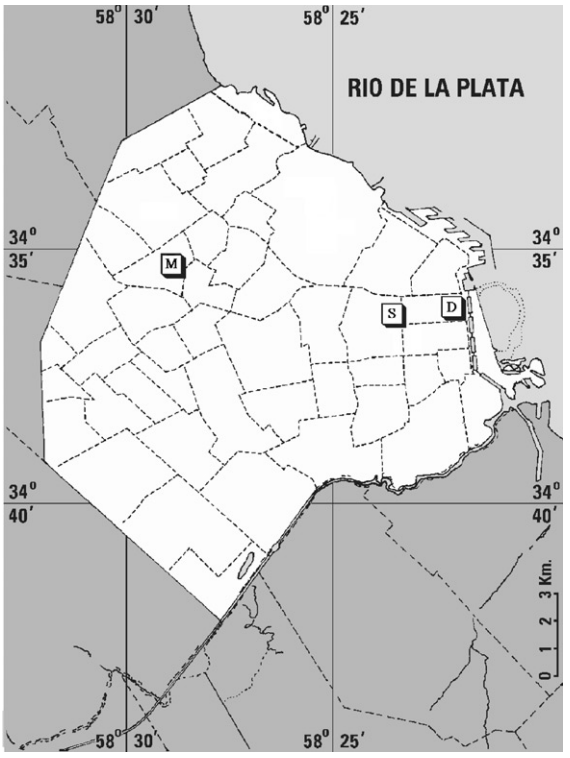

Fig. 1. Buenos Aires City and the sites of relevance to this work: S, site of measuring at Junín Street; M, meteorological station at Villa Ortuzar (National Meteorological Service); D, downtown.

carbon monoxide, CO (and also of NO_x). The concentration of CO is a result of the mixing of vehicle emissions with clean air masses. A very highly repetitive daily CO profile was obtained for periods with similar traffic distribution. The relatively high wind speed and the flat topology of the city do not allow the accumulation of pollutants during most days. Thus, the second conclusion of our previous works is that the atmosphere is cleaned up during the night when the traffic stops. Every morning a renewed atmosphere is observed (Bogo et al., 1999), except for situations of more than two consequent days of calm.

It is worth noting that the characteristics of the Buenos Aires atmosphere substantially differ of the above-mentioned cities in a fundamental aspect: there is no accumulation of gas pollutants. This is due to the relatively high average wind speed, a distinctive characteristic of Buenos Aires city in comparison to the other megalopolises. Consistently, photochemical processes due to secondary pollutants, seem to play a minor role.

Particulate matter (PM) concentrations were not measured in our previous studies, and there is a lack of information on PM in Buenos Aires. Although PM is of major concern for public health, no systematic studies were performed in the city. The main preliminary study is a short campaign supported by the World Bank during 1997, but the sampling period was only about 45 days. (The air quality situation in the Grand Buenos Aires area. World Bank Project ARG 96/019/B/01/99 Final Report November, 1997). Some studies have been performed through aerosol sampling, particularly focusing on the determination of lead concentration, which has decreased by a large factor since the introduction of unleaded gasoline (Onursal and Gautam, 1997).

Accordingly, the aim of the present work was to perform a systematic monitoring of PM during 9 months at a site close to downtown. The concentrations of atmospheric particles of diameter <10 or 2.5 μm (PM10 and PM2.5, respectively) were measured and we looked for its sources by simultaneously measuring CO levels at the site. Heavy metal and ion concentrations in the particles were determined, and different microscopies were obtained.

Hence, this work must be considered as a first attempt to cover the lack of information on PM in Buenos Aires city. The results can allow for a comparison of the atmospheric situation with respect to other relevant cities of Latin America, and try to be a benchmark for future studies in the region.

2. Experimental

2.1. Equipments

2.1.1. Sampling of particulate matter

A MiniVol (Airmetrics, Springfield, OR, USA) portable air sampler equipment was used to collect total suspended particulate (TSP), PM10 or PM2.5 (Baldauf et al., 2001; Pleasant, 1994). Impactors are available with a 10 μm cut-point (PM10) and a 2.5 μm cut-point (PM2.5). Operating the sampler without an impactor allows for collection of TSP matter.

An inlet tube downstream from the filter holder takes the air to a twin cylinder diaphragm pump. From the pump, air is forced through a standard flowmeter where it is exhausted to the atmosphere. The flow rate was 5 l/min for up to 24 h. A programmable timer turns the pump off at the end of a sampling period. The particles were collected in 24 h period. Hence, the reported values represent 24 h averages, except when indicated. The impaction inlets were used to selectively sample PM10 or PM2.5. For example, during a period of 24 h only PM10 is collected. After 24 h the impactor and the filter are changed and a new type of material (PM2.5 in this example) is collected. Therefore, although measurements were performed every day, it was never collected PM10 and PM2.5 simultaneously (1 day PM10 was collected, the next day was PM2.5). A discussion of the accuracy

associated with sampling frequency can be find in the paper of Rumburg et al. (2001).

2.1.2. Filter conditioning and weighting procedure

Different filters were used to collect the particulate material, depending on the experiments to be performed afterwards. Glass fiber filters were used for the gravimetric and ionic chromatography determinations. Nucleopore filters were used for the experiments of Particle Induced X-ray Emission (PIXE), while both types of filters, glass fiber and nucleopore, for the scanning electron microscopy (SEM).

Before the exposure, the glass fiber filters (Whatman, code #1851047, 47 mm diameter) were stored into a desiccator at room temperature in open plastic Petry dishes for at least 24 h. The desiccating material (silica gel with humidity indicator) was changed every week as routine and whenever the indicator turned pink. These filters (referred as non-exposed filters) were weighted in a microbalance (Sartorius, type XM1000P, weighting accuracy of $\pm 1\,\mu g$). Measurements were performed at room temperature. Room humidity was not controlled but was always between 30% and 50%. Filters were handled as fast as possible and for each sample three consecutive weight determinations were performed. If the difference of the three weights was $<5\,\mu g$, the average value was reported. If not, two additional measurements were performed and the average of the last three weights was reported (they were always within $5\,\mu g$). The standard deviation of obtained by this procedure was $\approx 3\,\mu g$.

