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Analysis of atmospheric aerosols by PIXE: the importance of real time and complementary measurements

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Abstract

Particle-Induced X-ray Emission (PIXE) has been used for more than 30 yr in many urban and background air pollution studies. The technique has certainly contributed to the understanding of source-receptor relationship for aerosol particles as well as to aerosol physics and chemistry. In the last few years, where aerosol issues were strongly linked to global climate change through the relationship between aerosol and atmospheric radiation points to new challenges in atmospheric sciences, where PIXE could play an important role. Also the recognition for the inter-relationship between aerosol and liquid and gas phases in the atmosphere makes important to integrate PIXE aerosol analysis with other complementary measurements. The use of Nephelometers and Aethalometers to measure scattering and absorption of radiation by aerosol particles can be done in parallel with particle filter collection for PIXE analysis. Parallel measurements of trace gases using traditional monitors as well as with new techniques such as Differential Optical Absorption Spectroscopy (DOAS) that can provide concentration of O_3, SO_2, NO_3, NO_2, HCHO, HNO_3, Benzene, Toluene, and Xylene, is also important for both urban and remote aerosol studies. They provide information that allows a much richer interpretation of PIXE data. Recently developed instruments that provide real time aerosol data such as the Tapered Element Oscillating Microbalance (TEOM) PM_{10} monitor and automatic real time organic and elemental carbon analyzers provide extremely useful data to complement PIXE aerosol analysis. The concentrations of trace elements measured by PIXE comprise only 10–30% of the aerosol mass, leaving the organic aerosol characterization and measurement with an important role. The aerosol source apportionment provided by PIXE analysis can be extended with other aerosol measurements such as scattering and absorption, estimating for example, the radiative impact of each discriminated aerosol source. The aerosol bulk PIXE measurements can be complemented with soluble concentrations provided by Ion Chromatography (IC) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Recent developments in remote sensing techniques and products also enhance significantly regional aerosol studies. Three-dimensional air mass trajectories should be integrated in aerosol studies for urban and remote areas. The applications of these techniques to study urban aerosols from São Paulo and Santiago de Chile have broadened extensively the scientific scope of these studies.

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1. Introduction

The three phases of the atmosphere: solid, liquid and gas are intimately linked. The interactions between these phases are very strong, and a dynamic equilibrium exists [1]. Many atmospheric studies have focused only on the aerosol component, and recent studies that integrate physical and chemical properties of aerosol particles as well as other atmospheric properties have shown that we can gain significantly with the integration of complementary measurements. Some of these measurements can be done in the same PIXE filter, such as gravimetric analysis for mass concentration measurements; ion chromatography for cations and anions; reflectance for black carbon concentration; Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) for soluble trace elements; Instrumental Neutron Activation Analysis (INAA), Proton Elastic Scattering Analysis (PESA), Particle-Induced Gamma Ray Emission (PIGE) and the analysis of individual aerosol particles by Electron Probe X-ray Micro Analysis (EPMA). Other atmospheric measurements that are useful for aerosol source apportionment studies include meteorological variables such as air mass trajectories, and aerosol physical properties such as size distribution, light scattering, light absorption, aerosol number concentration, hygroscopic properties and organic compounds characterization. Recent developments allow real time aerosol measurements with the use of the Tapered Element Oscillating Microbalance (TEOM) aerosol mass monitor. The organic aerosol component can be analyzed also in real time with the use of the Rupprecht & Patashnick Series 5400 Ambient carbon particulate monitor. For high temporal resolution and high sensitivity for black carbon measurements, the Aethalometer is a very useful instrument. The use of 3 wavelengths nephelometers for forward and backward aerosol light scattering, automatic tracking sunphotometers for real time aerosol optical thickness and diffuse and direct radiation measurements helps in the study of the climatic effects of aerosol particles [2,3].

Especially for urban aerosol studies, the measurements of the concentration of trace gases can help in the aerosol source apportionment [4]. Through the use of real time traditional gas monitors for measurements of carbon monoxide (CO), nitrogen oxides (NO, NO_2), sulfur dioxide (SO_2) and ozone (O_3) concentrations, it is possible to extend the scope of the study. New techniques such as the Differential Optical Absorption Spectrometry (DOAS) [5] technique allow the simultaneous measurements of 5–10 trace gases with detection limits that are adequate for urban studies.

