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A CONTRIBUTION TO THE CHARACTERIZATION OF THE AEROSOL SOURCES IN SÃO PAULO

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Fine and coarse particles in suspension in the atmosphere were collected on two Teflon filters with a dichotomous sampler. The concentration of Al, Br, Ca, Ce, Cl, Co, Cr, Fe, K, La, Mn, Na, P, Pb,, S, Sb, Sc, Se, Si, Sm, Th, V and Zn was determined by ED–XRF and INAA. The elemental concentration was analyzed by means of linear correlation coefficients, enrichment factors and principal factor analysis in order to identify the aerosol sources. The main sources of the aerosol particles were the marine ones, resuspended soil, fuel-oil combustion, phosphatic rocks, refuse incineration and residual high-temperature processes.

Introduction

Atmospheric pollution is a worldwide problem, the importance of which has grown, mainly in urban areas like São Paulo, owing to the increasing effects of pollutants on human health.

More than 15 million people live in the São Paulo metropolitan area, which is located on the Atlantic Plateau, 700 to 900 m above sea level, on the Tropic of Capricorn, 80 km from the Atlantic coast. The general topography is rather complex and the air flow is strongly influenced by local conditions.

The purpose of this paper is to contribute to characterizing the atmospheric aerosol of São Paulo, which is classified among the most complex in the world. The area has 150,000 industries such as cement, sulfuric acid, fertilizer and

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petrochemical plants, iron and steel works, refineries, chemical manufacturing, etc., and more than 4.5 million automobiles.

One of the most important problems in atmospheric aerosol studies is to determine the relation between the values measured in the environment and those emitted by sources.

Trace element concentrations on airborne particles have provided invaluable information about the locations and contributions of different types of sources at a given receptor.

Those elements are introduced into the air from sources ranging from natural origins, such as crustal weathering and the ocean, to anthropogenic activities such as industries producing emissions, oil combustion, incineration, etc.

Nowadays, special emphasis is being given to the application of models that lead from the elemental concentrations obtained in a receptor to the sources.

Many investigators have used correlation coefficients and enrichment factors to indicate the enrichment of an element in the atmosphere with respect to an investigated source.[1-3]

The enrichment factor (EF) is the ratio between the concentration of any X element and a R reference element, measured in the aerosol, and the same ratio calculated for a probable source. Even though useful, this technique of source research has a poor resolution power.

During the last 20 years, advances in computer science have allowed the development of powerful statistical methods and their application in the air pollution field.

The main methods can be classified into two categories: those based on regression and multiple correlation, and those based on multidimensional analysis, i. e., the various models of factor analysis.[4] In the first case, the model used, generally named chemical mass balance, determines the contribution of each source and its elemental chemical composition. The source signatures must, however, be known. On the other hand, factor analysis directly gives the number of emission sources responsible for aerosol chemical composition, without prior knowledge of these sources.[5-6]

Principal factor analysis (PFA) is a statistical technique that can be applied to a set of variables in order to reduce their dimensionality, replacing a large set of intercorrelated variables with a smaller number of new, independent variables that are simply linear combinations of the original ones. The answer that PFA gives is the number of sources and the correlation of each variable with these sources (factor loadings).

In this paper, correlation coefficients, enrichment factors and principal factor analysis of elemental concentration data obtained by energy dispersive X-ray fluorescence (ED-XRF) and instrumental neutron activation analysis (INAA), were used to characterize the aerosols of the city of São Paulo.

Experimental

Sample collection and analysis

Samples were collected with a Sierra Instruments model 244 Dichotomous Sampler (virtual impactor), which fractionated suspended particles into two size fractions, 2.5 to 10 μm (coarse particles) and less than 2.5 μm (fine particles). These two fractions were collected uniformly on two Teflon membrane filters with a flow rate of 1 m^3/h. Samples were collected at the western periphery of the city, 1.5 m above ground level. The collection time was 24 h.

The mass of particulate matter was determined gravimetrically with a precision of 1 μg with a microbalance and a ^{210}Po radioactive source to eliminate electrostatic effects, in a room with humidity controlled between 40 and 60%.

