Detection of Atmospheric Aerosol Sources in the City of São Paulo, by PIXE Analysis

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Abstract. Atmospheric aerosol samples collected every 3 h, from 14 to 18 July 2005, were used to study the sources of particulate matter at the São Paulo City. Samples were collected using a stacked filter system, in order to fractionate the aerosols in their fine and coarse fractions (equivalent aerodynamical diameter, $\phi<2.5\mu m$ and $2.5\mu m<\phi<10\mu m$, respectively). The concentrations of particulate matter on both fractions were determined; trace elements contents were also measured on both fractions using PIXE technique. Four sources of coarse particulate (soil, industrial process, fossil fuel burning and sulphates) and four sources of fine particulate (industrial process, fossil fuel burning, soil, and source of Al and K) were identified using Principal Components Analysis, and meteorological information. The results show that high resolution sampling could be a useful tool to provide a good definition of the principal components, despite the relatively limited number of samples used in this study.

Keywords: atmospheric aerosol, São Paulo, PIXE, sampling time resolution.

INTRODUCTION

The São Paulo Metropolitan Region (RMSP) is a complex and peculiar environment, especially concerning to its atmospheric pollutants. An inventory performed by the local environmental control agency evaluates that $2.3x10^6$ t of noticeable pollutants were injected in the RMSP airshed, on 2005 [1]. Nearly 95% of this were attributed to the fleet of 7.2 million vehicles, while the remaining 5% came from the operation of the 46.6 thousand industrial units in the greater metropolitan area.

The characteristics of the sources of atmospheric pollutants in São Paulo contrast with that in other world megacities. On one hand, we have the Brazilian energetic matrix, composed by 40% of renewable sources, or hydroelectricity, while word-wide 85% of energy is produced from fossil fuels. On the other hand, one must consider the variety of Brazilian vehicle fuels, whose compositions have been very dynamic. This is the case, for instance, of ethanol, used as pure fuel, mixed in the normal gasoline (22%, as antiknock agent) or in a fully variable proportion, as in the case of the recent flex-motors. There is also an increased tendency to adapt vehicles to the Natural Gas and the commercialisation of a mix of diesel and vegetable oils (called bio-diesel).

The atmospheric aerosol is one of the worst air pollution problems in the region, and has been studied in several works [e.g. ref. 2, 3, 4, 5, 6, 7 and 8]. Nevertheless, the complexity of this area and the dynamics of its source impose the permanent study of the atmospheric aerosol's behaviour. Its deleterious effects directly affects the life of 19.3 millions inhabitants, distributed over an area with 8051 km² [9].

MATERIALS AND ANALYTICAL METHODS

The sampling campaign started at 0 h, 14 of July 2005 (Thursday) and ended at 24 h, 18 of July 2005 (Monday), yielding a total of 40 samples, collected every 3 h. The sampling station was settled on the roof of the Institute of Geosciences (23K 032720 7393593 UTM), in the main campus of the University of São Paulo. Particles with equivalent average aerodynamical diameter (ϕ) less than $10\mu m$ (PM_{10}) were admitted in a staked filter unit [10]. The particles were retained on Polycarbonate filters (diameter of 47 mm); first the coarse ($2.5\mu m<\phi<10\mu m$ – $PM_{2.5-10}$) on filter with 8 μm holes, and after, the fines ($\phi<2.5\mu m$ – $PM_{2.5}$) on filter with 0,4 μm holes. The air inflow was of 16.6 l/min. The weighing of the collected mass was performed with a microanalytical balance, following standard procedures to eliminate electrostatic charging and contamination by suspended particles. One quarter

of some of the collected filters, in both fractions, was analysed by PIXE [11], given the concentration of chemical elements with atomic number higher than 12.

RESULTS AND DISCUSSION

Figure-1A shows the temporal series of the concentrations of fine, coarse and inhalable particulate. The national standards for daily and even for annual average concentrations of PM_{10}, 150 and 50 µg/m³ respectively, were not surpassed on those days.

The concentrations increased from Thursday till Friday, decreasing during the weekend. This could be explained by the typical reduction of urban activities on Saturdays and Sundays and, also, by the progressive increase of the wind speed during the experiment (Figure-1C), that facilitates the dispersion of pollutants. The concentration peak by the end of Friday is typical of the chaotic traffic in this day of the week. It could had been intensified by the prevailing N and NNW wind after midday (Figure-1B), bringing directly into play the emissions of an important, 12 tracks thruway that is close by (Marginal Pinheiros).