Recently developed remote sensing techniques allow the large-scale observation of aerosol particles. The new aerosol product from Total Ozone Mapping Spectrometer (TOMS) instrument and the Advanced Very High-Resolution Radiometer (AVHRR) aerosol optical thickness and fire count products have significantly contributed to the global scale analysis of aerosols. Future satellite instruments specifically designed for aerosol studies such as the NASA EOS MODIS instrument will allow much better aerosol quantification from space.

The purpose of this paper is to discuss some applications with the integrated use of PIXE with some of these modern techniques. The study of biomass burning in Amazonia shows the integrated use of PIXE, ion chromatography, aerosol optical thickness measurements and large-scale air mass trajectories. In urban studies in São Paulo and Santiago de Chile, the joint use of PIXE and real time aerosol and trace gas monitors is an example of successful integration of these techniques.

2. Aerosol studies in urban areas: Santiago de Chile

Several of the mega cities in Latin America suffer from severe air pollution, such as Mexico City, São Paulo and Santiago de Chile. The topographical configuration and the geographical location of Santiago de Chile together with an expanding population and severe traffic make air pollution in Santiago a very serious problem. A frequent inversion layer during wintertime adds to this unfavorable condition [6]. Strong enforcement of air pollution reduction in Santiago and São Paulo includes restriction of automobile circula-

tion and a strict industrial emission control. Aerosol sources apportionment studies were designed to determine the main aerosol sources in the urban area and to check the efficiency of the air pollution control regulations. Fine and coarse mode aerosol particles were collected in three sampling sites in the urban area of Santiago de Chile in 1997. Elemental concentrations were measured with the particle-induced X-ray emission (PIXE) method, measuring the concentration of up to 23 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, Sn, Se, As, Ba, Pb). A dedicated 5SDH Pelletron accelerator facility, Laboratório de Analise de Materiais por Feixes Iônicos (LAMFI), from the University of São Paulo was used for the PIXE analysis [7]. Two Si(Li) detectors are used in the PIXE system, one optimized for low Z elements and the second having a thick absorber to detect elements heavier than Ca. The arrangement with two Si(Li) detectors provides better detection limits and avoids some of the pile-up and dead time corrections. The two Kevex detectors have 12 μm Be window and 138 eV resolution for the Mn Kα line. The precision of the elemental concentration measurements is typically in the range of 4–10%.

The VARIMAX rotated factor analysis of fine mode aerosol for Santiago de Chile is shown in Table 1. Five factors explain 90.2% of the data variability and the values presented in Table 1 are the factor loadings for the five retained factors. It is possible to observe the large impact of the

Table 1
Aerosol source apportionment for fine mode aerosol from Santiago de Chile in the Las Condes sampling station (VARIMAX rotated factor loading matrix)[a]

Source	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
	Transport	Resuspended soil dust	Oil combustion	As + S	Cl + S
FPM	0.89	0.17	0.18	0.14	0.25
Sn	0.84	0	0.27	0	0
Br	0.83	0.44	0.17	0	0
S	0.80	0	0	0.39	0.36
Se	0.78	0.42	0	0	0.25
K	0.78	0.44	0	0	0.27
BC	0.75	0.50	0.27	0.15	0
Pb	0.74	0.51	0.32	0.10	0
Ni	0.63	0.42	0.57	0.18	0.17
P	0.60	0.43	0.10	0.51	0
V	0.60	0.50	0.51	0.14	0.17
CPM	0.58	0.42	0.16	0.20	0.36
Ca	0.16	0.94	0.12	0.15	0
Al	0	0.91	0	0	0.26
Si	0.36	0.87	0	0.16	0
Ti	0.25	0.86	0.18	0.23	0.20
Fe	0.35	0.84	0.32	0.19	0
Mn	0.43	0.68	0.45	0.27	0
Sr	0.44	0.67	0.21	0	0
Cu	0.53	0.60	0.29	0.27	0
Zn	0.42	0.58	0.60	0.24	0
As	0	0.25	0.13	0.90	−0.12
Cl	0.26	0.16	0	−0.11	0.91
Eigenv.	7.96	7.59	1.86	1.79	1.54
%Var.	34.6	33.0	8.0	7.7	6.7

[a] The total variance explained by the 5 factors for the fine mode Las Condes aerosol is 90.2% of the original data variability. FPM is the fine mode aerosol mass concentration. CPM is the coarse mode mass concentration and BC is the black carbon concentration. "Eigenv." is the eigenvalue of the factor analysis for each retained factor. %Var. indicates the percentage of variance explained by each factor.