After weighting, the non-exposed filters were assembled in corresponding cassettes and stored in the Petry dishes until delivery to the measuring station. Special care was put in handling, using a flat tool for assemblage. Transport to the measuring station was performed in a box, assuring that the filters remained in horizontal position. Extreme precautions were taken to avoid loss of filter material. After collecting the material the filters were stored in a desiccator for 24 h and then weighted under exactly the same conditions that the blanks.

Some non-exposed filters were transported (every week) to the measuring place, installed in the MiniVol and removed after 5 min, brought back to laboratory, and weighted again in order to test for possible material leakage after transportation. The total standard deviation, which consider the whole described procedure, was now $\approx 10\,\mu g$, which render a standard deviation of $1.5\,\mu g/m^3$ for the particulate material concentrations.

2.1.3. CO concentration

CO was continuously measured with a fully automatic Monitor Labs, ML 9830, instrument. The data are continuously acquired, stored in a personal computer, and recorded primarily as 1 min averages. The detection limit of the instrument is 0.02 ppm of CO. Other details, including the calibration procedure, are given elsewhere (Bogo et al., 1999).

2.1.4. Ionic chromatography

Only ions from PM10 material were analyzed. We have measured concentrations of Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, F^-, Na^+, K^+ and NH_4^+. A total number of 30 filters were used for the ion chromatography experiments, uniformly selected within the whole campaign period.

Glass fiber filters containing PM10 material were sonicated in a known volume of water (25 ml) during 30 min. The obtained solutions were analyzed by ion chromatography with a DIONEX DX-100 equipment. Two columns were used, AS4A (anionic) and CS10 (cationic). The detection limits for each ion are indicted in Table 1.

2.1.5. Particle induced X-ray emission

Few determinations of Fe, Ni, Cu, Zn and Pb, no related to the samples used for ions determinations, were performed by PIXE spectrometry from four filters containing PM2.5 particulate matter. The material was collected on nucleopore filters, that were used as targets of a 50 MeV ^{16}O beam produced in a Tandem Accelerator (Ozafrán, et. al, 1999). In this case, the collection time of PM2.5 was reduced to few hours in order to avoid self-absorption of the incident beam on the surface of the filters. The detection limits of heavy metals is about $2\,ng/m^3$, depending of the analyzed metal. PIXE analysis has been reported for São Paulo (Castanho and Artaxo, 2001) and Santiago de Chile (Jorqera et al., 2000; Artaxo et al., 1999).

2.1.6. SEM and AFM

SEM images were recorded with a Phillips XL-30 SEM equipment (20 kV) equipped with Energy Dispersive Differential X-ray Analysis (EDX) facility (Centro de Investigación Industrial, Fundación Para el Desarrollo Tecnológico, Organización Techint, Argentine). Nucleopore filters (policarbonate membrane kit, code #115100, of 47 mm diameter) coated with gold and glass fiber filters were used.

An AutoProbe CP contact mode scanning force microscope (Park Scientific Instruments, PSI, Sunnyvale, CA) was used for atomic force microscopy (AFM) imaging (topographic and error signal modes and scan rate between 0.5 and 2 Hz). (Köllensperger et al., 1999). Samples for AFM analysis were collected on nucleopore filters of $0.2\,\mu m$ pore.

2.2. Measuring places

The instruments for CO and PM measurements were placed since December 1998, at the beginning of the

Table 1
Anions and cations in PM10

	Mean concentration ($\mu g/m^3$)	Range concentration ($\mu g/m^3$)	Detection limit ($\mu g/m^3$)	Fraction of total mass (PM10) (%)	Reference[a] typical values ($\mu g/m^3$)
Anions					
Chloride	5.3	3.9–6.7	0.1	8	1–3
Nitrate	4.1	2.6–5.6	0.1	6	2–10
Sulfate	6.8	3.8–11	0.1	10	5–10
Phosphate	Lower than 0.2		0.2		
Fluoride	Lower than 0.1		0.1		
Cations					
Sodium	2.3	1.0–3.8	0.1	3.4	1
Potassium	0.6	0.5–1.3	0.1	0.8	0.1
Ammonium	2.6	1.9–5.7	0.2	3.9	2–6

[a] Reference = representative concentrations of individual chemical components of airborne particulate matter (taken from Airbone Particulate Matter in the United Kingdom, 1996, p. 135).

summer season, to September 1999 in a building at Junín street, in a populated area near downtown (Fig. 1). This site is referred as Junín. Measurements were performed at a horizontal distance of ≈ 4 meters from the traffic line and at a height of ≈ 15 m from the ground. This altitude is well below the mean altitude of most apartment buildings in downtown. The relevant sites are indicated in Fig. 1.

2.3. Meteorological variables

Relevant meteorological parameters, manly hourly values of temperature and wind velocity and direction, were taken into account for the analysis. Two meteorological stations are managed in the city by the National Meteorological Service. One is located in Villa Ortúzar (Fig. 1), well inside the urban area, and the other at Aeroparque, the local airport nearby the La Plata River. Data from the first station was used for the analysis at Junín. Although it is possible that some local effects could not be well represented, it has been tested that general trends, such as the seasonal variation of the monthly averaged wind speed or the calculated atmospheric boundary layer altitude, are similar when data from Villa Ortúzar or Aeroparque are considered (Mazzeo and Gassmann, 1990).

2.4. Traffic

National Transport Secretary (NTS) monitored the hourly number of vehicles at Junín Street on 7 July 1999. These measurements are in agreement with statistical data recorded by the NTS during many years at streets nearby Junín that share the same transit direction.

