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Trace Metals in the Atmosphere of Niterói City, RJ, Brazil

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Niterói City (Figure 1) belongs to the metropolitan area of Rio de Janeiro City and it is considered to have the 4th best environmental quality among all Brazilian cities. Despite this fact, there are no published data about atmospheric pollutants for this City except those of Pereira Netto et al (2001) who presented data on 17 PAHs in the atmosphere of this city. Even for Rio de Janeiro, capital of the Rio de Janeiro state and the 2nd biggest city of Brazil, the data already published about atmospheric trace elements are about 15 or more years old (Daisey, 1985; Trindade, 1981).

Atmospheric metals have natural and anthropogenic origin (Chow, 1995) and they have been associated with respiratory diseases such as asthma (Whittemore and Korn, 1989; Schwartz, 1993). The elements associated with anthropogenic activities are mainly originated in industrial activities or automotive pollution. Pb is a classical example since leaded compounds have longer been used as additives to gasoline and for many years it was ubiquitous in urban atmospheres.

MATERIALS AND METHODS

In this work, a simple methodology was employed to sample digestion and metal determinations in total suspended particulate (TSP). It consisted of a single step digestion in a closed system (microwave digestion) using an acid mixture of HNO_3 and H_2O_2, avoiding the use of HF. ICP-AES (Dean et al, 1998) was used to the determination of 5 elements (Fe, Cd, Pb, Mn and V). Winter and summer samples of TSP taken in Niterói during 1999 were analysed for those elements and their contents were compared. Most of those samples had been already analysed for their PAHs contents (Pereira Netto et al, 2001).

HNO_3 (65%) and H_2O_2 (30%) were purchased from Merck, Darmstadt. Purified water was prepared with a Milli-Q Plus System (Millipore, USA). All other chemicals used were P.A. grade from several dealers.

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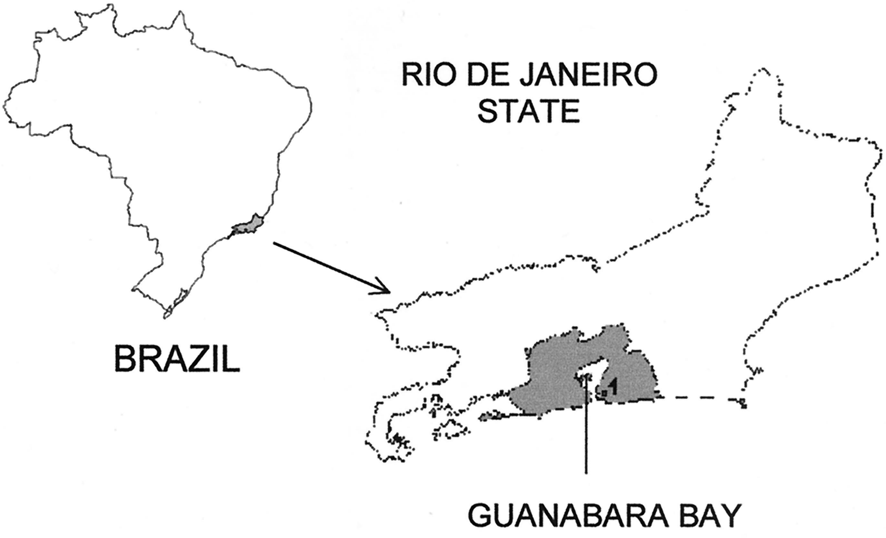

Figure 1. Map showing the localisation of Rio de Janeiro State in Brazil and the approximate localisation of the sampling point at Niterói (1). The grey area corresponds to the Metropolitan Area of Rio de Janeiro City.

Glassware and plasticware were decontaminated by immersion during 2 days in 10% solution of Extran (MERCK) followed by immersion during 3 days in 10% HNO_3 solution. After that they were rinsed several times with purified water. Working standards solutions were prepared by serial dilutions of stock solutions (MERCK). Urban Particulate Matter, SRM 1648 (NIST, USA) was used for external quality control.

A portable high volume air sampler (Sibata HVC-500, Japan) and glass fiber filter (Advantec Toyo, Japan) were used to collect TSP samples. They were collected at the Campus of Federal Fluminense University, which is located in a mixed commercial-residential neighbourhood representative of Niterói City centre. Hi-Vol samplers were placed in the library balcony facing open areas about 6 meters above ground and about 200 m away from Guanabara Bay margins. Loaded filters were stored in dark and at low temperatures until analysis. Further details about sampling procedure can be found elsewhere (Pereira Netto et al., 2001).