transport sector, represented by factor 1, being the dominant source of trace element variability and associated with both fine and coarse mode aerosol mass concentrations. The sampling site in downtown Santiago is heavily impacted by local traffic. The second factor, associated with resuspended soil dust is also linked with vehicular traffic. The other three components are residual oil combustion (V, Ni, and Zn), sulfates and a factor associated with Cl and sulfur that can be associated with sea-salt aerosol. For this aerosol source apportionment study in Santiago, carbon monoxide (CO) concentrations were measured in parallel with aerosol particles. More than 90% of the CO emissions in Santiago are associated with vehicular traffic. Fig. 1 shows the fine mode and PM_{10} aerosol mass versus carbon monoxide (CO) concentrations in Santiago de Chile. Both $PM_{2.5}$ and PM_{10} aerosol concentrations correlate with CO, indicating that traffic is indeed a major source of aerosols, not only for the fine mode, but also for the coarse mode through resuspended soil dust. Automobile emissions are rich in volatile organic gases that nucleate and coagulate forming fine mode aerosol particles. Fig. 2 shows the association between carbonaceous particles and aerosol mass in Santiago de Chile. There is a significant correlation between $PM_{2.5}$ and organic carbon, with organic carbon comprising a significant fraction of $PM_{2.5}$. The lower part of Fig. 2 shows that organic carbon comprises 40% of total carbon with the remaining 60% of total carbon being elemental carbon. This high percentage of elemental carbon indicates again the importance of vehicular traffic, and particularly diesel emissions in the particulate matter in Santiago. The measurements

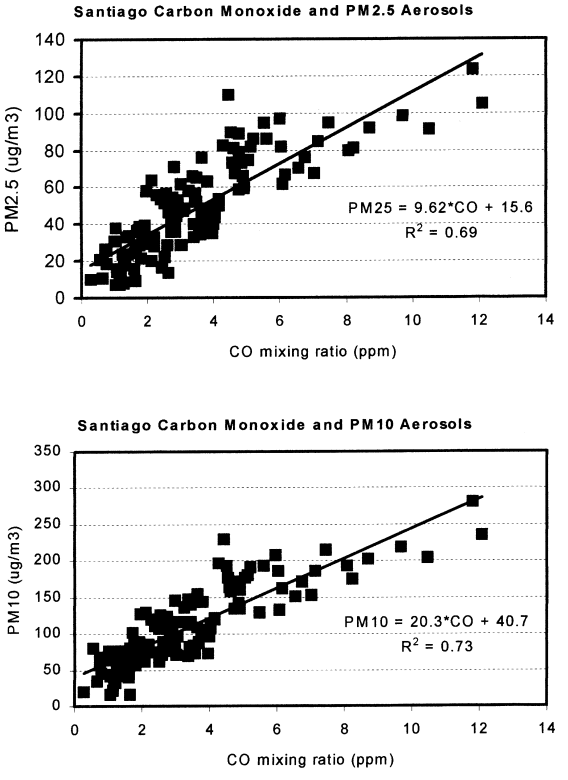

Fig. 1. Fine mode and PM_{10} aerosol mass concentrations versus carbon monoxide (CO) in Santiago de Chile. CO is an excellent tracer for traffic emissions in Santiago.

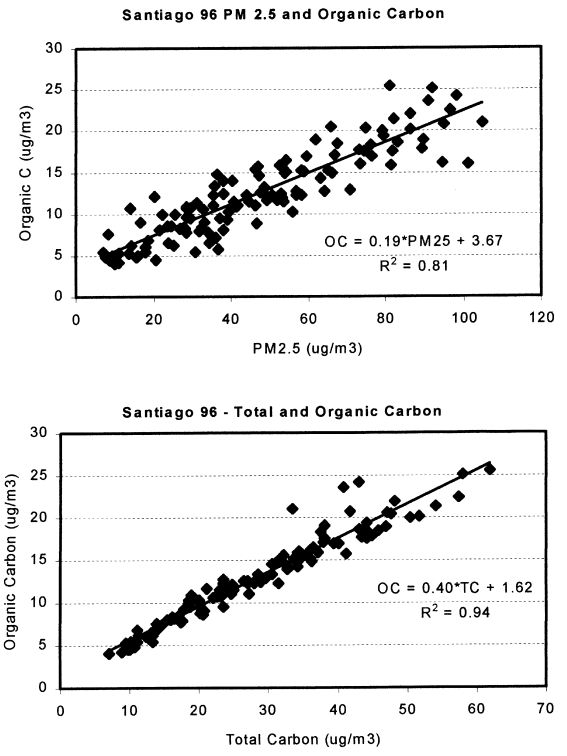

Fig. 2. Organic and total carbon in aerosols from Santiago de Chile. Measurements performed with the R & P 5400 organic carbon monitor, with 1 h time resolution.

of trace gases and organic aerosol components in Santiago significantly helped in getting a clear picture of vehicular emissions in this complex urban area.