3. Results and discussion

3.1. Ions and heavy metals

Table 1 shows the average values of different anions and cations. The total number of analyzed samples (equal to 30) is not enough to report seasonal averages. Therefore, the averages over the total sampling period are reported for each ion. The concentrations of ions shown in Table 1 constitute the first values reported in an international journal, as there are no previous reports of ions concentration in the atmospheric particles of Buenos Aires. It can be seen in Table 1 that the concentrations are similar to that reported for cites of the United Kingdom in a series of very well-documented studies of urban aerosols (Airbone Particulate Matter in the United Kingdom, 1996). It is noted that the fractional contribution of anions to the total mass of PM10 is relatively large. For example, the sum of Cl^-, NO_3^- and SO_4^{2-} concentrations represents a contribution of approximately 24% to the total mass in PM10. It is worth noting that the levels of Na^+ and Cl^- are higher than the typical interval that we used as a reference (see Table 1). This could be an indication of possible marine characteristics in the atmosphere of Buenos Aires, that should be investigated in a more systematic study.

Although the number of analyzed filters by PIXE is very low, the results of the measurements are in excellent agreement with the previously observed decrease of Pb concentration in Buenos Aires city since the introduction of unleaded gasoline.

In fact, the group of the National Atomic Energy Commission have reported high values of Pb in urban area in 1988 (Caridi et al., 1989), in the range from 1 to 4 $\mu g/m^3$, which exceed the limits permitted by national

government regulations (1 μg/m^3). The same group reported a significant decrease 10 years later (Ozafrán et al., 1999), measuring several elements at different urban places in Buenos Aires during 7 working days and a weekend (December 1998). The daily mean concentrations average values found in that work for Pb were always <0.3 μg/m^3. The average of the four determination of Pb concentration at Junín was (0.048 ± 0.08) μg/m^3. For the case of Fe, Ni, Cu and Zn we obtained the following values: (0.086 ± 0.007), (0.004 ± 0.002), (0.007 ± 0.002) and (0027 ± 0.002) μg/m^3, respectively, which are the arithmetical averages of the concentrations on the set of the analyzed samples at Junin and the errors correspond to the standard deviations. These values are always lower than the reported ones at Birmingham in the reference work, by a factor about 2 in all cases.

3.1.1. Microscopies

The optical microscopy allows to observe only particles of area (A) in the range $3\,\mu m^2 \leqslant A \leqslant 1200\,\mu m^2$, that is of diameters ($d$) in the range $2\,\mu m \leqslant d \leqslant 40\,\mu m$ ($A = \pi(d/2)^2$). The largest percentage (in the indicated range) was obtained for particles of area $<100\,\mu m^2$, with a maximum at $\approx 7\,\mu m^2$ which corresponds to a diameter of about 3 μm if a spherical size is assumed. This seems to be similar to the particle area distribution reported by Seinfeld and Pandis (1998) for a typical urban atmosphere in the interval of areas between 3 and $1200\,\mu m^2$.

Particles of diameters in the scale of hundred nanometers where observed by SEM images. These images confirm the approximately spherical shape of the finest particles (illustrated in Figs. 2a and b). Spherical shape images were also obtained by AFM in the range 100–300 nm (Fig. 3). The SEM images show that some particles with dimension in the scale of hundred nanometers appear as grouped into agglomerates, up to 300 nm large (illustrated in Fig. 2b). The presence of these agglomerates was confirmed by other SEM images (not shown).

We have analyzed the composition of some of the collected particles by EDX (data not shown). For some of the particles the analysis reveals the presence of Al, Si, Na, K, O and Fe, in addition to carbon, indicating that the source of those particles is ground dust, composed mainly by aluminum silicates (Seinfeld and Pandis, 1998). The SEM image of one of those particles is shown in Fig. 2a.

It was determined by EDX that some particles are composed mainly by carbon, using glass fiber filters (which do not contain carbon) to collect the samples.

In conclusion, the EDX analysis is consistent with two types of atmospheric particles: ground dust and carbon particles. Their sources and relative contributions are investigated in the next paragraphs.

3.1.2. CO and traffic

A representative traffic profile at Junín is shown in Fig. 4. The traffic intensity increases since 6 am, reaches a maximum between 9 and 10 a.m., remains almost constant during the afternoon, and then slowly decreases until night. This behavior, illustrated for a particular day in Fig. 4, is coincident with statistical studies performed during many years by the NTS. The hourly averaged CO concentration and the wind speed distributions are also illustrated in Fig. 4 for a particular day that is taken as an example of the typical behavior.

It can be seen in Fig. 4 that the CO levels follow the traffic distribution at the site, modulated by the meteorological parameters. Systematic measurements of CO during the whole campaign period confirm that behavior, which is the same than that measured at Belgrano Avenue, but with different traffic profiles for both sites. The difference of traffic distribution is due to the orthogonal directions of Junín Street and Belgrano Avenue. In Belgrano Avenue the traffic goes into downtown in the morning and out of the area in the evening, and the traffic profile reflects the rush hours. On the other hand, no traffic fluctuations during the day, after rising in the morning, are expected in Junín Street as noted in Fig. 4. In spite of the differences of the traffic profiles both sites share the same characteristic: the hourly averaged CO distribution follows the traffic profile, modulated by meteorological variables. It was shown in the previous works that the meteorological variables of relevance are mainly the wind speed and direction and the altitude of the atmospheric boundary layer. In Fig. 4 are shown the hourly variations of wind speed and direction for a particular day. In that example is illustrated the general characteristic observed during the whole campaign, of decreasing CO levels with increasing wind speed at constant traffic levels.

3.1.3. Particulate matter and CO levels

The values of PM2.5 (in μg/m^3) vs. the daily averaged CO concentration (in ppm), measured since the last week of March to the last week of August 1999, are shown in Fig. 5a. In spite of the scatter, the concentration of PM2.5 seems to be linearly correlated to CO levels in the mentioned period. No correlation was observed during the summer, when a notorious increase of wind speed, atmospheric boundary layer and temperature average values with respect to the other seasons have been reported (Mazzeo and Gassmann, 1990; Bogo et al., 1999). In this case, CO remains at relatively very low levels (below 1 ppm) and no significant variation of PM with CO concentration was noted.

