

## PIXE ANALYSIS FOR AIR POLLUTION SOURCE APPORTIONMENT IN URBAN AREAS OF BRAZIL

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PIXE analysis has been applied to an air quality monitoring and assessment program in south-eastern Brazil. Fine and coarse particle size fractions were sampled selectively, using Nuclepore in stacked filter units, once a week for one year in one background and five urban sites. The procedures used for sampling and analysis have been developed and refined in close conjunction with the application to aerosol studies, and 138 pairs of filters have been analyzed by PIXE. Once a national source signatures library for particulate matter has been created, the data are suitable for receptor modeling and source apportionment for anthropogenic and natural particulate constituents by chemical mass balance models.

### 1. Introduction

This work is an extension of a study previously reported [1] on the use of the SP-PIXE system in a national air quality monitoring program. We present here an account of the procedures developed for analyzing samples collected in the program, together with a summary of sampling procedures that are described more fully elsewhere [2] and an indication of the suitability of the database for source apportionment modeling.

All samples were collected in separated coarse and fine particle size fractions by stacked Nuclepore filters at one nonurban and five urban sites in coastal and nearby inland locations in south-eastern Brazil (fig. 1). At most sites samples were collected for at least one year, thus providing information over all seasons and many weather conditions. As shown in table 1, the sampling program commenced in 1982 and continued to early 1986. The samples were generally collected weekly for 1 to 5 day periods. They were then analyzed by PIXE at the University of São Paulo using the 8 MV tandem Pelletron accelerator.

### 2. Experimental

Emphasis was placed on developing a sampling procedure that contained quality control features. Stacked Nuclepore filter units (SFU) consisted of uncoated 47 mm diameter filters of 8.0 and 0.4  $\mu\text{m}$  pore diameter that, when operated at 3 l min<sup>-1</sup>, provided a particle size cut at 2.5  $\mu\text{m}$ , and, at 10 l min<sup>-1</sup>, a cut at 2.1  $\mu\text{m}$  diameter. Particles of diameter >15  $\mu\text{m}$  were excluded by a suitable inlet [3]. Before use, all filters were equilibrated at 50% relative

humidity and electrically discharged in the presence of a <sup>210</sup>Po source and then weighed on Mettler M3 microbalance three times to assure constant weight within  $\pm 10 \mu\text{g}$ . Of these, 10% were reserved as analytical blanks, and the remaining filters were loaded into SFU holders which then were shipped to the sampling locations and deployed by field personnel.

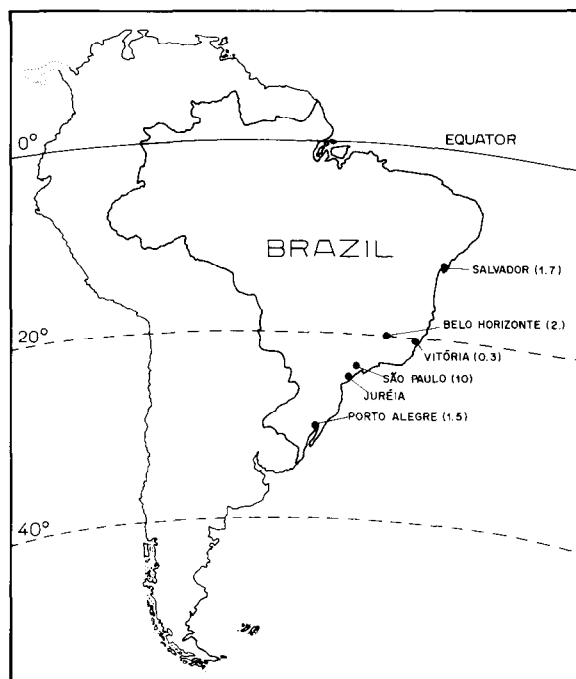


Fig. 1. Locations of the natural forest area of Juréia and five urban and industrial areas for aerosol composition measurements. Urban populations in millions are indicated.

Table 1.  
Samples collected by stacked filter units at six Brazilian sites.

Site	Dates	Sampling conditions	
		Average time (h)	Air volume (m <sup>3</sup> )
Juréia	9/82–8/84	96	17
Vitória	8/83–6/85	124	23
Salvador	3/83–7/84	72	13
P. Alegre	11/82–9/84	72	12
São Paulo	8/83–present	24	6
B. Horizonte	2/84–1/86	72	11

Sampling in the field was performed for 1 to 5 day intervals in a setup that was designed to assure accurate air flow measurement. The setup consisted of a sampling inlet, the plastic holder of the SFU, a quick disconnect joint, a rotameter, a critical flow orifice, a vacuum gauge, a diaphragm vacuum pump, and a factory calibrated dry gas meter. Satisfactory agreement between gas meter readings and volumes calculated from rotameter readings and sampling times was found. Moreover, the satisfactory condition of each vacuum pump could be verified from this information.

