Atmospheric inputs to ecosystems of the east coast of Rio de Janeiro state.

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Abstract

Precipitation can be an important source of nutrients, trace metals and acidity of aquatic and terrestrial ecosystems. Drawing on bulk precipitation and aerosol samples obtained at five sites located on the east coast of Rio de Janeiro state (a region marked by distinct levels of industrialization and urbanization), this work attempts to improve the understanding of three basic issues: 1) the role variation of precipitation chemistry; 2) the variability of element distribution within the dissolved and particulate phases of bulk precipitation, and 3) the relative importance of atmospheric inputs of trace metals for ecosystems located along the Rio de Janeiro state coastline. The results of this study confirm that seawater and crust are indeed the most important sources of material into the atmosphere of coastal the areas of Rio de Janeiro state, but the manmade sources are also influence precipitation chemistry. The results also indicate that while precipitation plays a minor role in the total flux of trace elements for contaminated environments, it becomes rather significant for unpolluted environments. Finally, this study confirms that long atmospheric transport is playing a direct role in the contamination of ecosystems located in areas not directly under the influence of urban and industrial activities and it is directly related to the strong activity of cold fronts on coastline of Rio de Janeiro.
Key words: atmospheric inputs, bulk deposition, trace metals, coast of Rio de Janeiro state.

Resumo

A precipitação atmosférica pode ser uma fonte importante de nutrientes, metais traços e acidez em ecossistemas aquáticos e terrestres. A partir de amostras de precipitação e de material particulado obtidas em cinco diferentes pontos ao longo da costa leste do estado do Rio de Janeiro (uma região marcada por níveis distintos de urbanização e industrialização), o presente trabalho procura melhorar o conhecimento atual em três questões básicas: 1) o papel das distâncias geográficas na variação da composição química da precipitação, 2) a variabilidade da distribuição de elementos nas fases dissolvida e particulada, e 3) a importância relativa das entradas atmosféricas de metais traços nas áreas costeiras do estado do Rio de Janeiro. Os resultados deste estudo confirmam que embora a água do mar e a crosta terrestre sejam as principais fontes de elementos na precitação das áreas costeiras do Rio de Janeiro, existem também a influência de fontes antrópicas. Os resultados também indicam que apesar da precipitação atmosférica ter apenas um papel secundário no fluxo total de elementos traços em ambientes contaminados, a mesma tem uma contribuição mais significativa para áreas que não estejam poluídas. Finalmente, este estudo demonstra que o transporte atmosférico de longa distância é importante na contaminação de ecossistemas que não estejam diretamente sob influências de fontes urbano-industriais, o que no caso da costa do estado do Rio de Janeiro está diretamente relacionado à forte presença

de frentes frias ao longo do ano.

Palavras-chave: aporte atmosférico, deposição, metais pesados, costa, Estado do Rio de Janeiro.

Introduction

Biogeochemical cycles of natural ecosystems are sustained by the input of materials from geologic, atmospheric and biological sources. Knowledge on the flux of elements from these sources is thus fundamental for the understanding of the functioning and management of such ecosystems (Bormann and Likens, 1967).

A variety of studies on rain water chemistry and atmospheric inputs have shown, that precipitation is an important source of plant nutrients, pollutants and acidity of ecosystems of the temperate and tropical coastal zone, including also of Brazil (Trindade *et al*., 1980; Silva Filho, 1985; Berner and Brener, 1987; Irwin and Williams, 1988; Oliveira and Lacerda, 1988; Santschi, 1988; Pedlowski *et al*., 1991). The few studies carried out on atmospheric inputs of nutrients and trace metals in the State of Rio de Janeiro have been performed on a local scale and have in large been restricted to the western Fluminense coast (Trindade et al., 1980; Silva Filho, 1985; Mello and Motta, 1988; Pedlowski, 1990; Silva Filho, 1997).

This study compares results on rain water chemistry and atmospheric inputs between five sites spiked along the western and eastern Fluminense coast, from Ilha Grande to Iguaba, covering a climatic gradient from humid in the west to semi-arid in the east. It discusses the contribution of dissolved and particulate phases to bulk deposition and the importance of inputs of trace metals between urban and remote areas.

Study area

The study covered the coastal zone of the Stae of Rio de Janeiro between Latitudes 22°58' and 23°10'S and Longitudes 42°12'and 44°10'W. It encompassed the sites of Ilha Grande, Sepetiba, Ilha do Fundão, Maricá and Iguaba (Fig.1).