The main information from Fig. 5a is that a local increase of CO is correlated with an increase of PM2.5 and that this change can be observed from one sample to another (collected in different days). Since the traffic

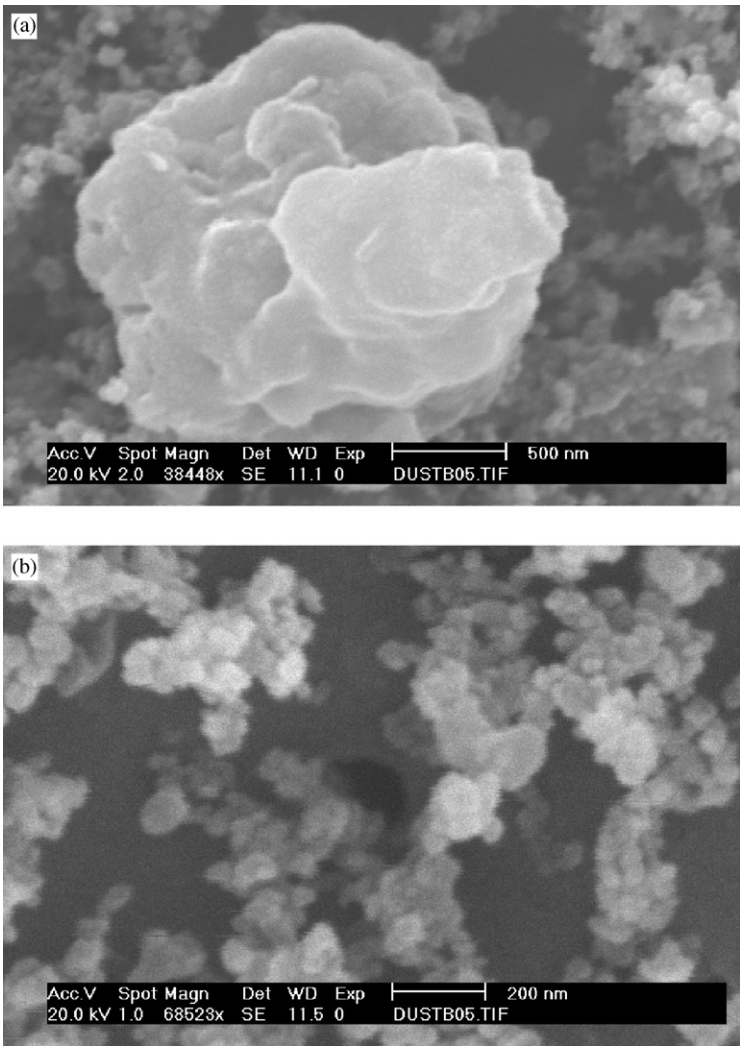

Fig. 2. (a) SEM image (38,448 ×) showing a particle whose elemental composition was analyzed by EDAX. (b) SEM image (68,523 ×) of atmospheric particles (PM2.5) collected on nucleopore filters.

intensity, as a daily average, is rather constant, Fig. 5a shows the response to different meteorological conditions. For example, the wind speed affects both the dilution of PM2.5 and CO, since both are generated locally. In Fig. 5a the points of higher levels of CO and PM2.5 corresponds to days with lower wind speed compared to those associated to low CO and PM2.5.

We made a least squares linear regression of PM2.5 as a linear function of both CO and wind velocity, V, (daily averages) for wintertime ($[PM2.5] = (30 \pm 4)[CO] - (0.7 \pm 0.7)V + (17 \pm 6)$; $R = 0.82$). The coefficient for the wind speed was very low compared to that for CO, and a 100% error was obtained for that coefficient. The same correlation coefficient was found when the wind speed was not consider ($[PM2.5] = (32 \pm 3)[CO] + (11 \pm 3)$; $R = 0.83$).

A lower correlation between PM10 and CO, in comparison to that observed for CO and PM2.5, was obtained in the autumn to spring period (Fig. 5b; $[PM10] = (30 \pm 5)[CO] + (25 \pm 4)$; $R = 0.63$). This indicates that PM10 concentrations measured in a 24 h sampling period have a more important contribution of re-suspended material than PM2.5. Note that larger value obtained for the ordinate to the origin in Fig. 5b than in Fig. 5a.

The summer scatter plots of PM vs. CO are shown in Figs. 5c and d. The seasonal scatter plots are of interest as in important issue for control actions because, as is shown in Fig. 6, high PM2.5 levels are produced in summer.

Fig. 6 shows the PM2.5 and CO monthly averaged values as a function of the month. It is shown in Fig. 6

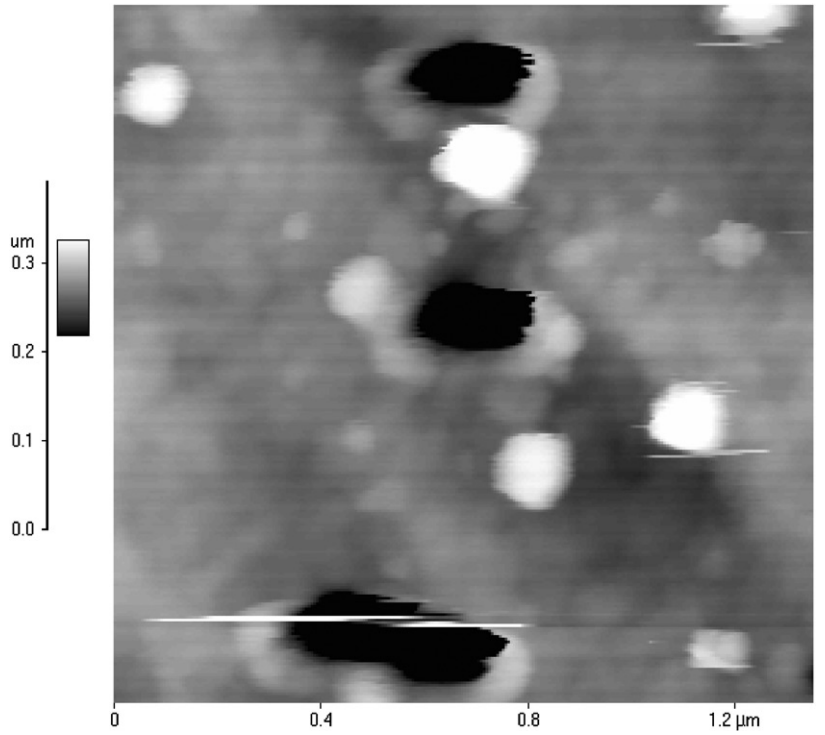

Fig. 3. AFM topographic image of particles on a 0.2 µm porous nucleopore membrane. The white spots represent the particles, while the black ones the nucleopore filter holes, respectively.

