CHARACTERIZATION OF ELEMENTS IN PARTICULATE MATTER COLLECTED IN SÃO MATEUS DO SUL, PARANA, BRAZIL

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ABSTRACT

Urban aerosol with aerodynamic diameter below 2.5µm has been consistently associated with adverse health effects. Since particle composition affects toxicity, chemical analysis of urban aerosol generated by different sources provides useful information for risk assessment on the exposed population. In this study we analyzed $PM_{2.5}$ collected in São Mateus do Sul - Paraná (South of Brazil), a region where the dominant source of $PM_{2.5}$ is shale oil extraction. Samples of particulate matter were colleted through filter and analyzed by instrumental neutron activation analysis (INAA) and X ray fluorescence (XRF) techniques. The particulate matter was collected in five sampling sites during five days using $PM_{2.5}$ impactor sampler and polycarbonate filter. The air was sampled about 24 hours per day at a rate of 10L min^{-1}. In these filter samples, the elements As, Br, Cr, Fe, K, La, Sb and Zn were determined using INAA and Al_2O_3, CaO, Co_2O_3, Cr_2O_3, CuO, Fe_2O_3, K_2O, MgO, MnO, P_2O_5, PbO, SO_3, SiO_2, TiO_2, V_2O_5, ZnO and ZrO_2 by XRF. These results indicated that the origin of some toxic elements found in the particulate matter can be attributed to oil shale plant emission.

1. INTRODUCTION

Among possible environmental contaminations by toxic agents, air pollution is one of the most wide-ranging, with capacity to disperse pollutants without precise geographic limits. The moving of primary pollutants by drafts, allied with the many formation processes of secondary pollutants, through photochemical reactions, makes the air pollution evaluation and its consequences on the human health one of the most complex problems in environmental toxicology.

Currently, the association between atmospheric particulate matter (PM) concentrations and adverse health effects on exposed population, especially on susceptible people with preexisting heart and lung disease, children, and the elderly, is widely accepted. Earlier studies of the effects of particulate matter on health evaluated a possible connection between air pollution and human health, and launched a wave of research to explore this connection. Recent research has showed

that even moderately high concentrations of particulate pollution may result in reduction of children's pulmonary function and increased risk for bronchitis and other respiratory [1]. Airborne particulate matter consists of a complex mixture of variable sized particles and physicochemical composition. The chemistry of ambient particle depends on several factors, including particle size and sources of particulate pollution in the local environment [2]. Recent studies have found biological effects to be even more pronounced for particles less than 2.5µm ($PM_{2.5}$), commonly referred to in the literature as the fine fraction of particulate matter [3 - 5].

The aim of this research was to study the environmental degradation (with consequences on public health) related to the particulate matter generated in São Mateus do Sul city in the State of Paraná, located in a rich region in shale, 150 km distant from the capital, Curitiba.

According to the SIX [6], the shale is extracted from the soil for the production of oil, gas and sulfur, from the heating of organic material (querogen) at a temperature around 500^0C. The residue from the shale extraction process is arranged in piles and left to cool down outdoors. During that process, gas and water vapor are emitted to the atmosphere, releasing organic and inorganic chemical compounds, potentially harmful to the environment and to the public health. In all the stages of the shale extraction process (mining, transportation, extraction and residues stockpiling), there is an intense production of particulate matter that is carried away by the wind, reaching neighboring areas.

2. EXPERIMENTAL

2.1 Particulate Matter Sampling

Particulate matter was collected at five sampling sites all located in São Mateus do Sul, Paraná in South, Brazil. These sites are shown in Figure 1. $PM_{2.5}$ samples were collected on polycarbonate filter (Isopore™ Membrane Filters Polycarbonate, 0.8µm, 37mm, Millipore, USA) using Harvard Impactors (Air Diagnostics, Harrison, ME) operating at 10 L min $^{-1}$ for 24h. The collection was carried out for five days, during October, 2006.

2.2 Gravimetric Analysis

In order to obtain total mass of particulate matter per volume of air, the quantity of collected particulate material was determined by weighing the filter before and after the collection.

2.3 Chemical Analysis

Two methods were employed to determine the composition of the elements in the material collected on the filter. These methods were Instrumental Neutron Activation Analysis and Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF).

2.3.1. Instrumental neutron activation analysis (INAA)

Half the filter containing particulate matter was irradiated along with synthetic standards of elements at the IEA-R1 nuclear research reactor. The quantities of elements in these standards (in μg) were: As = 1.5; Br = 5.0; Cr = 2.0; Fe = 350.0; K = 601.6; La = 0.6; Sb = 0.6 and Z = 35.0. The thermal neutron flux utilized was about 5×10^{12} n cm^{-2} s^{-1} for 16 hours. After two and ten days of decay times, samples and element standards were measured using an HGe detector coupled to a gamma ray spectrometer. The game obtained data were processed using an appropriate computer program. The quantities of the elements in each sample were calculated through comparative method. The following radioisotopes were used in these determinations: ^{76}As, ^{82}Br, ^{51}Cr, ^{59}Fe, ^{42}K, ^{140}La, ^{122}Sb and ^{65}Zn.

