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CHARACTERISTICS OF FINE AND COARSE PARTICLES OF
NATURAL AND URBAN AEROSOLS OF BRAZIL

by

C.Q. Orsini, M.H. Tabacniks, P. Artaxo,
M.F. Andrade, and A.S. Kerr

Instituto de Física, Universidade de São Paulo

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Instituto de Fisica da Universidade de São Paulo

GEPA - Grupo de Estudos de Poluição do Ar

Caixa Postal 20516

01498 São Paulo, SP, Brazil

A B S T R A C T

Fine and coarse particles have been sampled from 1982 to 1985 in one natural forest seacoast site (Jurèia) and five urban-industrial cities (Vitória, Salvador, Porto Alegre, São Paulo, and Belo Horizonte). The time variations of concentrations in air and the relative elemental compositions of fine and coarse particle fractions, sampled by Nuclepore stacked filter units (SFU), have been determined gravimetrically and by PIXE analysis, respectively. Enrichment factors and correlation coefficients of the trace elements measured lead to unambiguous characterization of soil dust and sea salt, both major aerosol sources that emit coarse particles, and soil dust is also a significant source of fine particles.

Key word index: Aerosol, air pollution, fine and coarse particles, PIXE, trace element, enrichment factor, sources.

INTRODUCTION

Many extensive experiments have been performed during recent years to investigate the characteristics of atmospheric aerosols of urban-industrial, rural, and natural-remote terrestrial areas of the Northern Hemisphere (Junge, 1972; Whitby et al., 1972; Hidy et al., 1975; Demuynck et al., 1976; King et al., 1976; Flocchini et al., 1981; Spengler and Thurston, 1983; Pacyna et al., 1984; Winchester, 1984). Considerably less attention has been paid to atmospheric aerosols of the Southern Hemisphere (Lawson and Winchester, 1979; Maenhaut et al., 1979; Adams et al., 1980; Vleggaar et al., 1980; Orsini et al., 1982). This situation is partially due to the fact that the Southern Hemisphere is mainly populated by developing countries which, as a rule, do not as yet place strong emphasis on emission control or environmental protection. However, a better understanding of atmospheric aerosols of both the Northern and the Southern Hemispheres is important, not only from a local air pollution control viewpoint, but in a more general sense: Emission sources in each of these regions of the earth plays a potential role in the global cycling of atmospheric trace substances.

Generally speaking, Brazil (about 8.5 million km^2) occupies half the South American continent and thus covers a quarter of the total land area of the Southern Hemisphere exclusive of Antarctica. Because of its continental extent, geographic location, and historical development, almost half of Brazilian territory still remains remote and partially unexplored, keeping its original characteristics, for example in the extensive areas covered by the Amazon forests and by the large swamplands of Mato Grosso. At present, many small areas of these natural lands are being transformed into national

parks or ecological reservations, a simplified procedure that is probably not sufficient to preserve their ecological identities.

Aiming at helping to improve our knowledge about atmospheric aerosol properties of both rural and urban-industrial areas of the country, an extensive project, based on the investigation of properties of airborne inhalable particles, is being carried out by the Group for Studies of Air Pollution at the University of São Paulo. The project started in 1982 as an attempt to evaluate air quality of the atmospheres of one rural and some important urban-industrial areas in Brazil and to perform preliminary identification of the main sources of their atmospheric aerosols. As the program advanced, its goal has been extended to more ambitious tasks, such as a more detailed characterization of the aerosols and, consequently, a more effective investigation of relationships between source emissions and observed atmospheric concentrations.

Figure 1 shows the geographic locations of the coastal rural and five urban areas in this investigation as well as the interior natural areas of the basins of Amazônia and Goiás that have been investigated in 1980 and 1982 and are described elsewhere (Orsini et al., 1982). Since 1982 regular atmospheric sampling has been carried out at the natural forest ecological reservation of Juréia and five urban-industrial areas - Vitória, Salvador, Porto Alegre, São Paulo and Belo Horizonte (ordered from seacoast to interior, east to west and south to north) - selected in collaboration with the Brazilian agency for environmental protection SEMA, Secretaria Especial do Meio Ambiente. At most of the sites the record of measurements extends over
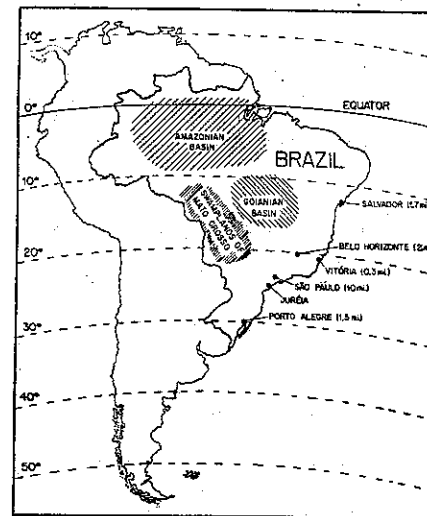
Figure 1. Locations of the one natural forest and five urban areas of this investigation. Urban populations in millions are indicated. Also shown are three interior regions under investigation (Orsini et al., 1982).

periods of more than one year.