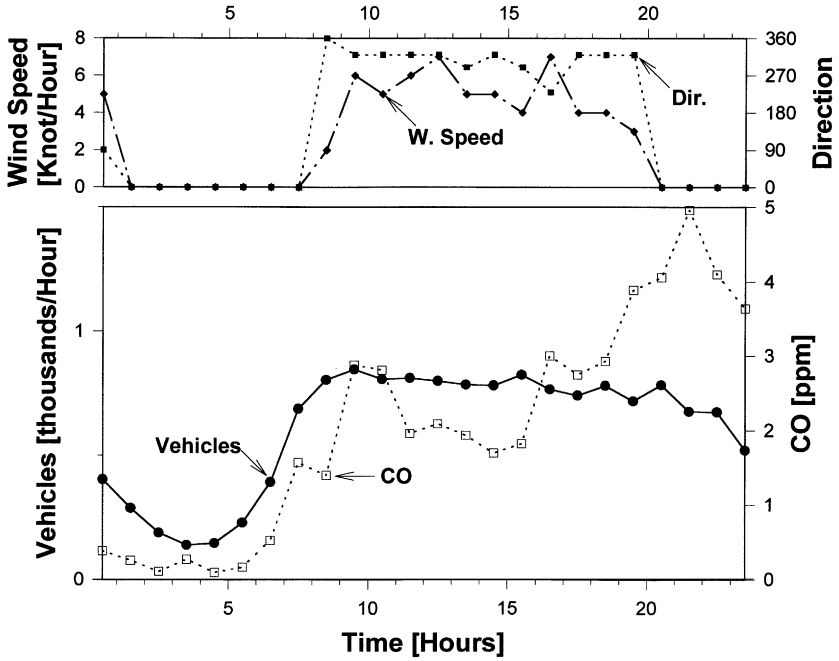

Fig. 4. CO and traffic distribution at Junín Street (7 July 1999). Values of CO are hourly averaged values (in ppm). Traffic is represented as number of vehicles per hour. Wind speed and direction are represented in the inset.

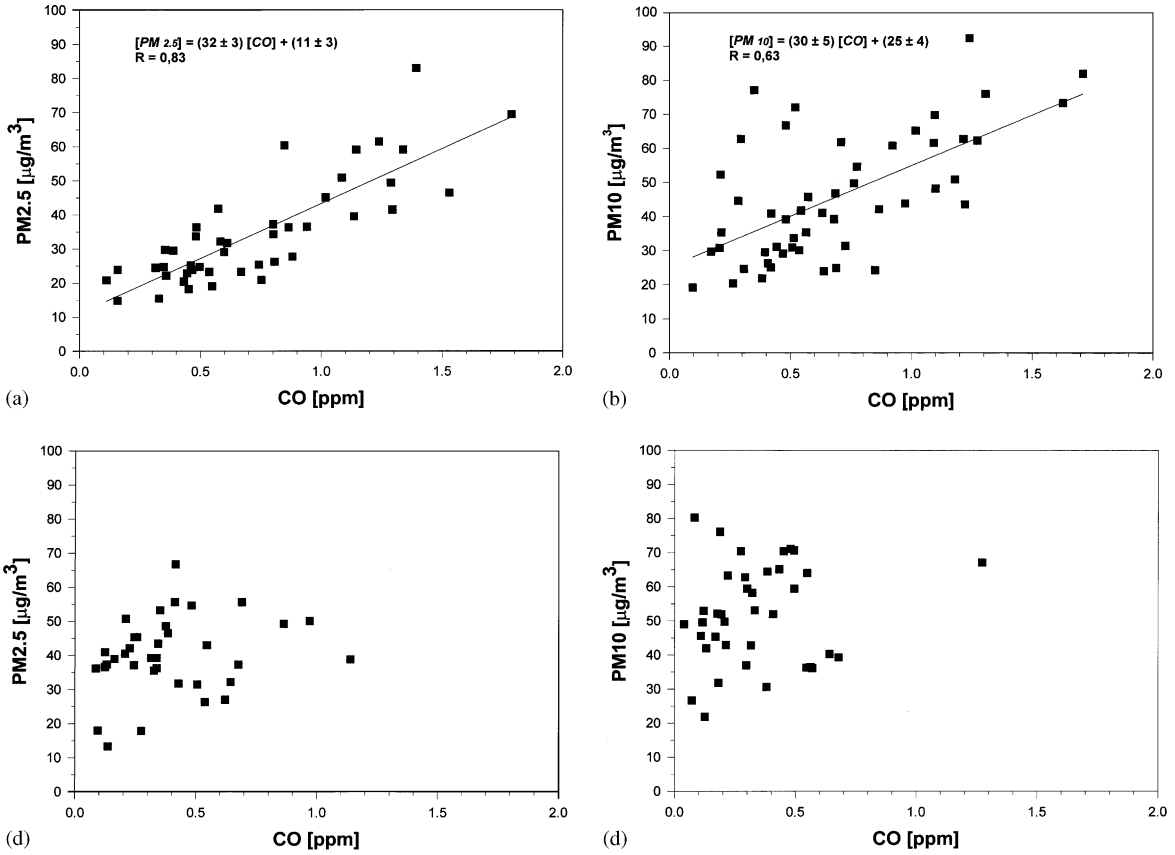

Fig. 5. (a) PM2.5 (in $\mu g/m^3$) vs. CO (in ppm) at Junín Street. Every point represents a 24 h sampling of PM2.5 and the average value of CO in the autumn–winter period. (b) PM10 (in $\mu g/m^3$) vs. CO (in ppm) at Junín Street. Every point represents a 24 h sampling of PM10 and the average value of CO in the autumn–winter period. (c) PM2.5 (in $\mu g/m^3$) vs. CO (in ppm) at Junín Street. Every point represents a 24 h sampling of PM2.5 and the average value of CO in the summer period. (d) PM10 (in $\mu g/m^3$) vs. CO (in ppm) at Junín Street. Every point represents a 24 h sampling of PM2.5 and the average value of CO in the summer period.

that while CO responds with generally higher average levels during wintertime, the PM2.5 levels are slightly higher during the summer. This suggests that there are other sources than traffic for PM2.5. An hypothesis for this is that the stronger winds during summer timer can generate more re-suspended material.