The blank of the filter was also analyzed and considered in these calculations. With the quantity of each element in the filter and having the volume of air suctioned, the concentration of elements in the air was calculated.

2.3.2. X - ray fluorescence analysis (XRF)

The energy dispersive X-ray fluorescence spectrometry analysis (ED-XRF) was carried out using an EDX equipment 700HS, Shimadzu Corporation Analytical Instruments Division, Kyoto, Japan. A low power Rh-target tube, voltage 5 to 50kV and a current from 1 to 1000 μA were used in the analyses. The characteristic X-ray radiation was detected by a Si (Li) detector.

The analysis was performed in a vacuum atmosphere on an surface of 10 mm diameter, for the elements Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, P, Pb, S, Si, Ti, V, Zn and Zr determination in oxide forms The non-exposed filter was also analyzed as a blank and its contribution was discounted from the results of samples. The results were obtained in units of percentage of each oxide of element. Once having the percentage of element oxide present in each filter, the mass of particulate matter per filter area and total area of filter exposed for collection the mass of the element oxide was calculated. The concentration of each oxide of element in the air was evaluated dividing this mass per volume of air suctioned for each filter.
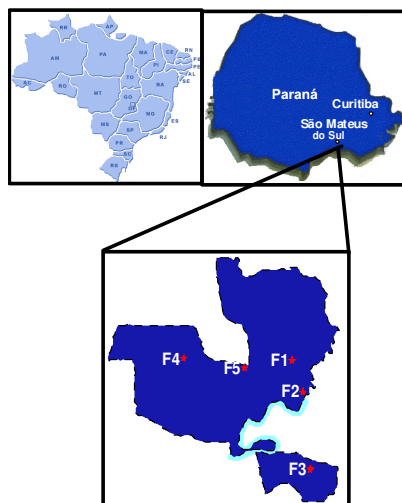

Figure 1. Sampling sites in São Mateus do Sul, Paraná, Brazil.

2. RESULTS AND DISCUSSION

Table 1 shows the mean concentration of PM$_{2.5}$ mass colleted in samples collected for 5 days in sites of São Mateus do Sul. According to these results, it was possible to verify that site 3 presented higher PM$_{2.5}$ mass concentration than those others obtained in other sites.

Table 1. Mean concentrations and standard deviation of PM$_{2.5}$ mass

Sampling sites	Longitude	Latitude	Mean mass ($\mu g\ m^{-3}$)[a]
1	558566	7190540	16.7 ± 5.9
2	562340	7138091	10.9 ± 6.5
3	562571	7135855	24.6 ± 8.6
4	558560	7139061	19.3 ± 11.9
5	560494	7138770	22.1 ± 6.7

[a] mean of five days of sampling

The results obtained in the analysis of PM$_{2.5}$ collected in filters by INAA (Table 2) indicate that there was a great variability among the element concentrations depending on the day of sample collection denoted by the standard deviation of the mean concentrations. Comparison among the data obtained for different sampling sites showed that sampling site 3 presented the highest levels of Br, Cr, La and Zn and site 5 of Fe. The levels of As, K and Sb were found at the same orders of magnitude in the five sampling sites.

Table 2. Mean concentrations of elements obtained by INAA of PM$_{2.5}$ collected in filters.

Elements	Sampling Sites				
	1	2	3	4	5
As (ng m^{-3})	0.44 ± 0.27	0.31 ± 0.18	0.41 ± 0.15	0.64 ± 0.42	0.43 ± 0.17
Br (ng m^{-3})	5.03 ± 1.47	3.10 ± 1.68	8.43 ± 7.07	3.05 ± 2.75	2.02 ± 0.61
Cr (ng m^{-3})	1.28 ± 0.35	1.85 ± 0.17	2.5 ± 1.75	0.91 ± 0.31	1.47 ± 0.53
Fe (µg m^{-3})	0.154 ± 0.075	0.133 ± 0.001	0.218 ± 0.038	0.426 ± 0,255	0.807 ± 0.675
K (µg m^{-3})	0.34 ± 0.15	0.16 ± 0.06	0.22 ± 0.03	0.570 ± 0.470	0.205 ± 0.124
La (ng m^{-3})	0.229 ± 0.06	0.147 ± 0.087	0.369 ± 0.195	0.359 ± 0.190	0.225 ± 0.050
Sb (ng m^{-3})	0.44 ± 0.19	0.29 ± 0.13	0.47 ± 0.11	0.38 ± 0.31	0.74 ± 0.32
Zn (ng m^{-3})	27.2 ± 16.6	19.1 ± 5.5	79.9 ± 52.9	19.9 ± 15.0	36.5 ± 2.10

Results obtained in the PM$_{2.5}$ analysis by ED-XRF technique (Table 3) also show great variation of element concentrations in PM$_{2.5}$ samples depending of the sampling day. Besides high concentrations of oxides of Si, V, Mn, Ni, Cu, Zn, Pb and S were found in the PM$_{2.5}$ samples collected in sampling site 3.

Table 3. Mean concentrations and standard deviation obtained for elemental oxides by ED-XRF of PM$_{2.5}$ collected in filters.