The filters were analyzed first by ED-XRF using a TEFA system which had a dual anode Mo/W / X-Ray tube. Mo and Cu primary X-ray filters were used to obtain monochromatic excitation. The X-ray spectrometer consists of a Si(Li) X-ray detector, an amplifier and a pulse height analyzer, which measures the energy and intensity of characteristic X-rays generated in the excitation procedure.

After that, filters were submitted to an INAA. Samples and standards were irradiated for 5 minutes under a neutron flux about 10^{12} n cm^{-2} s^{-1}, for the analysis of elements that give rise to short-lived radionuclides. To analyze long lived radionuclides, samples were irradiated for 24 h under a neutron flux of 10^{13} n cm^{-2} s^{-1}.

Standards were prepared by pipetting suitable aliquots of standard solutions obtained by dissolution of high-purity metals or oxides of elements on pieces of Whatman-41 filter paper and drying under an infrared lamp. The measurements were carried out after suitable cooling times with a Ge(Li) detector, Ortec model 8001-1022V, with a resolution of 2.6 keV at the 1332 keV gamma peak of ^{60}Co, coupled to a 4096 channel gamma-spectrometer, Ortec model 6240B.

Results and discussion

Accuracy of INAA method

To test the accuracy of the INAA method, two USGS standards (W-1 and AGV-1) and two filters from the IAEA (AIR 3/1 reference material) were analyzed. The results were compared with values reported in the literature. The relative errors were less than 1% for As, Ba, Co, Cr and Mn, while they ranged from 1 to 8% for Al, Fe, La, Na, Sc and Sm, being equal to 14% for Th.

Aerosol sample results

The above procedure allowed the determination of the following elements: Al, Br, Ca, Ce, Cl, Co, Cr, Fe, K, La, Mn, Na, P, Pb, S, Sb, Sc, Se, Si, Sm, Th, V and Zn in 52 aerosol samples. Range, geometric means and detection limits, calculated according to IUPAC criteria,[7] are presented in Table 1.

Sulfur was observed to be one of the most abundant elements. Certain sulfate compounds like zinc sulfate, sulfuric acid and ammonium sulfate are pulmonary irritants[8] and may produce chronic obstructive pulmonary disease.[9]

If all sulfur is assumed to be in the sulfate form, it is possible to calculate the maximum fraction of sulfate associated with each cation determined. Less than 34% of sulfate was bound to Al^{3+}, Ca^{2+}, Fe^{3+}, K^{+}, Pb^{2+} and Zn^{2+}. DZUBAY et al.[10] have suggested it may be bound to light cations such as H^{+} and NH_4^{+}. Besides, MOYERS et al.[11] have found a high degree of correlation between SO_4^{2-} and NH_4^{+}, while GAARENSTROOM et al.[12] have determined NH_4^{+} and SO_4^{2-} contents stoichiometrically consistent with the $(NH_4)_2SO_4$ chemical form. This compound was presumably formed in the oxidation and gas-to-particle conversion of SO_2 and subsequent neutralization by ammonia.[13] A sunny, warm and humid climate, like that of São Paulo, whose relative humidity ranges from 60 to 90%, favors these processes.

The elemental concentration data were analyzed by means of correlation coefficients, enrichment factors and principal

Table 1

Range, geometric means and detection limits for coarse and fine particulate matter (ng m^{-3})