The samples were returned in their holders to the laboratory, and the filters were treated and weighed using the same procedures as the blanks to determine the total gravimetric mass of coarse and fine fractions. Mass concentrations in air were calculated from air volumes measured to  $\pm 10\%$  by the gas meters. Thereafter, each filter was cut in two, one to be analyzed by PIXE and the other archived for either supplemental analysis by other chemical methods or for reproducibility tests of the PIXE procedure.

Of the total of 359 pairs of filters collected in the program and weighed for gravimetric mass, 138 have been analyzed by PIXE for elemental concentrations. Since the most recent descriptions of the SP-PIXE system [1,4], some modifications have been made to improve resolution of X-ray spectra, detection limits, and control of operations during sample bombardment. Unchanged is the basic system that consists of an 8 MeV alpha beam, a specially constructed target chamber in which the detector is at 120° to the beam, and an Ortec 7000 50 mm<sup>3</sup> Si(Li) detector, in a 30 l Dewar, with an 8  $\mu$ m beryllium window custom designed to be thin and long so as to provide a large solid angle (0.026 sr) for high X-ray counting efficiency. A funny filter of 103  $\mu$ m Mylar and 12% hole equalizes the sensitivity curve of the system in the low Z region. Micromatter standards, 50  $\mu$ g cm<sup>-2</sup> thick, are used for system calibration. Beam currents of 1–10 nA give X-ray counting rates less than 5 kHz so as to give less than 10% dead time in the X-ray detection system.

A new collimator of 3.7 mm diameter and a Faraday cup made of silver, which has a Coulomb barrier higher than the alpha beam energy, avoids the reac-

tion in carbon collimators <sup>12</sup>C( $\alpha$ , n)<sup>15</sup>O ( $\beta^+$ ,  $t_{1/2}$  = 122 s). Other possible metals were not selected owing to their potential interest in air quality measurements (e.g. Pb, Ni, Cu) or difficulty to machine (e.g. Ta).

The Ni beam diffuser foil is now closer to the target (75 cm) and thicker (0.5  $\mu$ m), thus giving the same scattering but being more durable, less likely to break during alpha bombardment, and without excessive energy straggling.

The target chamber now permits changing a load of 8 samples within 10 min, thus improving the number of analyses that can be carried out in the allotted time of accelerator use.

Nuclepore filter samples of 10 m<sup>3</sup> air bombarded with 10  $\mu$ C charge give detection limits of 30 ng m<sup>-3</sup> for 10 < Z < 16, 1 ng m<sup>-3</sup> for 16 < Z < 30, 30 ng m<sup>-3</sup> for 30 < Z < 40, and 80 ng m<sup>-3</sup> for Z = 82 (Pb). Precision ranges from 10% for 16 < Z < 30 to 30% for lighter and heavier elements, except for Z = 11 (Na) which is less precisely determined owing to its soft X-rays.

The X-ray spectra are resolved by a modified version of the program HEX [5] in the Burroughs B6900 computer at the University of São Paulo. The large amount of data to process in our air quality research program requires an integrated system that includes an automated computer code for spectrum resolution. In addition to speed, operator errors are avoided. Systematic errors are minimized by the analysis of standards that are fitted with a semi-empirical sensitivity curve of the elements.

### 3. Results

Detailed descriptions of the sampling sites have been given elsewhere [2]. A summary of elemental concentrations in ng m<sup>-3</sup>, expressed as geometric means (of values above detection limits) over all samples analyzed, is shown in fig. 2 for separate fine and coarse fractions. Also indicated for each site is the gravimetric mass concentration ( $M$ ) in  $\mu$ g m<sup>-3</sup> and the number of samples ( $n$ ) in each set. For comparison, the lower part of fig. 2 shows the elemental composition of average soil dust, sea salt, and bulk plant