Rio de Janeiro state is the second most important industrial and urban region in Brazil, with about 14 million inhabitants within the metropolitan region of Rio de Janeiro city alone. In the last three decades industrial, tourist, and urban expansion have intensified and led to a series of impacts on the environment. The southern part of Rio de Janeiro city shows the fastest growing rates of industrialization and urbanization in the state, due to transportation facilities (roads and railways), cheap and extensively available land and good freshwater supply. Large

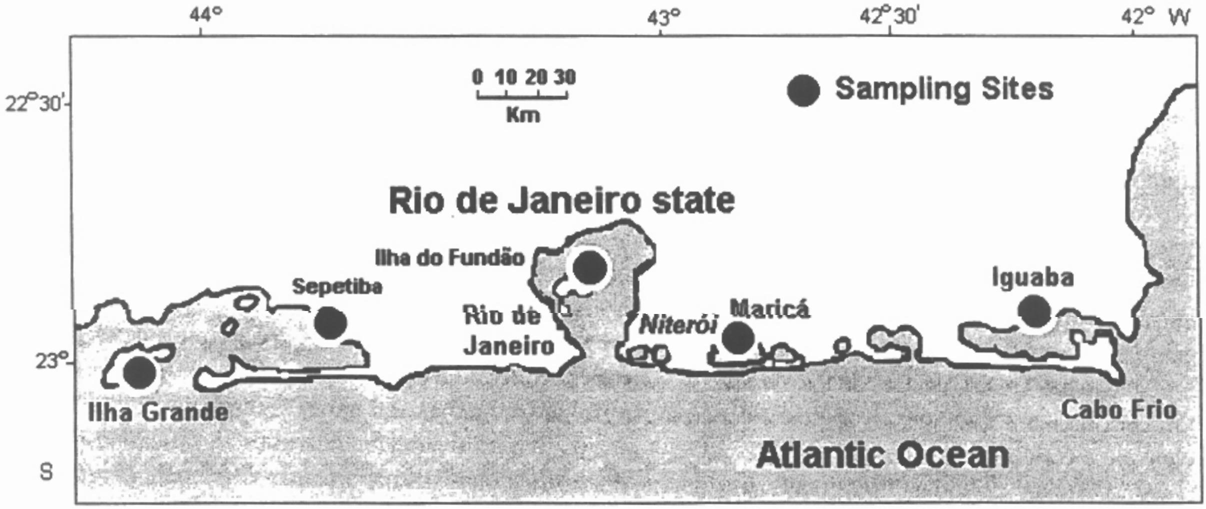

Fig. 1 - Map of sampling sites.

population flows and the construction of a large harbor in the early 1970s made the area even more attractive for industrial development. Currently, there are some 400 industries, that can be grouped into pyrometalurgic (including two large steel plants), aluminum and thermal power plants. This industrial park is responsible for the input of large amounts of heavy metals into the surrounding environments via rivers and the atmosphere (Pedlowski et al., 1991; Marins et al., 1996; Silva Filho, 1997).

Ilha Grande is a coastal island placed in the middle of semi-enclosed Ribeira Bay, located on the Southeast coast of Rio de Janeiro state (Fig.1). Ilha Grande is a particularly important environment which has been used in some studies to establish background levels for the region (De Paula et al., 1993). In spite of its quite natural condition, without any direct source of pollution, the island is subject to atmospheric inputs derived from the urban centers of São Paulo and Rio de Janeiro. The protected Biological Reserve of Praia do Sul, the southernmost basin of Ilha Grande is located here. The environment is characterized by the presence of a coastal rainforest (Mata Atlântica), aged circa 150 years. The region was occupied for agricultural activities until the early 19th century when the land was abandoned definitively (Oliveira et al., 1994).

The main sources of environmental impact in this area are tourist development and urbanization. The industrial park is restricted to a shipyard and small agroindustries with no major impacts in terms of environmental contamination.

On the northern coast of Rio de Janeiro state, the topography deserves especial attention because the coastline is oriented in an west to east axis, and the coastal elevations are oriented along a SW-NE axis (Perrin, 1986). In addition, on the eastern portion of the coast (Cabo Frio), the highest elevations tend to occur away from the ocean (Figure 2), which has a strong influence on the regional climate (Barbiére, 1975; Veloso, 1978).