Measurements of inhalable particles (diameter <15 um) have been made by sampling using a Nuclepore stacked filter unit (SFU) so as to collect separately the fine (<2.5 um, FP) and coarse (2.5-15 um, CP) components of the airborne inhalable particles (IP = FP + CP). The two sample fractions have been analyzed gravimetrically for determination of their mass concentrations and by PIXE (particle induced X-Ray emission, Johansson et al., 1976) for determinating their trace element concentrations.

The results can be examined from two viewpoints, by the analysis of the time variation of the FP and CP mass concentrations and by the analysis of inter-elemental concentration relationships by means of enrichment factors and correlation coefficients which may suggest aerosol source types. In a future paper, results obtained by receptor model analysis for source apportionment will be presented.

SAMPLING AND ANALYTICAL PROCEDURES

The main characteristics of the sites selected for sampling are the following:

Juréia (Federal Ecological Reservation), forest area of 30,000 hectares on the southern seashore of the State of São Paulo. It is a mountainous region, completely covered by the Atlantic Woodlands. The sampling site was inside the forest, 1.5 m above the soil level, about 1 km distant from the seacoast.

Vitória, a city 0.3 million on the seacoast of the State of Espírito Santo, about 6 km downwind of a large steel plant and the biggest iron ore harbor in Brazil. A few small industries are also located in around the city. The sampling site was first at Ilha do Boi, a small island just a hundred meters from the city, 6 m above the soil level and 50 m above sea level, on top of the building of the Senac Hotel, 200 m from the seacoast. Later, the sampling site was moved to the top of the 4 storey DMA building (state health office) near downtown, 300 m from the seacoast and 2 km from the previous station.

Salvador, a city of 1.7 million on the northeast seacoast of Brazil, State of Bahia. There are a large oil refinery, lead and other processing plants, and several medium size industries in its neighborhood. The sampling site was 1.5 m above the soil level in an army headquarters sports area within a residential area about 400 m from the seacoast.

Porto Alegre, a city of 1.5 million population about 50 km from the seacoast in the State of Rio Grande do Sul. There are many medium size industries, including iron and steel, a refinery, and a paper plant, spread across the city and its periphery. The sampling site was placed 15 m above the street level on top of the DMA building (the local state agency for environmental protection) about 100 m from a local subway construction site.

São Paulo, the largest industrialized city in Latin America, with about 10 million inhabitants in the city and 13 million in greater São Paulo. There are about 150,000 industries of all kinds and sizes, many of them large, and 2.5 million automotive vehicles. The sampling site was on the western periphery of the city 15 m above ground level on top of the main building of the Instituto de Física on the campus of the University of São Paulo.

Belo Horizonte, an inland city of about 2 million inhabitants with large industrial plants, including iron and steel in its neighborhood and many medium size industries spread over its area. Sampling was performed on the campus of the Catholic University of Minas Gerais (PUC-MG), situated on a hill at the periphery of the city. The samplers were placed 3 m above

the ground on top of a water reservoir.

It should be noted that today 80% of Brazilian automobiles use unleaded gasoline blended with 24% ethanol, and about 20% use pure alcohol fuel.

The experimental procedure, described more completely elsewhere (Orsini et al., 1984), consists of the following:

A 47 mm diameter Nuclepore stacked filter unit (SFU) sampler was installed in each previously selected site in the areas described above and operated for sampling intervals of 1 to 5 days (24-120 hours) from 1982 to 1985 as indicated in Figure 2. The SFU's were mounted with special inlets designed to admit airborne inhalable particles (IP, diameter <15 um) and operate with Nuclepore filters with 8 um and 0.4 um pores for separate collection of coarse (CP) and fine particles (FP), respectively (Cahill et al., 1979).

All the SFU's have been analyzed gravimetrically by weighing before and after exposure in a Mettler M3 1 ug sensitivity balance. Before each weighing the filters were equilibrated 24 hours at 50% relative humidity, and electrical discharge of the filters was assured by means of exposure to ^{210}Po radioactive sources before and during weighing.