Elements	Sampling Sites				
	1	2	3	4	5
SiO$_2$ (ng m^{-3})	291.5 ± 148.4	260.5 ± 278.6	549.5 ± 77.5	712.7 ± 52.6	370.8 ± 9.5
SO$_3$ (ng m^{-3})	569.9 ± 392.7	8.5 ± 13.6	1344.3 ± 971.3	313.5 ± 342.4	568.9 ± 96.2
V$_2$O$_5$ (ng m^{-3})	25.4 ± 11.7	14.6 ± 18.4	41.4 ± 53.2	9.0 ± 11.7	18.9 ± 17.7
MnO (ng m^{-3})	6.9 ± 3.8	11.7 ± 6.8	14.5 ± 4.2	7.5 ± 6.5	12.4 ± 7.7
Fe$_2$O$_3$ (ng m^{-3})	144.7 ± 65.9	121.4 ± 80.8	688.1 ± 829.2	354.4 ± 391.4	817.4 ± 67.3
NiO (ng m^{-3})	4.5 ± 5.7	6.8 ± 5.1	8.7 ± 7.3	2.3 ± 0.5	1.7 ± 0.5
CuO (ng m^{-3})	18.2 ± 8.8	30.4 ± 7.6	51.6 ± 48.3	16.8 ± 10.3	20.0 ± 6.0
ZnO (ng m^{-3})	15.3 ± 8.5	9.3 ± 5.9	40.6 ± 32.7	13.4 ± 11.1	23.8 ± 12.3
PbO (ng m^{-3})	16.3 ± 9.3	9.0 ± 3.8	27.6 ± 45.8	21.2 ± 20.2	9.8 ± 7.0

Concentrations of Fe and Zn obtained determined by ED-XRF are slightly lower than those obtained by INAA. This discrepancy can be attributed to the X ray radiation absorption by sample total components in the analysis by ED-XRF. Another factor that could cause this effect is the difference of filter area of a sample used in INAA and ED-XRF.

From the results obtained in gravimetric analysis and also chemical analysis by INAA and ED-XRF of aerosols collected in filters we can indicate sampling site 3 as being the most polluted area. Various studies related to particulate matter have suggested that transition metals are considered potential agents in the biological response. According to these studies, the oxidative stress is the possible mechanism of toxicity for the first-row transition metals [2 - 9].

4. CONCLUSION

Preliminary results obtained in this study showed that the particulate matters present in the atmospheric air of São Mateus do Sul contain a considerable content of toxic elements, such as transition metals and sulfur. Therefore the development of more detailed studies of the atmospheric air of São Mateus do Sul is of great importance and an environmental monitoring in order to control the emission of pollutants throughout the region is needed.

REFERENCES

1. C.A. Pope III. "Respiratory Disease Associated with Community Air Pollution and a Steel Mill, Utah Valley."*Am. J. Public Health*; **79**, pp 623-628 (1989).
2. T. Carnelley, X.C. Le, "Correlation between chemical characteristics and biological reactivity of particulate matter in ambient air." Science and Technology Branch Environmental Sciences Division, Alberta Environment. Pub. Nº: T/602, ISBN: 1709-8 (Printed Edition), ISBN: 1719-1 (On-Line Edition), (2001).
3. K.L. Dreher. "Particulate matter physicochemistry and toxicology: In search of causality – a critical perspective". *Inhalation Toxicol.*.,**12** (Suppl. 3), pp 45-57, (2000).
4. W.L.W. Hsiao, Z.Y. Mo, M. Fang, X.M. Shi, and F. Wang. "Cytotoxicity of PM2.5-10 ambient air pollutants assessed by the MTT and the Comet assays". *Mutat. Res.*., **471**, pp 45-55, (2000).
5. C.A. Pope, III. "Epidemiology of fine particulate air pollution and human health: biologic mechanisms and who's at risk?" *Environ. Health Perspect.*, **108** (Suppl. 4), pp 713-723, (2000).
6. Unidade de Negócio da Industrialização do Xisto, Processo Petrosix. Available at: <http://www2.petrobras.com.br/minisite/refinarias/portugues/six/conheca/ProcPetrosix.html> Access: in 23 april 2007.
7. M.W. Frampton, A.J. Ghio, J.M. Samet, J.L. Carson, J.D. Carter, R.B. Devlin. "Effects of aqueous extracts of PM10 filters from the Utah Valley on human airway epithelial cells". *Am. J. Physiol.*, **277**, pp 960-967 (1999).
8. P.S. Gilmour, D.M. Brown, P.H. Beswick, W. MacNee, I. Rahman, K. Donaldson, "Free radical activity of industrial fibers: role of iron in oxidative stress and activation of transcription factors". *Environ. Health Perspect.,* **105** (Suppl. 5), pp 1313-1317, (1997).
9. J.D. Carter, A.J. Ghio, J.M. Samet, R.B. Devlin, "Cytokine production by human airway epithelial cells after exposure to an air pollution particle is metal-dependent." *Toxicol. Pharmacol*. **146**, pp180-188 (1997).