One quarter of each particulate-loaded filter was weighed, placed in a Teflon vessel and digested with an acid mixture consisting of 10 mL of concentrated HNO_3 and 2 mL of H_2O_2. Two quarters of each filter were analysed independently. Digestion of filters was carried out on a microwave system SPEX CDS-7000 under PULP program during 27.5 minutes and at 190 psi. The resulting solution was diluted up to 25 mL with Milli-Q water. Metals were determined by ICP-AES using a spectrometer ARL 3410ICP equipped with a minitorch. Instrumental parameters for all determinations were: pressure 75 militorr, coolant flow 22 psi; carrier flow 32 psi; plasma flow 42 psi and at a power of 650 W.

Filter and reagent blanks were carried on in parallel with all determinations and the results were adjusted to the filter blanks.

RESULTS AND DISCUSSION

Results obtained in the analysis of SRM 1648 are presented in Table 1. Good agreement between our results and the certified values was obtained. The recoveries of the 5 selected metals (Fe, Pb, Cd, V and Mn) were greater than 80% indicating that the method accuracy is suitable for their determinations. Standard deviations of concentrations found also were consistent with those reported to SRM 1648. Relative standard deviations between 1.2 and 7.9 were found indicating that the method overall precision is suitable to those determinations.

Our results to SRM 1648 also agree well with those of Yamashige et al (1989) who used the same decomposition procedure (HNO_3-H_2O_2) although with a different technique (batch digestion) (Table 1).

Table 1. Concentrations ± standard deviations (μg/g, n=3) of selected metals in the SRM 1648 Urban Particulate Matter.

Metal	Certified Value	Measured Value	Recovery (%)	Yamashige et al.(1989)
Fe	39100 ± 1000	32000 ± 400	81,8	30500
Pb	6550 ± 80	6600 ± 300	101	6420
V	140 ± 3	117 ± 2	83,6	112
Cd	75 ± 7	63 ± 5	84,0	72.5
Mn [#]	860	802 ± 45	93	780

[#] Information value only

Diurnal samples were collected during summer and winter of 1999. TSP concentrations together with those of the analysed metals are shown in Table 2 and 3 respectively. Data precision for individual metals in each sample was coherent with those obtained with SRM 1648 (Table 1) and relative standard deviations lower than 13% were found.

Fe was the most abundant metal present in all samples with concentrations between 4000 and 7000 ng/m^3. This element is associated with several sources and at the sampling point it can mostly be related to motor vehicle emissions and to resuspension of road and soil dust (Chow, 1995).

The results for V and Mn are comparable with those of Daisey et al. (1987) and Trindade et al (1981). When compared to previous results of Trindade et al (1981) to Rio de Janeiro City, lower concentrations of Pb were obtained in this work. This decrease of Pb concentration is certainly related to the fact that there is no addition of leaded compounds to Brazilian gasoline.

The sample taken on February, 9th showed the highest concentrations of the analysed metals among all samples except in the case of Cd. No significative increase of PAHs concentrations was also observed in this sample (Pereira Netto et al, unpublished results). Probably the observed metal differences are related to some kind of atmospheric or meteorological event (Dannecker, 1986), such as wind direction out of control in this study.

Table 2. Concentrations of TSP (mg/m^3), concentrations and their geometric means ($\mu g/m^3$) of selected metals in the atmosphere of Niterói City during the winter of 1999.

Date	01/25	02/09(*)	02/23	GM(#)
TSP	110	195	166	151
Fe	4770	6970	4020	5113
Pb	32.8	77.2	27.6	41.2
V	9.7	39	13	17
Cd	0.62	3.2	1.9	1.6
Mn	55	130	64	77

(*) single determination
(#) geometric means

Table 3. Concentrations of TSP (mg/m^3), concentrations and their geometric means ($\mu g/m^3$) of selected metals in the atmosphere of Niterói City during the summer of 1999.

Date	07/26	08/23	08/30	09/12	GM(#)
TSP	207	166	183	160	178
Fe	5510	4380	4450	5780	4991
Pb	44.5	27.5	54	40.9	40.5
V	17	11	12	12	13
Cd	0.86	1.7	6.5	1.8	2.0
Mn	66	69	63	72	67

(#) geometric means

The mean concentrations of the 5 elements in winter and summer also are shown in Table 2 and 3. Higher mean metal contents were found in summer but due to the few data available it is not possible to clearly state that the differences are related to seasonal variations because the differences between both seasons are in the same range of the differences observed in each season.

These data came from a preliminary part of the study of seasonal and spatial concentrations of trace metals in the atmosphere of Niterói City, RJ which is being carried on at our laboratories. This also includes two different sampling points in Niterói City. Assessment of climatological data as well as Principal Component Analysis probably will provide us information about the relative importance of the sources of metals to the atmosphere in Niterói.

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