3. Aerosol studies in urban areas: São Paulo

The city of São Paulo (latitude 23°32′s, longitude 46°38′W) is one of the largest urban areas in the world. It has a populations of about 18.4 million inhabitants in 1990 and is expected to have about 24 million in year 2000 [8]. There are two main air pollution sources in the metropolitan area: industrial emissions and transportation. In the urban are of São Paulo, there are about 5 million vehicles. During the winter months (May–September), a strong inversion layer at low altitude makes the dispersion of air pollutants difficult in the urban area. Low wind speeds and low precipitation rate leads to very high levels of air pollution in wintertime. The main pollutants in the urban area particulate matter, SO_2, ozone and carbon monoxide [9].

Stacked filter units [10] were used to collect fine and coarse mode aerosol samples during wintertime 1997 in São Paulo. In this study, several other instruments were also employed such as the TEOM real time aerosol monitor, R&P ambient 5400 carbon monitor, Magee Scientific Aethalometer for black carbon measurements, an OPSIS DOAS system for real time trace gases and TSI Nephelometers for light scattering. Fig. 3 shows the time series of aerosol mass concentration for the period 10 June to 9 September 1997. The average PM_{10} aerosol mass concentration is a high 76.6 μg/m^3. Large variability is observed due to changes in source strengths and meteorological conditions. Fig. 4 shows the hourly black carbon concentration measured with an Aethalometer. The high values of black carbon indicate the importance of vehicular emissions, and in particular diesel emissions in the São Paulo atmosphere. The advantage of having several different methodologies for aerosol measurements is that it is possible to compare parameters measured by two different techniques. Fig. 5 shows the aerosol mass concentration measured by gravimetric analysis of SFU filters and with the real time TEOM aerosol mass monitor. The TEOM data was reduced to the same 12 h collection time of the SFU. The similarity for both measurements is remarkable, and the TEOM

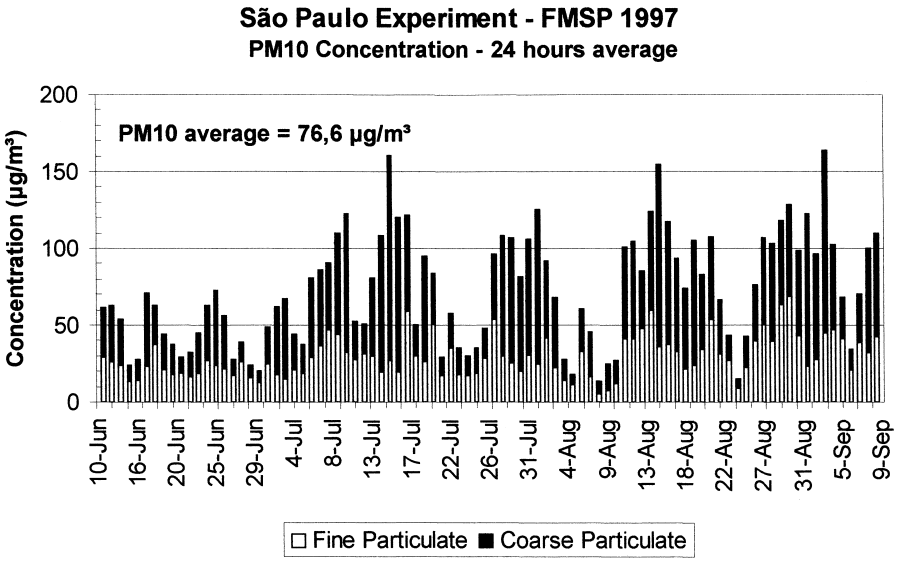

Fig. 3. Concentrations of fine and coarse mode aerosol mass measured from 10 July to 10 September in São Paulo. Measurements with gravimetric analysis of SFU.