Element	Coarse		Fine		Detection limits
	Range	Geometric means	Range	Geometric means	
Al	349-2396	1041	49-258	115	1.1
Br	0.82-3.07	1.78	3.04-27.74	8.21	6.7
Ca	100-4631	818	21-236	109	0.7
Ce	0.60-4.07	1.56	0.06-1.57	0.36	0.14
Cl	81-1128	356	17-558	71	34
Co	0.15-0.90	0.47	0.12-0.80	0.37	0.03
Cr	2.03-19.89	12.3	0.52-21.65	11.5	0.3
Fe	176-1564	706	79-408	216	17
K	66-533	214	74-639	297	17
La	0.31-1.56	0.74	0.06-0.40	0.19	0.01
Mn	5.5-126.5	27.5	5.4-161.8	26.5	0.2
Na	89-1077	215.8	134-894	254.8	12
P	49-260	104.4	57-216	120.7	8.2
Pb	9-118	30.7	31-160	72.2	8.2
S	174-3882	714	672-4051	2096	139
Sb	0.77-7.17	2.57	1.02-8.42	3.18	0.01
Sc	0.04-0.39	0.13	0.003-0.026	0.009	0.003
Se	0.08-1.84	0.35	0.33-5.84	1.31	0.2
Si	694-4387	2040	142-535	342	16.1
Sm	0.02-0.28	0.09	0.011-0.244	0.049	0.001
Th	0.05-0.39	0.16	0.004-0.271	0.03	0.01
V	1.78-11.52	4.7	4.16-27.15	10.8	0.2
Zn	13-125	53.8	32-326	95.3	2.4
MP	8000-33900	17198.6	12200-52500	26492.4	

factor analysis in order to obtain information about aerosol sources.

Correlation coefficients and enrichment factors

The usual correlation coefficients were calculated. It was observed that the number of significant correlations was higher in the coarse particulate matter than in the fine. The elements Al, Ce, Fe, La, Sc, Si, Sm and Th were clearly associated in the coarse particles, while in the fine fraction the elements most frequently associated were Br, P, S, Sb and V.

In order to evaluate the contribution of anthropogenic aerosol sources, the enrichment factors (EF) were calculated using the average concentration of earth's crust and sea water reported by MASON et al.[14] and GOLDBERG,[15] respectively. The results are presented in Table 2.

Since Fe is the second most abundant element in the earth's crust[14] and its analytical uncertainty was less than 4%, this was chosen as a reference element for this source. On the other hand, Na was chosen as a reference for sea water because it is one of the major marine constituents and had an analytical uncertainty of less than 2%.

The investigation of sources using the criterion established by RAHN,[16] where elements with an EF less than 7 have their origin in the source investigated, while those with an EF greater than 10 are enriched in relation to that source, allowed us to observe that elements Br, Cl, Cr, Pb, S, Sb, Se and Zn were enriched in relation to the earth's crust while the probable source of Al, Ca, Ce, Co, K, La, Mn, Na, Sc, Si and Th was resuspended soil since they presented EF values of less than 7 in both fine and coarse particles. Only the element V presented a different behavior, with an EF greater than 10 in fine and less than 7 in coarse particulate matter. On the other hand, all elements were

Table 2

Enrichment factors calculated in relation to earth's crust (EF soil) and sea water (EF sea) average composition[14,15]

Element	Coarse		Fine	
	EF soil	EF sea	EF soil	EF sea
Al	0.91	>1000	0.33	>1000
Br	50.5	1.3	758	5.2
Ca	1.6	99.5	0.69	11.2
Ce	1.84	>1000	1.39	>1000
Cl	194	0.91	125	0.19
Co	1.34	>1000	3.46	>1000
Cr	8.73	>1000	26.5	26.5
Fe	1	>1000	1	>1000
K	0.58	27.4	2.65	32.2
La	1.74	>1000	1.43	>1000
Mn	2.05	>1000	6.44	>1000
Na	0.54	1	2.08	1
Pb	167	>1000	>1000	>1000
S	194	39.2	>1000	97.6
Sb	912	>1000	>1000	>1000
Sc	0.41	>1000	0.1	>1000
Se	491	>1000	>1000	>1000
Si	0.52	>1000	0.28	>1000
Sm	1.02	-	-	-
Th	1.58	>1000	0.1	>1000
V	2.47	>1000	18.4	>1000
Zn	54.5	>1000	314	>1000

enriched in relation to sea water except Br and Cl, which probably are of marine origin, since their EF values were less than 7 for both fine and coarse particles.

Principal factor analysis

The PFA was carried out using Statgraphics, software of the Statistical Graphics Co., on the elemental concentration data. After extraction of the principal factors, an orthogonal rotation (Varimax) was carried out to make the interpretation of the factors easier. Coarse and fine particulate matter were treated separately.