After gravimetric analysis the filters were stored until the PIXE elemental analysis could be performed. The SP-PIXE system operates with the 8 MV Tandem Pelletron accelerator of the University of São Paulo (Sala and
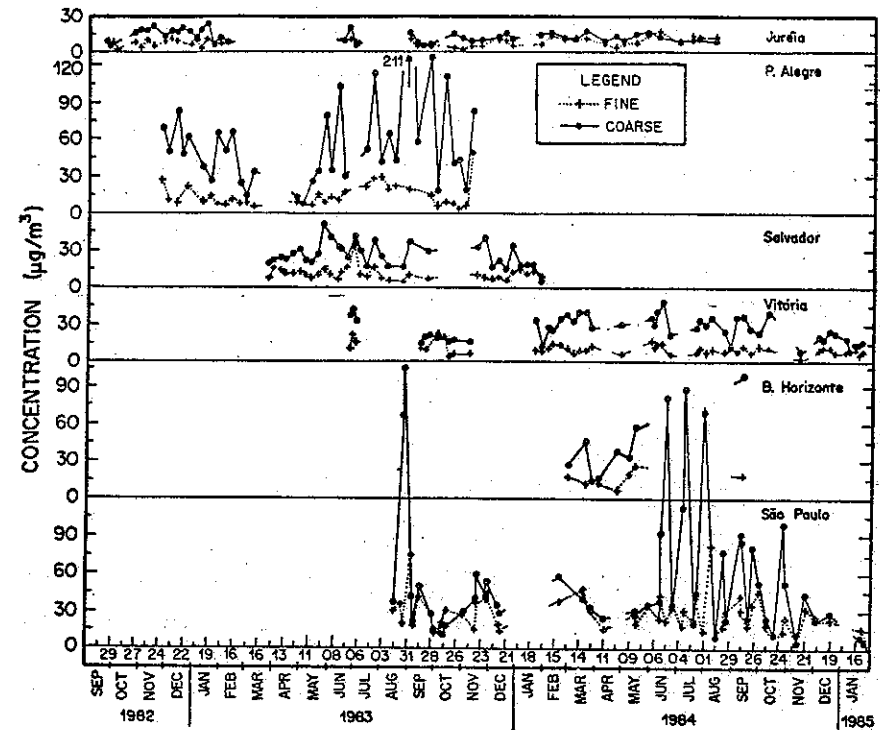

Figure 2. Time variation curves of the FP and CP mass concentrations for the six areas investigated.

Spalek, 1974; Tabacniks, 1983). Samples are bombarded with an 8 MeV alpha-particle beam, and their X-ray spectra are detected by an Ortec 7000 Si(Li) detector with an 8 um window (Orsini and Boueres, 1977). Detection limits

for ranges of elements are 30 ng m^{-3} for 10<Z<16, 1 ng m^{-3} for 16<Z<30,

30 ng m^{-3} for 30<Z<40, and 100 ng m^{-3} for Pb. Precision of the analysis

ranges from 10% for medium Z elements (16<Z<30) to 30% for light and heavy

elements (10<Z<16 and Z>30), except for Na which may be systematically

overestimated by up to 30%. The PIXE X-ray spectra have been reduced and

processed using the computer program HEX (see Kaufmann et al., 1977.) and the

B6900 Burroughs computer of the University of São Paulo.

A summary of the sampling schedule and analyses performed is presented

in Table 1.

Table 1 - Samples Collected by Stacked Filter Units at Six Brazilian Sites

Site	Sampling		Samples Collected by 12/85	Samples Analyzed	
	start	status		Gravimetric	PIXE
Juréia	9/82	stopped 8/84	52	46	49
Vitória	8/83	stopped 6/85	64	48	13
Salvador	3/83	stopped 7/84	45	33	10
P. Alegre	11/82	stopped 9/84	44	35	30
São Paulo	8/83	operating	98	62	30
B. Horizonte	2/84	operating	56	8	7

RESULTS AND DISCUSSION

First we present the gravimetric results and comment on their signifi-

cance for aerosol properties and air quality. Next, we present the trace

element results obtained by PIXE analysis, noting their significance for

aerosol characterization and relationships with their sources.

Gravimetric results

The time variation curves for the FP and CP concentrations, obtained by

gravimetric analysis of the SFU samples from the six sampled sites, are

presented in Figure 2. A visual examination of these curves shows several

characteristics: The low concentration values measured in the natural forest

area of Juréia contrast with the high values measured in the urban-industrial

areas; concentrations of the coarse particles are systematically higher than

of the fine; a seasonal effect is apparent, where winter (June-September)

concentrations in São Paulo and Porto Alegre are higher than in other

seasons; little correlation exists between FP and CP concentrations; and

absolute variability of CP concentrations is much greater than of FP.

Some of these conclusions can be quantified: Table 2 shows arithmetic (m_a)

and geometric (m_g) means and geometric standard deviations (S_g) of mass

concentrations, together with the correlation coefficients r between FP and

CP at each sampling site.

Several features can be seen in Table 2: Fine concentrations average

lower than coarse; arithmetic means are only slightly greater than geometric,

indicating only slightly skewed distributions; differences between the

geometric standard deviation values are significant, both between FP and CP

and between different sites; and FP and CP concentrations are not correlated

with each other. These features reflect the independence of the sources and

the mechanisms responsible for the generation of fine and coarse components

Table 2 - Arithmetic means m_a, geometric means m_g, geometric standard deviations S_g, and linear correlation coefficients r of fine with coarse mass concentrations (ug m^{-3}) in n samples.