The seasonal average values of PM2.5 and PM10 are shown in Table 2. This table allows a rapid comparison with values reported for other large cities (Table 3) and with standards and recommended values for air quality control. The values are similar to that obtained in other large cities (see Table 3), and to those measured at a place near downtown during a short period campaign organized by the World Bank in June 1997. It can be seen that PM2.5 exceeds the US standards (15 $\mu g/m^3$ for annual averages) by a factor of 2, and PM10 exceeds the local standard for the Province of Buenos Aires (which is 50 $\mu g/m^3$ for the annual averages).

The histograms of the measurements and cumulative counts (percentiles distribution) are shown in Figs. 7a–d as function of PM intervals concentration for the autumn–winter and summer periods. The obtained distributions are different for summer and autumn–winter. In summer, a normal-Gaussian distribution was obtained. In agreement, the graphs of the cumulative distribution function on a probability scale (upper plot of Figs. 7a and b) are straight lines.

On the other hand, the autumn–winter distribution is clearly not normal-Gaussian, but it resembles a log-normal-Gaussian distribution. Accordingly, the cumulative distribution function on a probability scale (upper part of Figs. 7c and d) is not a straight line in this case.

3.1.4. *Relationship between PM2.5 and PM10 levels*

As PM10 and PM2.5 were not measured simultaneously, we only can compare averages and percentile distribution over a defined period. When the whole measuring period is considered, it is observed that 80% of PM10 is PM2.5. This is a result of high relevance for health aspects, as the fine particles are those of highest

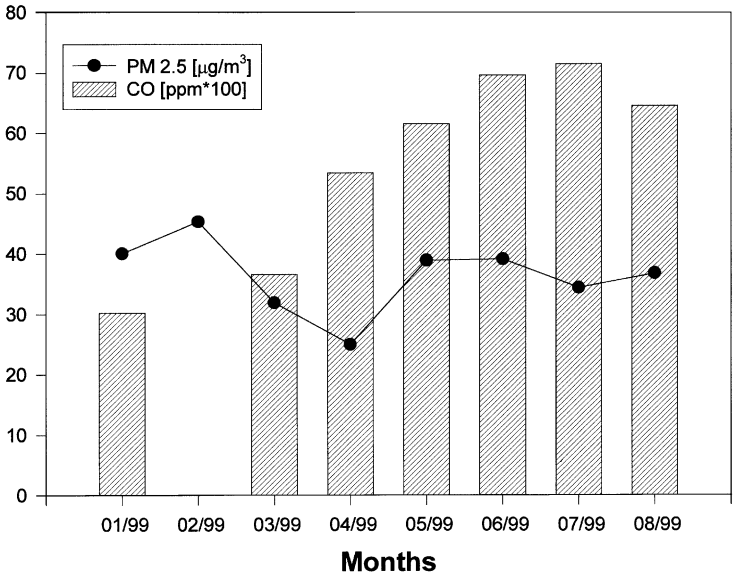

Fig. 6. Monthly average values of PM2.5 and CO for different months.

Table 2
Particulate matter in Buenos Aires City

Material	Average values[a] ($\mu g/m^3$)	Maximum recorded values ($\mu g/m^3$)	Number of collected samples
In summer			
PM2.5[b]	41 ± 9	67	45
PM10[b]	52 ± 14	80	45
TSP[c]	68 ± 22	101	21
In autumn and winter			
PM2.5[d]	33 ± 15	83	45
PM10[d]	44 ± 17	92	53

[a] The reported values are the arithmetical averages on the respective period. The standard deviations are indicated.
[b] Measured since the first week of January to the last week of March 1999.
[c] Measured during November 1998.
[d] Measured since the first week of April to the last week of August 1999.

negative impact on health and have the largest residence time in the atmosphere.

In the previous section it was mentioned that the measured concentrations are comparable to that find in other large cities. In this section we compare the obtained fractional relationship between PM2.5 and PM10, with fractional values that are calculated using statistical models developed for USA and European urban atmospheres, in order to make a more precise comparison. Therefore, we have compared the experimental relative percentages of PM2.5 and PM10 with those that are obtained using a well-described model distribution for urban particles (Seinfeld and Pandis, 1998; Jaenicke, 1993). This model has been used by Riley et al. (2002) in studies of indoor particle matter of outdoor origin. In that model the number distribution is described as the sum of three log-normal distributions:

$$n_N^0(\log D_p) = \sum_{i=1}^{3} \left\{ \frac{N_i}{(2\pi)^{1/2} \log \sigma_i} \times \exp\left[-\frac{(\log D_p - \log \langle D_{p_i} \rangle)^2}{2 \log^2 \sigma_i} \right] \right\}, \quad (1)$$

where N_i is the number concentration, $\langle D_{p_i} \rangle$ is the mean diameter and σ_i is the standard deviation of the ith mode. The volume distribution (which is proportional to the mass distribution assuming constant density) can be obtained from the number distribution. Then, if the values of N_i, $\langle D_{p_i} \rangle$ and σ_i $(i = 1, 2, 3)$ are known, the ratios PM10/TSP and PM2.5/PM10 can be calculated by integration of the volume distribution and compared with the experimental values. For the calculations, we used the values of N_i, $\langle D_{p_i} \rangle$ and σ_i suggested by Seinfeld and Pandis (1998) for urban aerosols.