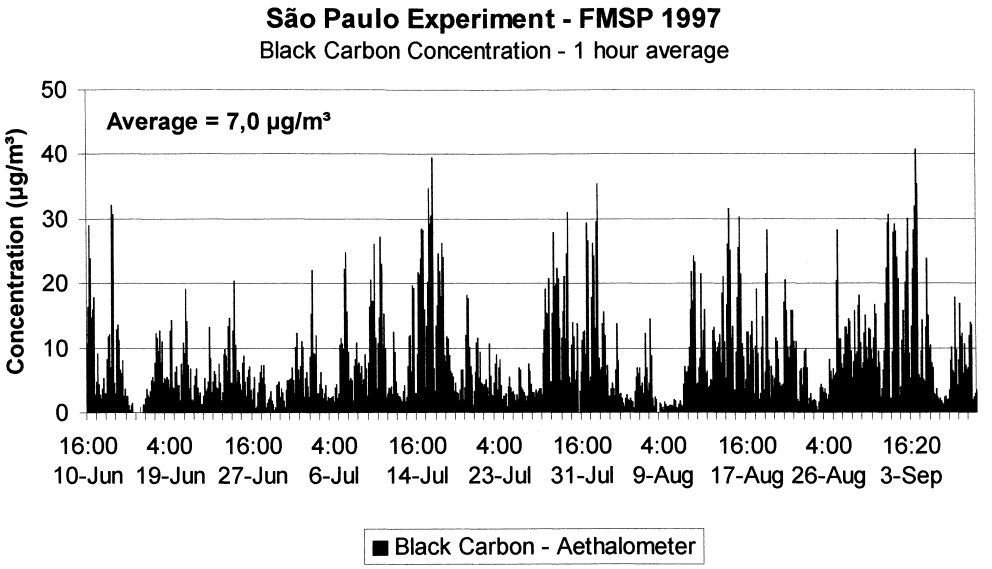

Fig. 4. High resolution (1 h) black carbon concentrations, measured from 10 July to 9 September in São Paulo. Measurements performed with the optical absorption technique from an Aethalometer.

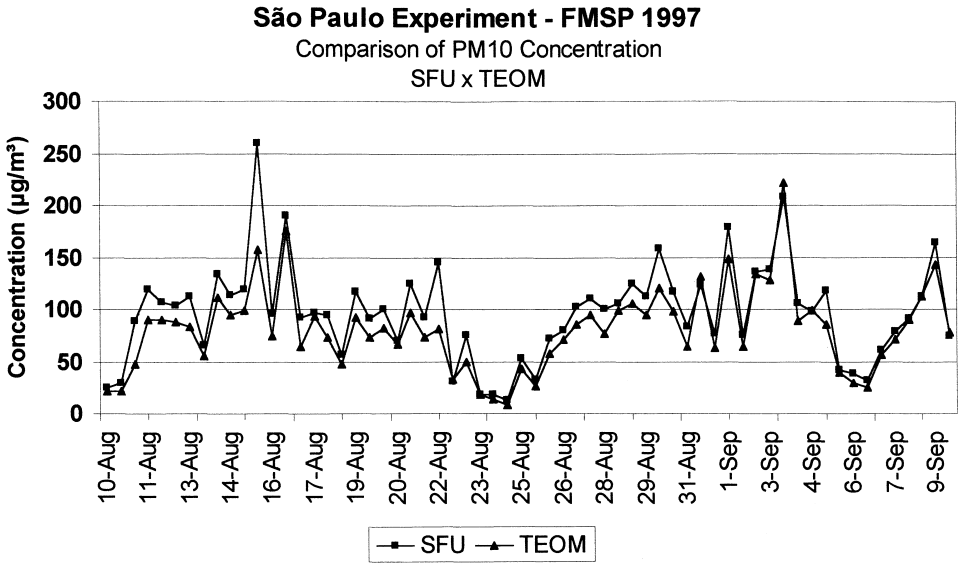

Fig. 5. Temporal series of two different measurements of aerosol mass concentration. SFU is the PM_{10} concentration obtained by gravimetric analysis of Nuclepore filters. TEOM is the PM_{10} concentration obtained by the TEOM real time aerosol mass monitor.

measure slightly lower concentrations, possibly because it has to heat up the air before collection to about 50°. This could cause the loss of some of the organic volatile compounds. Fig. 6 shows the correlation between two different measurements of black carbon concentration, given by the Aethalometer and the R&P 5400 ambient carbon monitor. The ratio between the concentrations is 1.0,