Site	n	Fine m_a	m_g	S_g	Coarse m_a	m_g	S_g	r
Juréia	44	8.4	7.7	1.59	12.6	11.6	1.55	.15
Vitória	47	10.8	10.3	1.39	26.7	24.7	1.48	0.42
Salvador	33	11.9	11.0	1.47	26.1	24.1	1.56	0.44
P. Alegre	33	14.3	12.1	1.78	56.5	45.3	2.0	0.32
São Paulo	62	29.0	25.6	1.68	52.4	34.6	2.58	0.15
B. Horizonte	8	16.5	15.5	1.50	41.3	34.5	1.90	0.39

LOCAL	J	PA	S	V	BH	SP
NUMBER OF CASES COARSE	46	35	33	48	8	62
FINE	44	33	33	46	8	62

Figure 3. Average values of the FP and CP mass concentrations. For comparison, the proposed U.S.E.P.A. annual air quality standard is about 50 ug m^{-3}.

of the inhalable particles (e.g. gas-to-particle conversion of pollutants for the FP and mechanical pulverization and dispersion of dust for the CP).

For air pollution control purposes the FP and CP concentrations have been averaged (m_a) in Table 2 and plotted in Figure 3 in histogram format. These results may be compared with the annual standard for inhalable parti- cles (about 50 ug m^{-3}) suggested by the U. S. Environmental Protection Agency. Both Porto Alegre and São Paulo exceed this standard, and it should be kept in mind that the sampling sites were not located in the most polluted parts of any of the cities. If these concentrations are compared with the natural forest site of Juréia, the effect of urban activities on aerosol concentration is seen in all the cities.
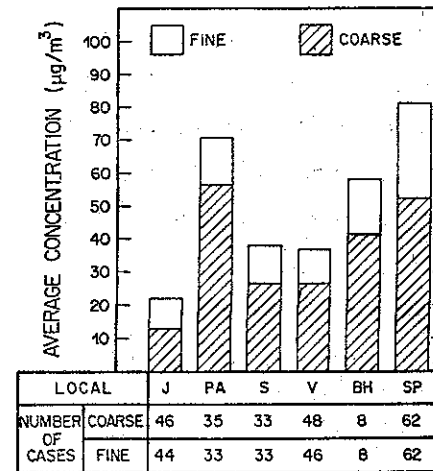
Brazilian legislation has established annual and daily standards for TSP using high volume samplers: 80 ug m^{-3} for the geometric mean of weekly measurements during one year and a maximum of 240 ug m^{-3} for any 24-hour measurement. We may convert our measured concentrations for inhalable particles to TSP using data that are currently available for Porto Alegre. Figure 4 shows the correlation between IP and TSP to be good, and the slope of 0.83 may be used to convert inhalable particles to TSP at other sites. After making this conversion it is seen that concentrations at the Porto Alegre and São Paulo sampling sites are in excess of the Brazilian annual standard.

PIXE results

The estimated contributions of likely chemical compounds of the trace

elements measured by PIXE are consistent with the gravimetrically measured masses of the FP and CP, as we can see in Table 3. The remaining mass may be mostly soot carbon and water held in combination with the compounds under the conditions of weighing the filters at 50% relative humidity.

Geometric means and geometric standard deviations of elemental concentrations at each of the sampling sites are given in Tables 4 and 5 for the FP and CP fractions. At Vitória the means for the two different sampling sites have been calculated separately. The number of data used for the means is also listed.

In order to obtain information about likely aerosol sources, enrichment factors (EF) and correlation coefficients (r) have been calculated, where

$$EF = (X/R)_{aerosol}/(X/R)_{reference}$$

X and R represent concentrations of any element X normalized to a selected element R, and r is the usual linear correlation coefficient. Geometric mean concentrations have been used for X and R in calculating EF.

If the aerosol is enriched in normalized elemental concentration relative to a reference composition (e.g. sea water or soil dust), EF>1. Soil dust and sea salt have been selected as reference compositions for EF analysis since these are the only cases with unambiguous results. Si and Na have been used for normalization (except in São Paulo where Si had exceptionally low fine particle values and was replaced by Ti). If other elements are
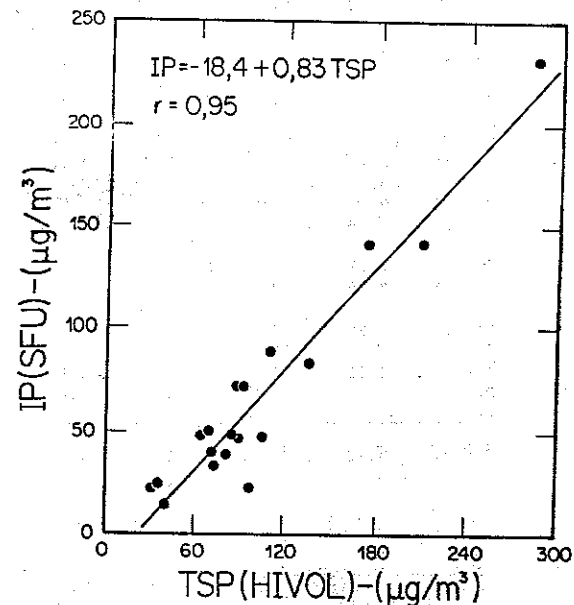
Figure 4. Regression of IP measured by Nuclepore stacked filter units versus TSP by high volume samplers in Porto Alegre (data from DMA, the state agency for environmental protection).