The geology is characterized by the presence of pre-Cambrian metamorphic rocks with intrusion of granitic rocks and occurrences of diabase dikes (especially in the municipality of Maricá). The rock formations are concealed by sediments of more recent origin (Santos, 1987). Three major geomorphological domains are found recent slopes covered by iron soils (red and red-yellow pdzols); lowlands with dominance of hydromorphic soils and the presence of a reductor gley soil associated with fluctuations of the water table, and extensive areas of sand and sand ridges which resulted from the last sea level regression

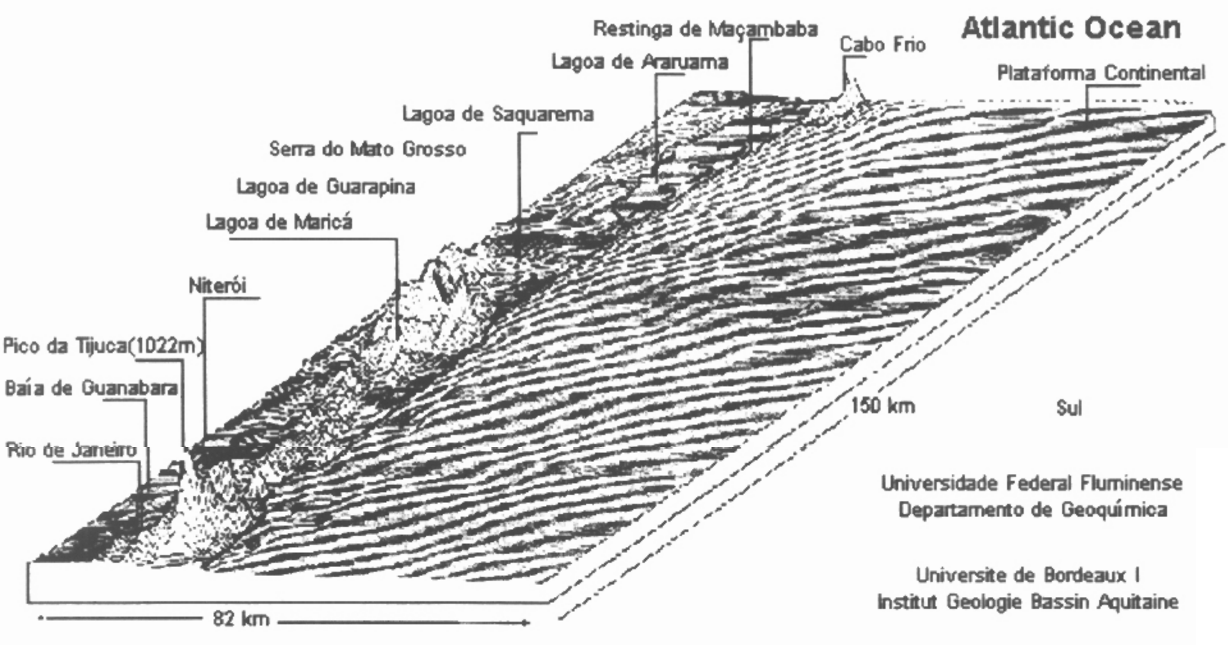

Fig. 2 - Block diagram showing the relief of the study area (Coe-Neto et al, 1986).

(Perrin, 1986; Ovalle et al., 1990).
An important tourist area has been developed on the east coast of Rio de Janeiro state, where natural beaches and lagoons represent an attraction for summer vacationers. The population of this area with the cities of Cabo Frio, Iguaba and Araruama, more than doubles during the summer season. Industries are not heavily represented in this area, except for salt mining from the hypersaline Araruarama Lagoon. Nevertheless, significant input of Pb has been recorded from atmospheric deposition (Patchineelam et al., 1988), but the main source of elements in this area are domestic wastes and urban runoff.
The eastern Fluminense coast between the municipalities of Niterói and Cabo Frio is characterized by marked climatic differences. For example, the dry climate that dominates Cabo Frio and Iguaba is a startling exception to the Southeast Brazilian coast including Rio de Janeiro, which is predominately humid (Bernardes, 1952, Barbiére, 1975; Barbiére and Coe-Neto, 1996). (Table 1).