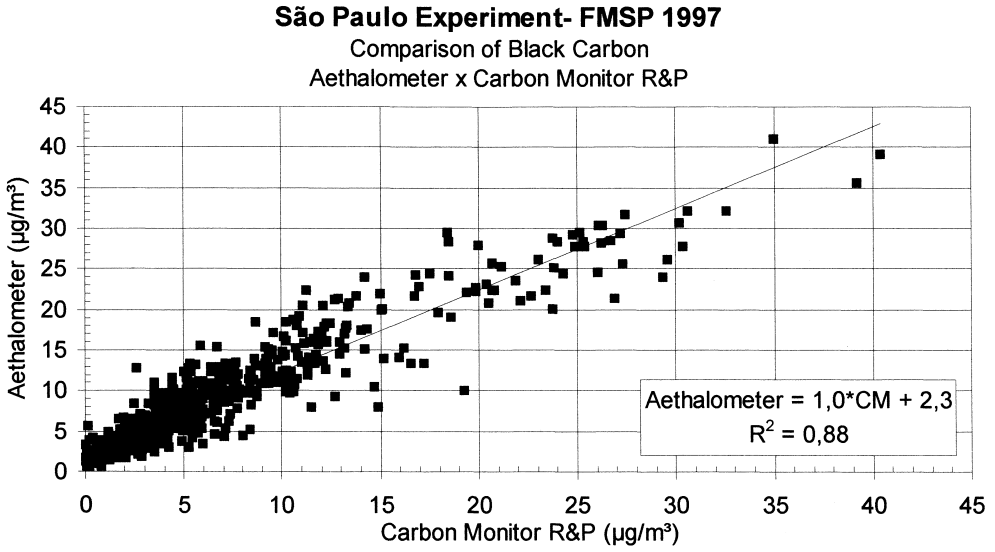

Fig. 6. Correlation between two different measurements of black carbon concentration, given by Aethalometer and the R&P 5400 ambient carbon monitor. The Aethalometer measures optical absorption, and the carbon monitor measures carbon converting it to CO_2.

meaning that the optical equivalent of the black carbon in urban areas can be adequately measured by the Aethalometer. The carbon monitor is an absolute carbon analyzer, but it has problems with the temperature for separation between organic and elemental carbon. The agreement between both instruments for urban areas gives confidence in the measurement of this important parameter, the black carbon concentration.

Aerosol sampling during 12 or 24 h in urban areas averages over many atmospheric conditions. The source strengths and meteorological conditions vary dynamically, especially in urban areas. Fig. 7 shows an example of this feature, with the daily variability of black carbon concentration for 7 days in this sampling campaign in São Paulo. In the early morning, when atmospheric conditions are stable, black carbon concentrations can go up to 40 $\mu g/m^3$. Only 5 h later, it drops to less than 5 $\mu g/m^3$. This extreme hourly variability is common in polluted urban areas. Fig. 8 shows the aerosol mass concentration (PM_{10}) daily variability in São Paulo. In the morning, concentrations can go up to 250 $\mu g/m^3$, going down to 50 $\mu g/m^3$ in a few hours. Sampling with a 12 h integration time evidently does not allow observing this important structure in the urban aerosol concentration. Independent of the variations in absolute concentrations along the day, ratios of aerosol properties in urban areas also vary significantly, and it is possible to learn about urban air pollution processes with these ratios. Fig. 9 shows the ratio of black carbon to PM_{10} concentrations. In the early morning, BC accounts for a high 18% of PM_{10}. This is mostly caused by the low inversion layer in the morning and the stable atmospheric conditions during the night. This condition accumulates emissions, and enhances BC concentrations, because soil dust is resuspended in smaller amounts during the night because of the stable meteorological conditions, and low wind speed and traffic. During the day, PM_{10} increases more than BC because of additional sources to PM_{10} that do not enhance in the same proportion the BC concentrations, such as resuspended soil dust, industrial emissions, secondary aerosol formation and other processes. During the weekend, the daily variability for this ratio is much smaller, because of the decrease in industrial and traffic source strengths. Also, during weekends, because of the lower traffic