Table 3 - Average percentage of fine and coarse particles accounted for by compounds of the measured elemental constituents.[a]

Fraction	Juréia	Vitória	Salvador	P.Alegre	São Paulo	B.Horizonte
Fine	24.4	35.1	35.9	23.7	36.1	17.8
Coarse	27.3	47.6	55.8	40.5	41.1	91.8

[a]Carbonates of Na^+, K^+, Mg^{++}, Ca^{++}. NH_4^+ salts of PO_4^{3-}, SO_4^{2-}, Cl^-, Br^-. Oxides of Al, Si, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb.

Table 4. Fine particle trace element concentrations, ng m^{-3}, from PIXE analysis[a].

	Juréia			Vitória-IBOI			Vitória-DMA			Salvador			Porto Alegre			São Paulo			Belo Horizonte		
	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g
Na	32	76.74	3.13	6	462.38	1.59	5	250.61	1.34	10	200.91	3.33	27	101.20	3.55	30	247.57	2.34	7	52.36	3.45
Mg				6	75.51	1.69	5	13.61	1.43	4	106.41	1.50	22	57.28	1.79	5	178.28	2.40	5	25.41	3.77
Si	44	87.70	2.50	6	175.79	2.12	5	214.29	1.14	9	311.17	1.92	25	146.76	2.97	20	96.83	3.78	6	234.42	1.86
P							1	4.10	-	0						10	38.31	2.27			
S	49	365.59	2.00	6	448.75	1.47	5	426.58	1.21	10	426.58	2.41	30	458.04	2.19	30	1842.89	1.60	7	297.17	1.59
Cl	21	9.27	2.28	3	27.99	11.22	4	7.00	3.11	5	19.82	2.51	15	18.25	4.55	24	25.47	3.36	5	10.30	3.09
K	48	35.08	2.37	6	101.39	2.01	5	108.14	1.29	10	119.12	2.55	29	93.71	2.62	30	240.60	1.62	7	103.28	1.84
Ca	46	9.10	2.59	5	47.86	1.55	5	34.67	1.24	10	58.21	2.60	29	31.31	2.78	29	52.18	3.22	7	31.41	2.12
Ti	11	3.19	1.62	5	5.40	2.32	5	8.47	1.18	4	9.64	1.39	22	5.10	1.99	25	9.63	2.16	5	5.26	2.08
V				2	1.71	1.27	3	2.75	1.33	8	11.89	2.58	11	6.07	1.62	26	24.11	1.65	4	3.66	1.61
Cr	9	2.99	1.21	3	0.25	4.43				4	7.52	2.04	16	2.59	1.63	4	7.81	5.41	2	0.24	3.93
Mn	15	2.86	2.22	2	3.52	1.64	5	4.91	2.58	9	55.46	2.74	19	3.08	2.21	26	21.08	2.07	6	4.14	1.85
Fe	49	14.69	2.99	6	240.44	2.54	5	274.79	1.26	10	89.33	3.57	24	39.13	3.35	30	203.38	2.47	7	188.36	2.20
Ni	24	1.29	1.44	2	2.24	1.89	5	3.01	1.68	6	4.79	2.06	17	2.30	1.73	29	8.57	1.53	7	2.69	2.24
Cu	37	2.10	2.02	2	2.88	1.71	5	3.37	1.73	7	16.79	3.69	21	3.30	1.88	30	11.32	2.83	5	5.51	2.25
Zn	45	5.71	2.49	6	14.00	5.89	5	119.12	2.34	9	29.92	3.62	28	26.76	2.32	30	125.72	2.10	7	9.89	1.63
Pb				2	18.66	1.47	2	62.66	1.80	7	115.08	6.90				13	94.28	2.43	3	20.09	1.16
PP[b]	44	8.26	1.47	6	13.21	1.77	5	10.05	1.26	10	11.4	1.04	30	12.74	2.01	33	28.91	1.55	7	14.26	1.44

Table 5. Coarse particle trace element concentrations, ng m^{-3}, from PIXE analysis[a].