FIGURE 1. Temporal series for: (A) PM_{10} concentrations
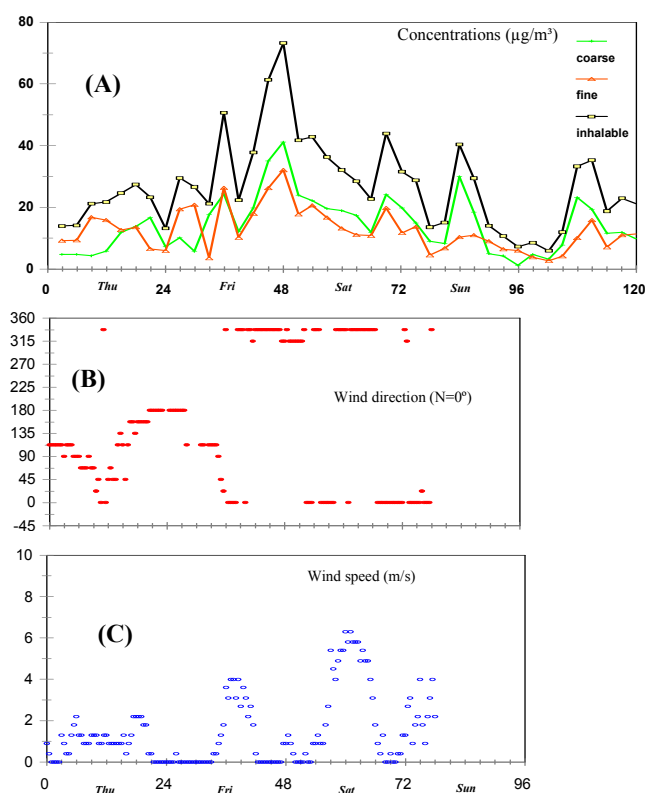
(inhalable), $PM_{2.5}$ (fine) and $PM_{2.5-10}$ (coarse); (B) Wind direction; (C) Wind speed. The time scale is in hours and begins at 0 h, 14 July 2005.

The average concentrations of the trace elements in the filters and the respective standard deviations were determined. Principal Component Analysis (PCA) was applied to all the database obtained, revelling four components for both, $PM_{2.5-10}$ and $PM_{2.5}$. These results are on Tables 1 and 2 (the highest loads in each component are in boldface), together with the eigenvalues and the explained cumulative variance of the components and, also, the communalities for each chemical element. Missing values were substituted by the respective average concentration, but elements present in less than 80% of the total number of cases (26) were neglected. The Cr was also eliminated of the PCA in the $PM_{2.5-10}$ due to Cr contamination in some filters. At least 82% of the variance is explained by the extracted components, in both cases - fine and coarse particulate.

The first component of the $PM_{2.5-10}$ is identifiable as soil resuspension. The main load (0.85) of TCC (Total Coarse Concentration) was on this component. Zn, Cu and Mn, in the second component, could be associated to industrial activities, especially those involving metallurgical process. The significant load of Cl in this component could be attributed to sea salt transported by the E and SE wind, often enhanced by sea breeze, and arriving to the sampling point after passing through the largest industrial area of the RMSP. Nevertheless, the association of Cl with industrial sources persists with N and NO wind, when we look at the temporal series of these elements. Pb and Br, relatable to fossil fuel burning, define the third component. In that case, the Pb should come from the petroleum mineral composition itself. The fourth component is characterised by S, mainly associated to sulphates.

The first component of the $PM_{2.5}$ may be associated to industrial process, especially metallurgy (Table-2). The Cl could be mainly associated to industrial sources, like in the case of $PM_{2.5-10}$. The second component, grouping Pb, S and TFC (Total Fine Concentration) should be from the usage of fossil fuel (Br was not detected in the fine filters because they were contaminated with it). The majority of TFC is related to this factor (load of 0.63), being coherent with the source inventory for the RMSP [1]. The third component, with high load of Ti and Ca, may be attributed to the fine fraction of soil resuspension. The forth component groups Al and K, were expected to be together with soil resuspension, but in this case arose as a specific undetermined source.

It is remarkable that although the highest load of the TFC is in the second component, it also has significative loads in the other three components, which totalize more than half of its explained variance. It indicates that actions to control $PM_{2.5}$ (the worst cause of health damage due to air pollution) should take into consideration all these sources.

Only a small amount of the Cu variance was explained (0.484). It could means that its sources are diffuse, needing to be better evaluated (they may be brushes of the many electric motors used on vehicles, home appliances and tools, etc).

No substantive differences were found among the source groups associated to the components in this experiment and those obtained in previous works. Nevertheless, it was evident that the 3 h sampling time resolution enabled a sharper definition of the elements belonging to each component, even with a relatively limited number of cases, what, in principle, could make unviable the use of PCA. The components definition was very similar to that obtained by Andrade [12, 3] in the Spacex experiment (135 samples), using a resolution of 6 h for daytime sampling and 12 h for nigh-time. Other experiment, EIF (137 samples), described by Andrade [12] with less resolution (12 h) at summer time, showed less definition of the components. The same could be observed in Castanho and Artaxo [6] with an experiment conducted with 12 h resolution, at summer time, at the School of Public Health (142 samples collected nearly 8 km farther from our station).