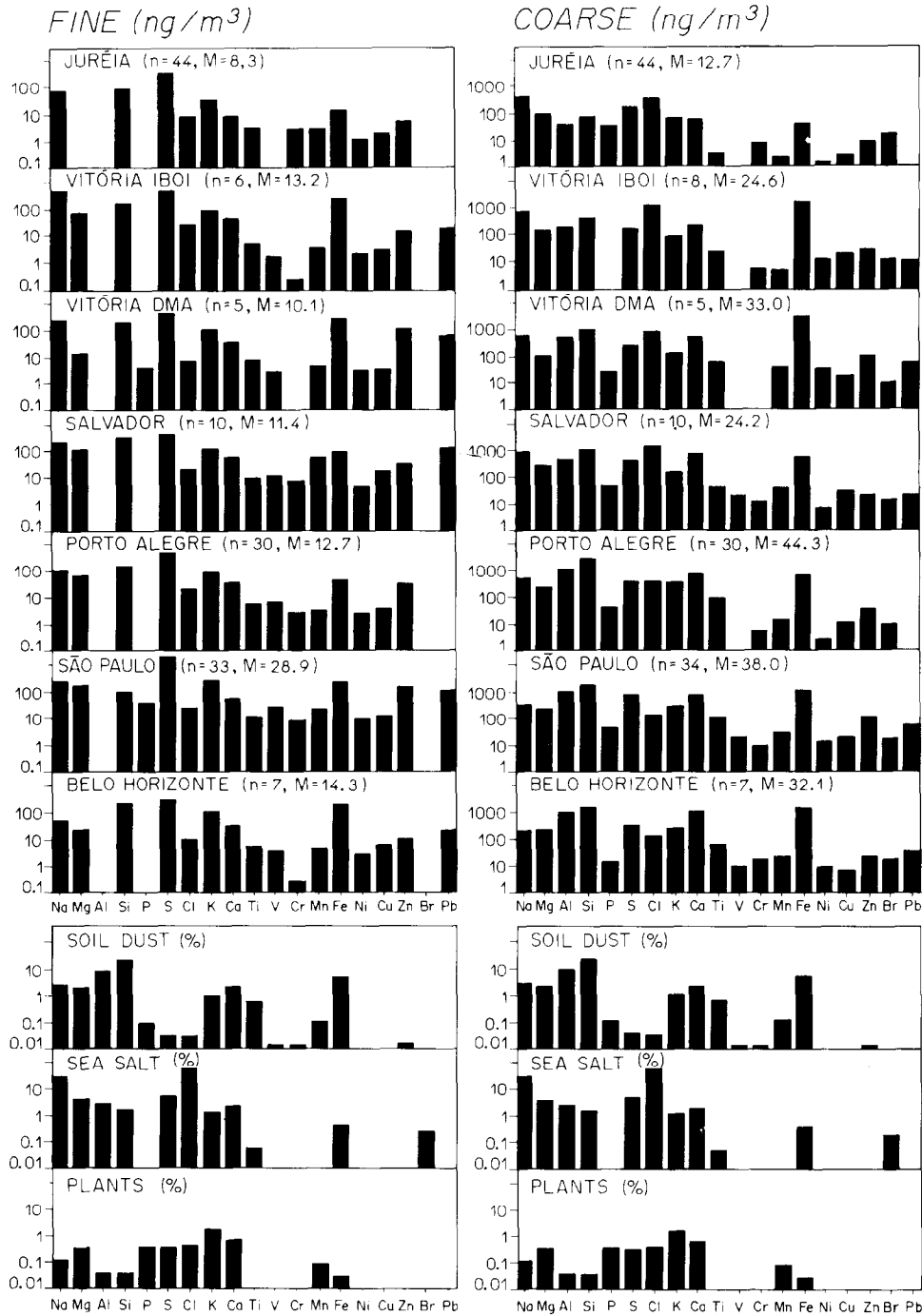


Fig. 2. Geometric mean concentrations, in ng m<sup>-3</sup>, of fine and coarse particles, for *n* samples. Gravimetric masses, in μg m<sup>-3</sup>, are given by *M*. Percent compositions of three major natural source types are given below for comparison.

material. The first two are convenient references for inorganic constituents of background aerosol [6] whereas the third has been found to explain a considerable fraction of remote aerosol in Brazil [7].

By inspection of fig. 2, where the sites are arranged in approximate order of expected marine to interior

atmospheric characteristics (cf. fig. 1), coarse particle relative abundances of Na, Mg, and Al at first decrease, and then increase, with increasing *Z*, reflecting a reduction in sea salt and a rise in soil dust contribution. On closer examination some additional features may also be seen, as pointed out elsewhere [2].

#### 4. Discussion

In principle, the data may be more quantitatively evaluated using chemical mass balance (CMB) and other receptor modeling techniques. For example, in CMB a constraint is applied such that the aerosol composition at the receptor site must be a material balance of the contributions from a finite number of known aerosol sources.

The quality of data obtained here is suitable to see the effect of mixing different source signatures in complex urban atmospheres, but a complete resolution of these must await a compilation of source compositions for Brazilian urban areas, such as has been accomplished for the United States [8].

The present program was designed for multiple purposes. The first objective was to obtain estimates of average concentrations of elemental constituents in suspended particulate matter in selected urban areas and background sites. For this, the choice of sampling frequencies of weekly or longer times between samples was optimum for minimum analytical effort. The quality control features and improvements in detection limits made during the program also simplified requirements for sampling in the field, while assuring high data quality and results that are useful in a practical sense by a public regulatory agency.

The second objective was to determine the effect of different natural and pollution sources on ambient air quality, an objective which is both practically useful and of considerable scientific interest. Ideally this is best done with sampling times and frequencies comparable to the variability in the source and transport processes that are linked to atmospheric chemical composition variability. Although our samples averaged over much of this variability, nevertheless, some trends can be seen in the data. However, a more comprehensive source signature library is required for our sampling sites before statistical analysis of our data may succeed in resolving the major sources.

PIXE is a valuable and cost effective method applicable to network studies like the one presented here. During the program improvements in procedures were made to avoid particular difficulties as they were recognized. The recent use of receptor models applied to PIXE data enhances the value of measurements by this and other multielemental and sensitive methods.

The improvements of detection limits and extension to low Z (Na), features achieved by refinements in procedures, are real needs to obtain better and more reliable source apportionment.

The present study represents a step in applying PIXE analysis to a practical evaluation of air quality in Brazil and to design further studies for distinguishing pollution from natural sources so that anthropogenic emissions may be controlled.

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