The results of the integration using Eq. (1) show that 60% of TSP correspond to PM10 and 72% of PM10 correspond to PM2.5. These values are in good agreement with the experimental ones that we obtained at Junín Street for the fractional relationship between PM10 and PM2.5, considering the limitations and approximations of the model calculations. Thus, the model calculations confirm that the fractional

Table 3
Particulate matter in other cities

Site	Date	Material	μg/m^3
New York City	1977 (50 days)	TSP	70.5
Washington, DC	1976 (summer)	TSP	65
Birmingham (central)	Annual mean 1993	PM10	26
Birmingham (Hodge Hill)	1995 January–June	PM2.5	13
Liverpool	1994 annual average	PM10	25
Buenos Aires, Paraguay Street	1997, winter, downtown	PM2.5	37
	average on 28 working days	PM10	49
Buenos Aires, Isla Maciel	1997, winter	PM2.5	35
	average on 19 working days	PM10	59
		TSP	116
Buenos Aires, Isla Maciel	1997, winter	PM2.5	35
	average on 27 days (include weekends)	PM10	54
		TSP	101

Note: For the Province of Buenos Aires (not including the Federal District of Buenos Aires City) the standard for PM10 is 50 μg/m^3 for annual averages.
Source: Taken from Seinfeld and Pandis (1998); Airbone Particulate Matter in the United Kingdom (1996) and World Bank Project (1997) "The air quality Situation in the Grand Buenos Aires Area, 1997"

relationship between PM2.5 and PM10 measured at Buenos Aires are (statistically) in excellent agreement with the typical fractions reported for urban atmospheres in other cities. The results of the model calculation for TSP cannot be compared to our experimental results because TSP was measured only in 1 month (November).

4. Conclusions

The data reported here constitute the results of the first long-term monitoring campaign of daily PM10 and PM2.5 concentration levels in Buenos Aires city. The only previous reported PM data in Buenos Aires showed very few measurements of TSP levels exclusively (not discriminated in PM10 and PM2.5), measured before 1986 (Kretzschmar, 1994). Indeed, in the work of Kretzschmar it is mentioned that the situation of Buenos Aires was not clear at all due to a lack of reliable data. Thus, we expect that preliminary studies as the one reported here can be considered as reference works for further investigations of particulate matter in the region, where there is a lack of systematic studies on atmospheric particles.

The levels of ions and heavy metals are similar to those measured for West-European large cities. In statistical term, about 30% of PM10 is composed by ions of salts, mainly Cl^-, NO_3^-, and SO_4^{2-}. In particular, the levels of chloride and sodium are quite high, suggesting that probably sea salt plays some role in the atmosphere of Buenos Aires. Concerning the levels of lead, the present study confirms the observed decrease of lead concentrations down to accepted levels (1.5 μg/m^3, maximum arithmetic mean, averaged over a calendar quarter, US-EPA), since the introduction of reformulated gasoline.

It was demonstrated in a previous work that the main source of CO is the traffic emission (and also for NO_x, Bogo et al., 1999). In the present work, we have shown this fact holds at the site of Junín for one particular day, although the traffic distribution is different than the previous one.

Additionally, a linear correlation between CO and PM2.5 concentrations was found at Junin. Therefore, this work demonstrates that traffic emissions have an important impact on the PM2.5 levels. Nevertheless, traffic emission is not the only source on PM2.5, shown by the fact that a non-zero ordinate was found in autumn–winter and that the levels of PM2.5 does not decrease the same percentage than CO in summer.

Both CO and PM are strongly influenced by common meteorology. The scatter in the PM2.5 vs. CO plots for wintertime are due to the meteorological factors in each day.

Besides, the higher wind speed levels presented in summer have the effects to decrease significantly the levels of CO avoiding to observe the correlation between CO and PM2.5 in summer.

Additionally, it was observed a change of the concentration particle distribution from log-normal-Gaussian-like in autumn–winter to a normal-Gaussian-like in summer.

The spherical shape of the particles, in the hundred nanometer and micrometer scales, was confirmed by SEM and AFM images.

The PM2.5 and PM10 levels are high compared to typical North-American and West-European