	Juréia			Vitória-IBOI			Vitória-DMA			Salvador			Porto Alegre			São Paulo			Belo Horizonte		
	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g	n	m_g	S_g
Na	44	443.61	2.03	8	968.28	1.69	4	683.91	1.43	10	933.25	1.46	28	514.28	2.32	28	356.70	1.85	7	214.29	1.33
Mg	49	96.83	1.39	8	187.93	1.62	4	125.60	1.42	9	272.27	1.33	26	244.91	1.78	27	249.57	1.53	7	220.29	2.84
Al	30	44.57	2.07	8	257.63	2.31	4	620.87	1.56	10	487.53	1.73	30	1204.20	2.19	29	1050.27	2.22	7	1016.25	2.04
Si	49	71.45	2.23	8	609.54	1.95	4	1218.99	1.44	10	1039.92	1.86	31	3360.47	3.38	29	1810.92	2.14	7	1520.55	1.88
P	34	38.90	1.51				4	30.06	1.21	4	50.93	1.35	17	43.46	1.98	21	49.26	5.68	1	13.58	-
S	49	170.61	1.53	8	234.42	1.48	4	316.96	1.33	10	419.76	1.63	31	400.31	2.39	29	787.59	1.75	7	319.89	2.53
Cl	49	404.58	3.25	8	1845.02	1.80	4	979.49	1.17	10	1396.37	2.22	31	403.55	3.72	29	146.69	3.45	7	127.35	2.57
K	49	69.82	1.57	8	118.03	1.43	4	174.58	1.44	10	162.18	1.90	31	363.75	2.76	29	303.74	2.30	7	246.04	2.29
Ca	49	56.23	1.73	8	318.42	1.38	4	606.74	1.31	10	724.44	1.82	31	814.70	2.62	29	742.68	2.04	7	988.55	1.73
Ti	24	4.42	2.20	7	36.64	2.21	4	85.51	1.35	10	47.21	1.99	30	102.31	2.00	29	104.45	1.98	7	56.89	1.80
V							3	22.80	2.23				24	19.99	1.96	4	8.41	1.52			
Cr	7	7.78	1.39	7	5.98	2.59				5	11.04	1.51	10	5.95	2.39	8	8.95	2.77	4	14.19	2.22
Mn	21	1.99	1.87	6	6.10	1.64	4	38.64	2.09	10	41.78	3.10	27	13.74	2.43	27	29.22	2.27	7	18.66	2.74
Fe	49	33.19	2.59	8	1674.94	1.93	4	2992.26	1.51	10	545.76	1.91	31	714.33	2.92	29	1040.64	2.06	7	1355.19	1.78
Ni	22	1.34	1.63	4	12.82	2.24	4	30.97	1.79	4	6.70	1.43	21	2.93	2.22	28	12.92	2.58	6	7.29	2.40
Cu	39	2.49	2.23	6	25.47	2.74	4	18.62	1.55	9	31.70	5.00	30	12.25	2.73	29	18.91	3.07	4	6.18	3.04
Zn	32	8.38	3.79	8	30.27	2.33	4	111.43	4.41	9	22.08	2.95	29	39.96	2.21	29	94.67	2.52	5	19.82	2.69
Br	15	15.03	1.39	6	14.59	1.79	4	10.02	1.46	8	14.89	2.62	27	10.43	2.29	29	16.23	2.58	6	16.60	2.52
Pb				3	13.58	2.28	4	56.10	3.21	5	23.01	2.09				20	51.32	2.16	6	28.12	1.96
CP[b]	44	12.68	1.48	8	24.55	1.44	5	33.04	1.15	10	24.21	1.7	30	44.28	1.80	34	38.02	2.05	7	14.26	1.44

[a]Key: n = number of values above detection limit of the samples analyzed.
m_g = geometric mean of n values.
S_g = geometric standard deviation.
[b]CP = coarse particle concentration from gravimetric analysis of samples analyzed by PIXE.
PP = fine particle concentration from gravimetric analysis of samples analyzed by PIXE.

chosen as references, slightly different results are obtained for EF, but the overall conclusions are virtually the same.

The data sets for Juréia, Porto Alegre and São Paulo were large enough to give meaningful correlations, and logarithms of FP and CP trace element concentrations were used for computing r. The calculated EF and r values are presented in Tables 6, 7, 8, and 9, together with the source profiles that were used (Lawson and Winchester, 1977; Artaxo, 1985).

Enrichment factors and correlation results

If EF is close to unity, a common origin of the trace elements involved is suggested. In this case, we expect the r values also to be close to unity. For coarse particles this is generally observed (see Tables 7 and 9) where the r values reinforce the conclusions based on EF. In addition, high r values are found for FP elements at some sites, and their corresponding EF values are also high; this could be a consequence of meteorological effects. Differences in the statistical significance levels of r values for the same number of samples are due to different numbers of paired concentrations used.

Some features can be derived from the values given in Tables 6 to 9:
(1) In general, soil dust or sea salt are the dominant sources of coarse particles, depending on the site location being far from or close to the seacoast. Soil dust is noticeable in all aerosols and is an effective producer of fine particles. In fact, in Table 7 the EF and r values show clear predominance of soil dust for the interior sites of Belo Horizonte, São Paulo, and Porto Alegre, while in Table 9 sea salt predominates for the

coastal sites of Juréia, Vitória and Salvador. Looking mainly at the EF values for Ca, Ti and Fe (important tracers of soil dust) in Table 6, a slight presence of fine soil dust for all sites can be observed. However, results in Table 8 do not lead to a similar conclusion for sea salt, even for coastal sites.