TABLE 1. Trace elements concentrations and Principal Components in the $PM_{2.5-10}$ fraction

Concentrations			Rotated Principal Components					
Average (µg/m³)	Deviation (µg/m³)	Cases (N)	Comm.	Element	1	2	3	4
0.0487	0.037	25	0.937	Ti	**0.93**	0.23	-0.14	0.01
0.468	0.36	26	0.865	Ca	**0.86**	0.24	-0.03	-0.05
16.5	9.6	26	0.927	TCC	**0.85**	0.44	-0.10	-0.01
0.640	0.49	26	0.953	Fe	**0.84**	0.50	-0.04	0.04
0.00328	0.0022	21	0.783	Sr	**0.83**	0.256	0.10	-0.12
0.822	0.56	22	0.762	Al	**0.72**	0.08	0.39	0.30
0.162	0.13	26	0.955	K	**0.71**	0.14	0.04	0.66
1.18	1.4	26	0.583	Si	**0.70**	0.08	-0.31	0.00
0.0366	0.035	26	0.829	Zn	0.15	**0.87**	0.23	-0.07
0.00640	0.0063	25	0.784	Cu	0.36	**0.80**	0.08	0.076
0.0966	0.061	25	0.652	Cl	0.19	**0.76**	0.18	0.07
0.0174	0.0088	26	0.898	Mn	0.64	**0.70**	-0.02	-0.01
0.00739	0.0067	26	0.757	Pb	0.04	0.16	**0.85**	-0.06
0.184	0.083	26	0.792	Br	-0.22	0.20	**0.82**	0.16
0.0873	0.13	23	0.962	S	-0.13	-0.01	0.06	**0.97**
0.00342	0.0040	21		Cr				
				Eigenvalues	5.94	3.17	1.79	1.53
				Cumulative Variance	39.6	60.8	72.7	82.9

TABLE 2. Trace elements concentrations and Principal Components in the $PM_{2.5}$ fraction

Concentrations			Rotated Principal Components					
Average (µg/m³)	Deviation (µg/m³)	Cases (N)	Comm.	Element	1	2	3	4
0.0101	0.0090	26	0.926	Mn	**0.95**	0.02	0.16	-0.05
0.0304	0.030	22	0.935	Cl	**0.91**	0.00	-0.09	0.32
0.203	0.15	20	0.927	Fe	**0.77**	0.07	0.324	0.15
0.0595	0.053	26	0.916	Zn	**0.77**	0.51	-0.10	0.22
0.285	0.17	26	0.833	S	0.01	**0.90**	0.06	-0.14
0.0114	0.009	26	0.846	Pb	0.09	**0.87**	-0.20	0.19
15.2	6.5	26	0.815	TFC	0.37	**0.63**	0.39	0.36
0.0927	0.074	25	0.837	Ca	0.03	0.00	**0.91**	-0.03
0.0185	0.012	26	0.879	Ti	0.10	-0.19	**0.81**	0.43
0.00953	0.011	26	0.484	Cu	0.39	0.30	**0.44**	0.22
0.267	0.26	21	0.814	Al	0.13	0.01	0.04	**0.89**
0.185	0.12	26	0.886	K	0.26	0.22	0.36	**0.80**
0.00101	0.0007	15		Sr				
0.654	0.92	20		Si				
				Eigenvalues	3.32	2.41	2.15	2.03
				Cumulative Variance	27.6	47.7	65.6	82.5

Nevertheless, the increase of the time resolution reduced the collected mass and, in consequence, the capability to detect some trace elements. Hence, some care is needed to determine an appropriate compromise between time resolution and detection limit for those elements. In our case, for instance, only one more sampling hour means a mass increase of 25%. Increase in the sampler's airflow also provides a proportional addition in the collected mass, although care must be taken so as to comply with the specifications for the samplers cut off diameters.

CONCLUSIONS

The use of PCA in a database collected with resolution time of 3 h, at the RMSP, enhanced the components definition (and respective groups of sources). Considering the complexity of the megalopolis, such procedure was important to increase the correlation between the chemical elements related to each source, or group of sources. Variability and correlation are bases of the PCA. Database obtained with large time interval sampling may highly smooth out its variability. That could compromise the distinguishably between the different group of correlated elements, that are related to the different sources. That could happen even if a large number of samples are available. Therefore, the increase of time resolution in experiments where the use of PCA is intended may improve its results.

The sources discriminated in the present study, in the $PM_{2.5-10}$ fraction, were: soil resuspension, industrial process, fossil fuel burning, and sulphates; in the $PM_{2.5}$ were: industrial process, fossil fuel burning, soil resuspension, and a source of Al and K. The main load of the TFC was in the second component (fossil fuel burning). Nevertheless more than half of its explained variability was connected to the other three factors, indicating that air control actions in the fine particulate fraction should take care of all the specified sources.

ACKNOWLEDGMENTS

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