Results for coarse particles

The results of PFA for coarse particles are presented in Table 3. Six factors explained 89% of the data variance. All elements presented high communality, indicating a good data fit. Although the sixth factor presented an unrotated eigenvalue less than 1.0, it was considered in the analysis because it presented an eigenvalue greater than 1.0 after rotation.

The first factor was responsible for 31.8% of the variance and had high loadings for Al, Fe, Sc, Th, V and rare earths. It appeared to represent the contribution from the resuspended soil.

The second factor presented a high correlation with Ca, K, P, S and Si, whose presence was attributed to a fertilizer plant located 4 km away from the sampling site. Phosphatic rocks are typical raw material for this kind of plant.

Only elements Cl and Na were separated in the third factor, which was clearly associated with marine aerosol.

The fourth factor was highly associated with Br and Sb, and seemed to represent emissions from high-temperature processes.

Refuse incineration, a source known to be enriched in Zn,[17] appeared to be represented in the fifth factor. This approach

Table 3

Principal factor analysis results for coarse elemental concentration data

Element	Factor						Communality
	1	2	3	4	5	6	
Al	0.89						0.93
Br				0.84			0.77
Ca		0.96					0.93
Ce	0.84						0.92
Cl			0.90				0.95
Co	0.69						0.77
Cr						0.75	0.74
Fe	0.83						0.86
K		0.93					0.97
La	0.89						0.95
Mn					0.89		0.87
Na			0.83				0.90
P		0.93					0.95
Pb		0.65				0.63	0.87
S		0.83					0.95
Sb				0.70			0.82
Sc	0.94						0.97
Si	0.58	0.77					0.96
Sm	0.76						0.92
Th	0.74						0.81
V	0.76						0.83
Zn					0.83		0.85
Eigenvalue	7.0	5.0	2.1	2.1	1.8	1.6	
Variance (%)	31.8	22.7	9.5	9.5	8.2	7.3	

seemed to be reasonable since there was a municipal incinerator in operation near the sampling site during sample collection.

The sixth factor had high loadings for Cr and Pb and was attributed to emissions from industrial processes.

Table 4

Principal factor analysis results for fine elemental concentration data

Element	Factor 1	2	3	4	5	Communality
Al					0.79	0.90
Br		0.58				0.59
Ca				0.85		0.81
Ce		0.78				0.90
Cl			0.89			0.91
Cr				0.54		0.88
Fe		0.74				0.85
K	0.82					0.90
La		0.82				0.88
Na	0.87					0.89
P	0.67					0.81
Pb	0.51	0.67				0.83
S	0.63					0.82
Sb			0.73			0.82
Sc			0.59		0.52	0.79
Se			0.54			0.87
Si	0.72					0.87
V		0.59				0.72
Zn	0.87					0.80
Eigenvalue	5.0	4.2	2.5	2.3	1.8	
Variance (%)	26.3	22.1	13.2	12.1	9.5	

Results for fine particles

The Varimax rotated factor matrix for fine particulate matter is presented in Table 4. Five factors were responsible for 83.2% of the total variance. All elements were well explained by this fitting, except the element Br, whose communality was 0.59.

In general the interpretation of many of these factors was similar to that of the coarse particles.

The influence of phosphatic rocks (high loadings for K, Na, P, S and Si) and refuse incineration (high loading for Zn) appeared in the first factor.

The third factor had high loadings for Cl and Sb and was associated with high-temperature processes.

A little contribution of soil appeared in the fifth factor. This seems reasonable since most of the soil went to the coarse particles fraction.

The source associated with the fourth factor, with a high loading for Ca and intermediary ones for Cr, was not clearly identified.

The element Pb was distributed between the first and second factors. In the factor 2, Pb was associated with Br, and this emission is frequently associated with leaded-gasoline automobiles.[18,19] A CETESB report[20] has shown Pb concentration decreasing in São Paulo during the period from 1978 to 1983 due to the "Alcohol Program" that stimulated the use of pure alcohol and gasoline blended with 20% alcohol as vehicle fuel.

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