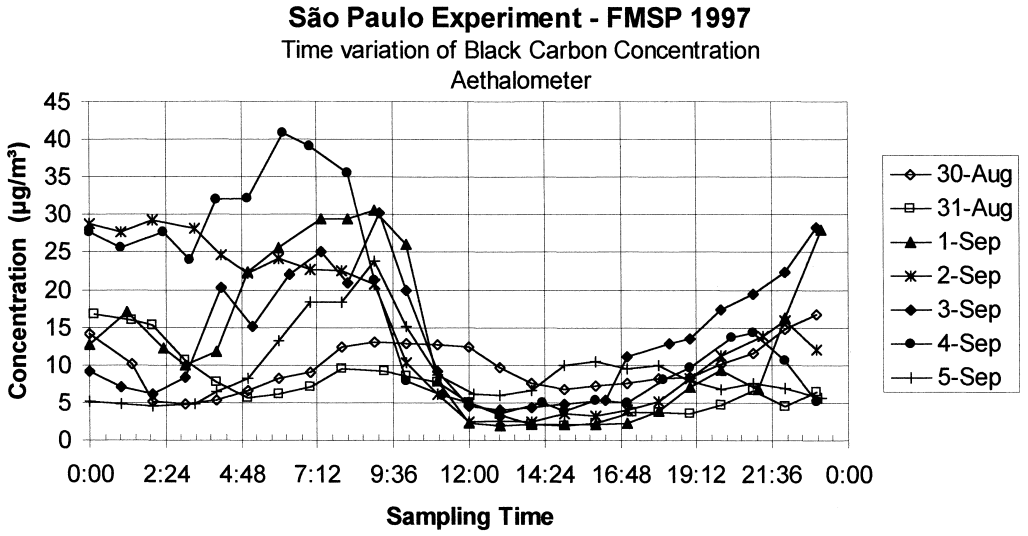

Fig. 7. Daily variation of black carbon concentration in São Paulo, measured with an Aethalometer with 10 min time resolution.

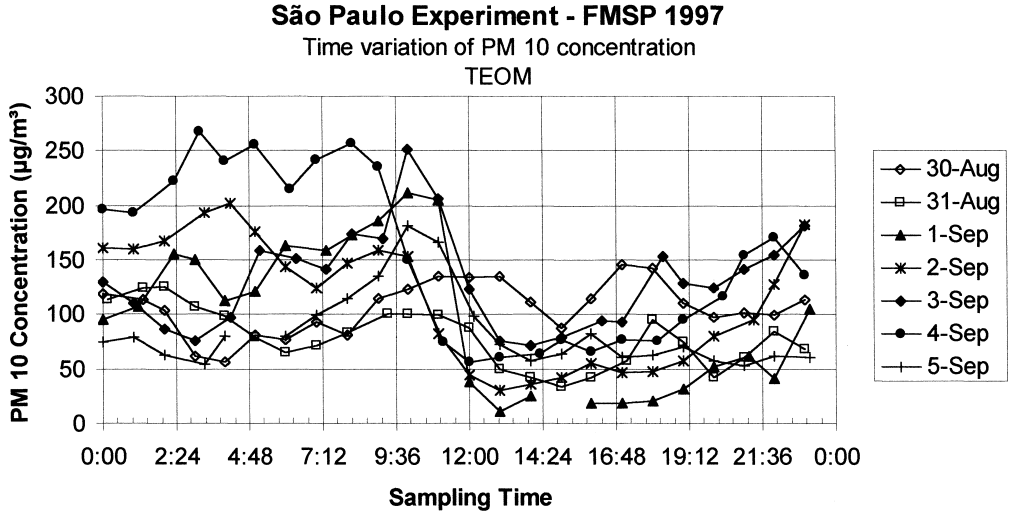

Fig. 8. Daily variation of PM_{10} concentration in São Paulo obtained with the TEOM real time aerosol mass monitor with 1 h time resolution.

emissions, the participation of BC in PM_{10} is smaller than during working days.

Fig. 10 shows the ratio of black carbon to the organic carbon concentrations for São Paulo. In the early morning, the BC concentration is about 50% of the organic carbon. Late afternoon, this ratio is only 20% in sunny days. This reduction is mostly caused by the increase in organic carbon along the day. The traffic emits significant amounts of organic volatile compounds that are quickly converted to aerosol particles. This newly formed organic aerosol enriches the PM_{10} and $PM_{2.5}$ along the day, reducing the ratio of BC to organic carbon and aerosol mass.