(2) A gradual degradation of the marine-like characteristics of the CP aerosols is noticeable as we move from seacoast to interior sites (downward in Tables 6 to 9). This can be observed for coarse particle EF relative to both sea salt and soil dust in Tables 9 and 7. In fact, the EF values of Table 9 increase as we move from Juréia to Belo Horizonte, the most interior site, while soil dust coarse particle EF values (Table 7) move in the opposite direction. This is especially evident for Mg, K, and Br in Table 9 and practically all elements in Table 7.

(3) Element-by-element examination reveals some common behaviors. In fact, in Table 9 we can observe a slight general enrichment of all elements relative to sea salt at seacoast sites, except for Cl. EF values relative to sea salt (Tables 8 and 9) show Cl depletion at all sites, even at Juréia where Cl exhibits high and significant correlations with Na. Coarse Cl depletion increases as we move away from the seacoast. Since soil dust is not a Cl source, this could be evidence of release of Cl from coarse particles due to its high chemical reactivity.

Finally, a site-by-site analysis makes evident some particular characteristics of the aerosols investigated here:

Table 6. Fine particle enrichment factors, EF, relative to soil dust, and correlation with reference element, r (in parentheses).

Site	n	Reference element	Fine EF, soil (r)[a]						
			Na	Mg	K	Ca	Ti	Fe	Si
Juréia	49	Si	7.5(-.37)	-	9.0(ns)	1.1(ns)	1.5(ns)	0.8(.32)	-
Vitória IBOI	6	Si	22	4.8	13	3.0	1.2	8.2	-
Vitória DMA	5	Si	10	0.7	11	1.8	1.6	5.8	-
Salvador	10	Si	5.5	3.8	8.6	2.1	1.2	1.3	-
P. Alegre	30	Si	5.9(.48)	4.4(ns)	14(ns)	2.3(.45)	1.4(.46)	1.2(ns)	-
São Paulo	30	Ti	5.5(.57)	5.2(ns)	14(.66)	1.5(.50)	-	2.4(.76)	0.25(ns)
B. Horizonte	7	Si	1.9	1.2	9.9	1.5	0.9	3.6	-
Soil dust weight ratio element/Si			0.117	0.0891	0.0444	0.0911	0.0249	0.222	1.0

[a] significance: P<0.001, double underline; 0.001<P<0.01, underline; 0.01<P<0.1, no underline; P>0.1, ns.

Table 7. Coarse particle enrichment factors, EF, relative to soil dust, and correlation with reference element, r (in parentheses)[a].

Site	n	Reference element	Coarse EF soil (r)[a]							
			Na	Mg	Al	K	Ca	Ti	Mn	Fe
Juréia	49	Si	52(ns)	15(ns)	1.5(.88)	22(ns)	8.6(ns)	2.5(.40)	6.2(ns)	2.1(.72)
Vitória IBOI	8	Si	14	3.5	1.0	4.4	5.7	2.4	2.2	12
Vitória DMA	4	Si	4.8	1.2	1.2	3.2	5.5	2.8	7.0	11
Salvador	10	Si	7.7	2.9	1.1	3.5	7.7	1.8	8.9	2.4
Alegre	31	Si	1.3(.57)	0.8(.91)	0.9(.989)	2.5(.84)	2.7(.94)	1.2(.985)	0.9(.82)	1.0(.66)
São Paulo	29	Si	1.7(ns)	1.6(.58)	1.4(.98)	3.8(.93)	4.5(.93)	2.3(.94)	3.6(.70)	2.6(.96)
Horizonte	7	Si	1.2	1.6	1.6	3.6	7.1	1.5	2.7	4.0
Soil dust weight ratio element/Si			0.117	0.0891	0.041	0.0444	0.0911	0.0249		0.222

[a] significance: P<0.001, double underline; 0.001<P<0.01, underline; 0.01<P<0.1, no underline; P>0.1, ns.

Table 8. Fine particle enrichment factors. EF, relative to sea salt, and correlation with _reference element, r (in parentheses)[a].

Site	n	Reference element	Mg	Fine EF sea salt (r)[a] S	Cl	K
Juréia	49	Na	-	30(ns)	0.06(.63)	12(ns)
Vitória IBOI	6	Na	1.2	6.2	0.03	5.5
Vitória DMA	5	Na	0.4	11	0.01	11
Salvador	10	Na	4.0	14	0.05	15
P. Alegre	29	Na	0.8(.57)	29(.66)	0.1(ns)	23(.38)
São Paulo	30	Na	-	47(.57)	0.05(.59)	25(.51)
B. Horizonte	7	Na	3.7	36	0.1	50
Sea salt weight ratio element/Na			0.1313	0.1569	1.90	0.0397

[a]Significance: P<0.001, double underline; 0.001<P<0.01, underline; 0.01<P<0.1, no underline; P>0.1, ns.