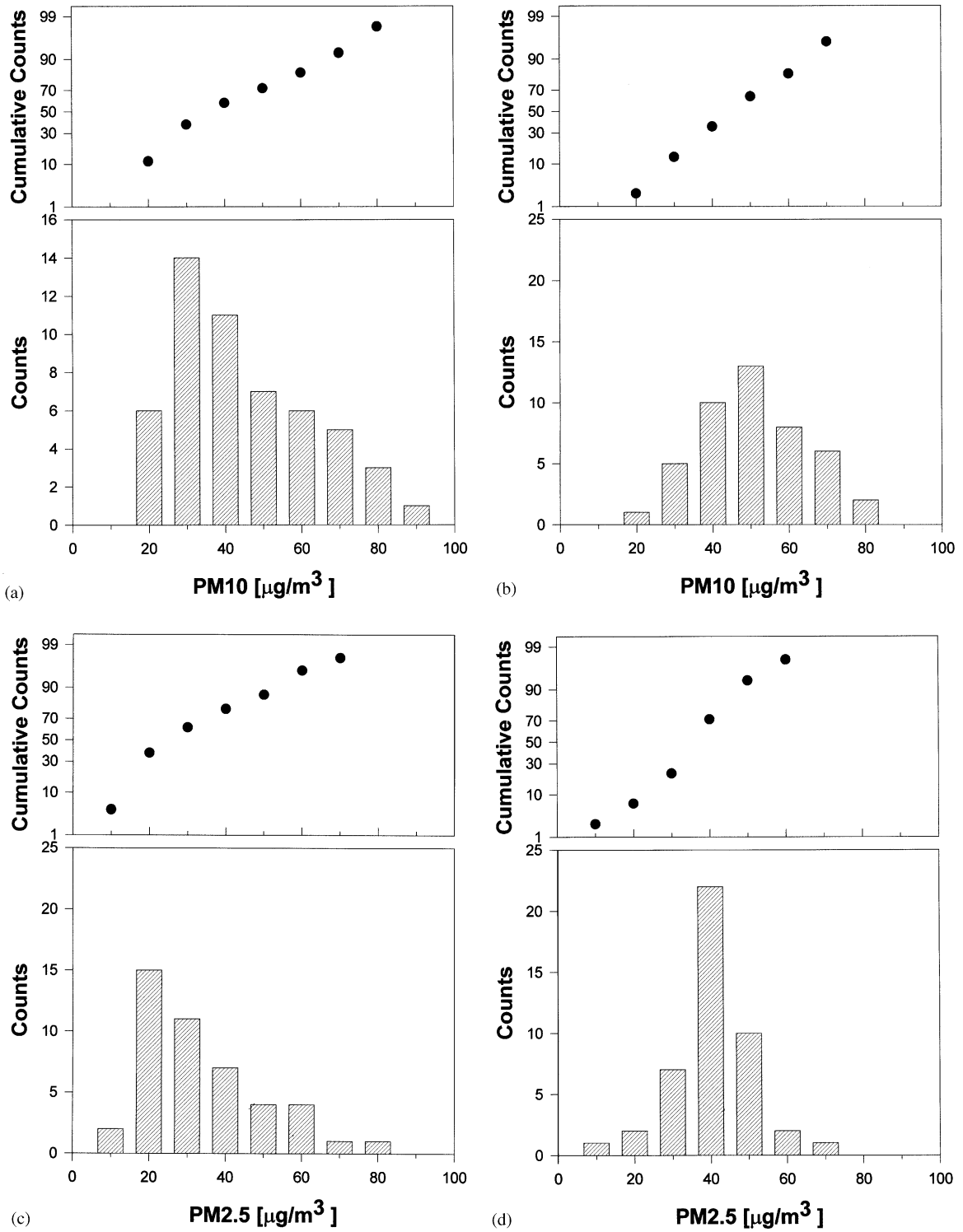

Fig. 7. (a) Histograms and cumulative counts on a probability scale (upper plot), in the autumn–winter period for PM10 (in $\mu g/m^3$). (b) Histograms and cumulative counts on a probability scale (upper plot), in summer period for PM10 (in $\mu g/m^3$). (c) Histograms and cumulative counts on a probability scale (upper plot), in the autumn–winter period for PM2.5 (in $\mu g/m^3$). (d) Histograms and cumulative counts on a probability scale (upper plot), in summer period for PM2.5 (in $\mu g/m^3$).

Table 4
Comparison between Buenos Aires, São Paulo and Santiago de Chile

	Buenos Aires (this work)	São Pablo (Artaxo et al., 1999)	Santiago de Chile (Jorqera et al., 2000)
PM2.5	33 (winter) 41 (summer)	30 (winter) 15 (summer)	40 (annual averages)
PM10	44 (winter) 52 (summer)	76 (winter) 24 (summer)	84 (annual average between different sites)
PM2.5/PM10	0.75 (winter) 0.79 (summer)	0.39 (winter) 0.63 (summer)	0.48

concentrations. The concentration levels of PM2.5 are near or larger than the US-EPA alarm value. Hence, the levels of PM2.5 are dangerous and it is expected an important impact on the inhabitants, since the finest particles are the more dangerous for health. Unfortunately, there are no medical statistics on allergy or respiratory diseases at present in Buenos Aires.

The results also suggest that the so-called coarse fraction, the difference between PM10 and PM2.5 concentration (Harrison et al., 1997), has a very important contribution of ground dust or re-suspended material, which is composed mainly by aluminum silicates. This is in agreement with the small seasonal variability of PM10 and PM2.5 levels. A further and more systematic study should include quantitative separation between exhaust particles and particles generated from re-suspension.

The main percentage of PM10 corresponds to the smallest particles, PM2.5. The relative percentages of PM2.5 and PM10 are in excellent agreement with the predictions of the Jaenicke model. As it was indicated, 80% of PM10 is PM2.5. It is possible to compare these relationships with values reported for other cities of South America, such as São Pablo, Santiago de Chile, Rio de Janeiro and Bogota (Onursal and Gautam, 1997; Artaxo et al., 1999). For these cities it was reported that the percentages of PM2.5 in PM10 are in the range from 40% to 60%, which are systematically lower than the values reported here for Buenos Aires.

For the case of São Paulo the absolute levels of PM2.5 are similar to that of Buenos Aires for winter while PM10 is higher in Buenos Aires in summer (Table 4). This explains that the ratio PM2.5/PM10 is lower in São Pablo than in Buenos Aires. The same holds when comparing Buenos Aires and Santiago de Chile, although annual averages are considered for the case of Santiago.

It is very interesting to note that the levels of PM in Buenos Aires decrease from summer to autumn–winter, while the opposite behavior was observed in São Paulo (Table 4). This is probably due to the different topography and meteorological characteristics. In fact, São Paulo is surrounded by hills and the city is at a valley, while Buenos Aires is located in a very plain area. In consequence, Buenos Aires is more "windy" than São Paulo, being very rare to find two consecutive days of calm (almost no wind) in Buenos Aires, even in winter (Bogo et al., 1999). In general, the atmosphere of Buenos Aires is renewed every day, the levels of CO and NO_x are very low at night during the whole year, and the average speed of wind increases significantly in summer. Therefore, the higher values of PM found in summer with respect to winter are in agreement with the abundance of re-suspended material in summer at Buenos Aires, due to the effect of wind. This effect seems not to be present in São Paulo.

It is also worth noting that the ratio PM2.5/PM10 is almost equal for summer and winter in Buenos Aires, while is higher in summer than in winter in São Paulo (Table 4). This is in agreement with the description of the above paragraph, that is, the meteorological and topographic conditions of Buenos Aires are less favorable than those of São Paulo for the formation of secondary aerosols of small size, which requires a more quiet atmosphere. The possibility of secondary aerosols formation is an open issue in Buenos Aires city, which requires further systematic studies in future.

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