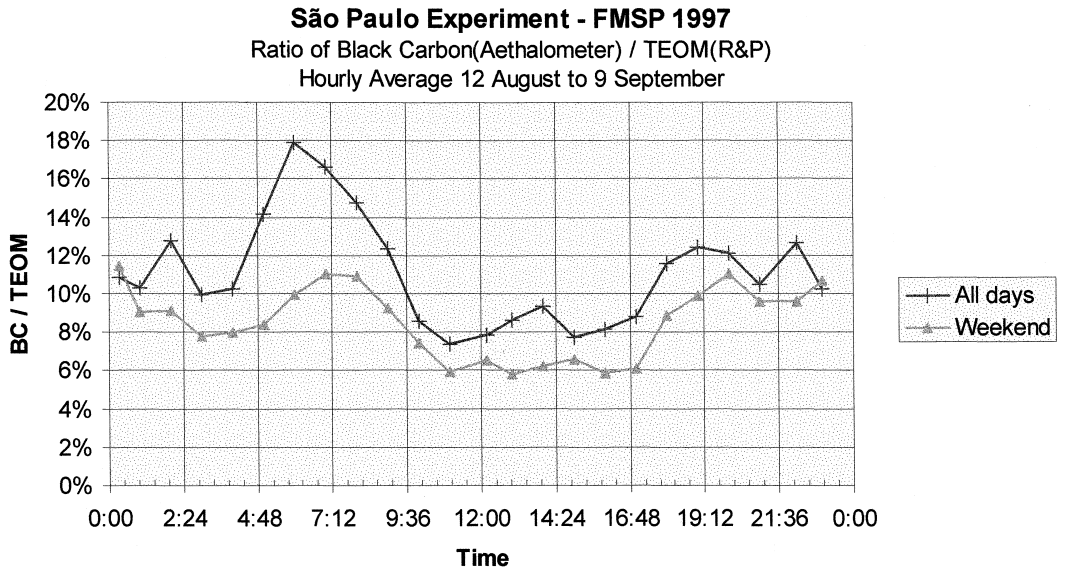

Fig. 9. Ratio of black carbon to PM_{10} aerosol mass in São Paulo, as a function of time.

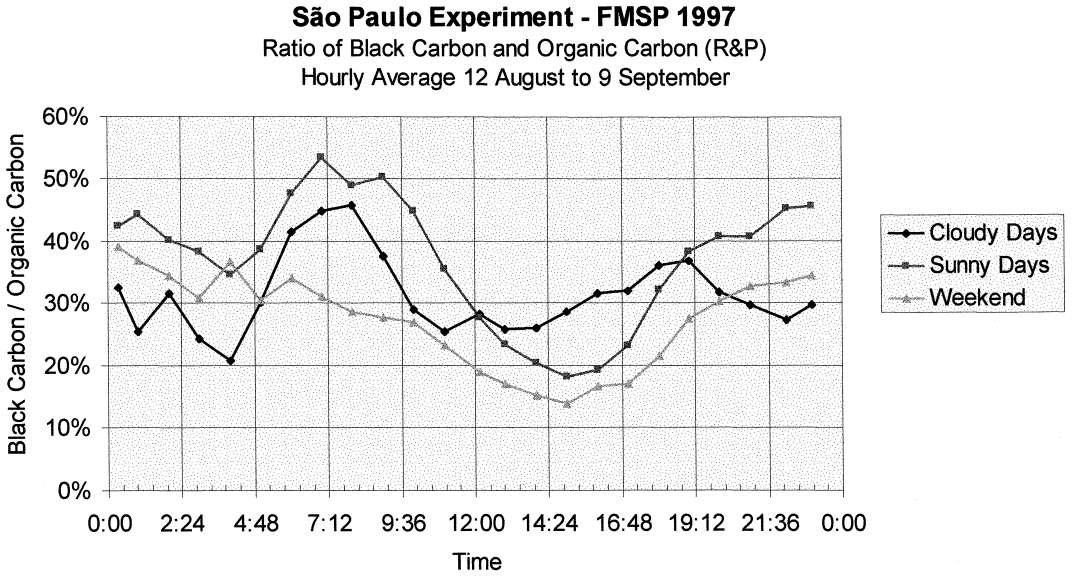

Fig. 10. Ratio of black carbon to organic carbon aerosol in São Paulo, as a function of time.

Three-dimensional air mass trajectories are getting more reliable and easier to obtain in recent years. The availability of several centers such as NOAA, ECMWF, AES Canada and others that provide 3D trajectory analysis make this tool an important one to be integrated in air pollution studies. The backward trajectories indicate the possibility of São Paulo to receive air masses originating from areas with strong biomass burning activities in the Amazon basin [11]. The forward trajectories show that pristine areas of Southern Brazil can receive significant amounts of

air pollution generated by activities in the urban area of São Paulo. Dry and wet deposition of important pollutants can be traced using this methodology. The effects of megacities emissions are certainly much far from their urban centers.

4. Conclusions

The combined use of aerosol analysis by PIXE with real time aerosol and trace gases monitors can significantly enhance the scope and completeness of urban and background aerosol studies. The recent advances in aerosol and trace gases instrumentation allows much more integrated studies, with interesting new scientific problems that would have been difficult to address a few years ago. The impact of aerosol particles in the global climate system has advanced significantly with the integrated use of aerosol analysis by PIXE with aerosol radiative properties measurements. The large aerosol picture can be obtained through the use of newly developed remote sensing techniques. Three-dimensional air mass trajectories can be integrated more easily with urban or background aerosol studies.

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