Table 9. Coarse particle enrichment factors. EF, relative to sea salt, and correlation with reference element, r (in parentheses)[a].

Site	n	Reference element	Mg	Fine EF sea salt (r)[a] S	Cl	K	Br
Juréia	49	Na	1.7(.79)	2.5(.51)	0.5(.86)	4.0(.46)	5.1(.64)
Vitória IBOI	8	Na	1.5	1.5	1.0	3.1	2.3
Vitória DMA	4	Na	1.4	3.0	0.8	6.4	2.2
Salvador	10	Na	2.2	2.9	0.8	4.4	2.4
P. Alegre	31	Na	3.6(.77)	5.0(.72)	0.4(.83)	18(.40)	3.0(ns)
São Paulo	29	Na	5.3(ns)	14(ns)	0.2(ns)	21(ns)	6.8(.55)
B. Horizonte	7	Na	7.8	9.5	0.3	29	12
Sea salt weight ratio element/Na			0.1313	0.1569	1.90	0.0397	0.0067

[a]Significance: P<0.001, double underline; 0.001<P<0.01, underline; 0.01<P<0.1, no underline; P>0.1, ns.

Juréia. The marine characteristic of the aerosol is evident only in the coarse fraction, while in the fine fraction soil dust is certainly an important source. Fine K is highly enriched (Tables 6 and 9) without any correlation with the reference elements Na and Si. On the other hand, K, Ca, and Mn are also enriched without being correlated with their reference element Si. This picture, reinforced by the fact that these elements are significantly correlated with each other (K with Ca, 0.73; K with Mn, 0.58), suggests a new aerosol source, in addition to sea salt or soil dust. Further studies with principal factor analysis and chemical mass balance receptor models have identified vegetation as probable for this new source (Artaxo and Orsini, 1986). Fine S may become enriched by decomposition of biological material and by gas-to-particle conversion since the station was located inside a subtropical forest.

Vitória. In both sampling sites (IBOI and DMA), the characteristic of the coarse marine-like aerosol is still quite apparent in Table 9. Soil dust characteristics are also seen in Table 7, although somewhat contaminated by urban-industrial pollution, especially from the large iron ore harbor and steel plant which enrich Mn and Fe. Fine soil dust particles are enriched in K, probably due to wood burning in a bakery very close to the sampling site, and Fe, due to the iron ore harbor and steel plant.

Salvador. The results here are similar to those at Vitória, except for the iron. Concentrations higher than 1 ug m^{-3} of fine Pb were measured in only 2 samples, leading to a not so high average value of 115 ng m^{-3}. The occasionally high values might be caused by a lead plant located 40 km from

the sampling site, but only under favorable wind conditions.

Porto Alegre. The marine-like characteristics are almost absent in the CP aerosol (see Table 9), with their EF values for Mg, S and K increased by a factor of 2 to 4 compared to Juréia. Soil dust characteristics on Table 7 are quite visible, with K and Ca slightly enriched. The high correlation of the soil dust elements and the high levels of these same elements (Table 5) indicate soil dust as a strong and important local air pollution source.

São Paulo. The complete disappearence of any marine-like characteristics of its CP aerosol is remarkable, since the respective EF values show high enrichments for all the trace elements considered. That is, the marine aerosol is completely obscured by particles of continental composition, plus contamination from local urban-industrial pollution. Again, soil dust seems to be an important aerosol source. A much more extensive aerosol characterization by receptor modeling is now being performed (Andrade, 1986).

Belo Horizonte. The situation here is similar in many respects to the one described for São Paulo, except for a strong natural iron enrichment of its soil.

CONCLUSIONS

First of all, it must be emphasized that the experiments performed show a simple way of investigating natural and urban-industrial aerosols by using inexpensive techniques accessible to developing countries. The SP-PIXE system we have used is installed in a Tandem Van de Graaff accelerator

specifically intended for nuclear physics research. The investigations performed have brought to light important characteristics of the atmospheric aerosols sampled, including the level of their concentrations, their time variations, and also their elemental composition relationships. The application of enrichment factor and linear correlation analysis leads to unambiguous identification of sea salt and soil dust as dominant sources of the sampled coarse particle fraction. In addition, soil dust is effective in producing finer particles.

Our results are consistent with the current understanding that marine aerosol is produced mainly by the mechanical process of bubble bursting, causing the formation of coarse particles of seawater composition. In contrast to this, the enrichment factor (EF) values for the fine particles suggest that soil dust aerosol, known to be produced as coarse particles by the dispersion of soil by wind, a typical mechanical process, also contains a fine particle component in practically all the aerosols investigated. A marked diminution of marine aerosol is evident as one moves from the seacoast to the interior of the continent.

The measurements that have been accumulated constitute a rich data set for further studies on source apportionment by receptor models, now being carried out by GEPA.

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