Materials and methods

Rain water samples were collected at the stations of Ilha Grande, Sepetiba, Ilha do Fundão, Maricá and Iguaba, all located close to the shore. The rain water samplers were equipped with an acrylic funnel (area of 0.0625 m^2) and a polyethylene plastic bucket attached to a narrow end. The samplers were fixed 1.5 m above the ground. The gauge collected bulk samples (wet and dry deposition). All devices used for sampling were pre-cleaned with metal-free acids and distilled water (Milli-Q$^{\Diamond}$) and the samples were collected using standards procedures (National Atmospheric Deposition Program, Vermette et al., 1995). Rain water samples were collected monthly for one year, from August 1993 to August 1994 (except for February 1994 at Iguaba, since no rain was recorded). After measurements of total volume, rain samples were filtered through acid washed and pre-weighed 0.45 µm Millipore$^{\Diamond}$ membranes (47 mm diameter), dried for 1 week at room temperature in a laminar flow hood and henceforth weighed.
The aerosol elemental concentrations were determined by instrumental neutron activation analysis (INAA). Membranes, folded into pre-cleaned polyethylene bags, and element standards were irradiated for 5 minutes (to determine Al, Mn, Na, Ti and V) and for 8 hours (to determine As, Ba, Ca, Co, Cr, Fe, K, La, Sm, W, Th and Zn) under a thermal neutron flux 10^{12} n cm^{-2} s^{-1} at the IEA-R1 nuclear reactor of the IPEN-CNEN/SP. Measurements of gamma rays induced in samples and standards were carried out in a hyperpure Ge detector after different decay times. Spectrum analysis were carried out using the VISPECT software developed at IPEN-CNEN/SP by Dr. Piccot from Saclay, France. Two reference materials, Coal Fly Ash (ICHTJ-CTA-FFA-1) and Urban Particulate Matter (NBS-SRM-1648), were analyzed in order to check the precision and accuracy of the method. The accuracy and precision was lower than 10% for most elements.
The elemental concentrations of rain samples filtered were determined by ICP and conducted in the Instituto de Geociências of the Universidade de Brasília using a Spectro Spectroflame FVM03. This method has advantages for analyzing rain samples of non-remote locations because it does not require pre-concentration. Despite the fact that coefficients of variation for this technique are expected to vary around 10%, the values found in this study were below 5% (Silva Filho, 1997).

Table 1 - Comparison of climatic parameters for the two major climatic domains in the Eastern Fluminense region.

Local	Precipitation (mm)	Evaporation (mm)	Balance (mm)	Period	Source
Iguaba	898	1372	-474	1971-1980	Barbiére, 1985
Rio de Janeiro city	1190,9	1174,8	+16,1	1974-1991	CRCM/RJ

Results and Discussion

Precipitation patterns

Seasonal and annual precipitation values for Iguaba, Serra do Mato-Grosso, Maricá, Niterói, Aterro do Flamengo, Floresta da Tijuca, Santa Cruz and Ilha Guaíba show a marked spatial variation along the coast of Rio de Janeiro state (Table 2). Iguaba presents the lowest and Floresta da Tijuca the highest precipitation. The remaining sites exhibit rainfall within the same order of magnitude. With the exception of Serra do Mato Grosso and Floresta da Tijuca, most sites are subject to a dry winter and wet summer and spring seasons.

The climatic conditions are defined by 3 features:1) the progressive distantiation of the mountain range from West to east along the coast (Fig. 2); 2. the orographic barrier represented by the Serra do Mato Grosso which acts as a virtual climatic front between the lagoon systems of Maricá-Guarapina and Saquarema-Araruama (Fig. 2), and, 3) the occurrence of the upwelling phenomena at Cabo Frio, which is in part responsible for the semi-arid conditions in the east (Valentin et al. 1987; Turcq et al., this volume). Given the small geographic distance (about 25 km), precipitation totals between Santa Cruz and Ilha Guaíba are remarkably different. The difference can be explained by the regional topography and heavy urbanization characterizing Santa Cruz. Wind speed and direction seem to confirm the precipitation patterns: while west and south winds predominate at Ilha Guaíba, north winds and calm conditions predominate at Santa Cruz (except for the period October-November when pattern changes to S and SW winds). Wind speed is very low at both locations and thermic inversions are very common in the region (Pedlowski, 1990). In addition, Barbiére and Kronemberg (1994) show the existence of a homogenous wind pattern in the region, with dominance of west winds in the spring and south winds during summer, with average speeds around 3,7ms^{-1}.

Chemical characteristics and deposition patterns of precipitation

The concentration values of SO_4, Na, K, Ca, Mg, Fe, Mn, Si, Al, Zn, Ba, Ti, Sr and P, dissolved in the rain varied greatly reaching two orders magnitude for some elements (Table 3). For example, SO_4 had a minimum value of 0,18 at Iguaba and a maximum value of 14,3 mg L^{-1} at Ilha Grande. Trace metals such as Fe, Al, Mn, Na, Ca and Mg show similar concentration ranges in all locations included in the study. If Rio de Janeiro City (Ilha do Fundão) and Sepetiba are taken as focal points, concentrations tend to decrease both to the

Table 2 - Seasonal and annual distribution of precipitation along the coast of Rio de Janeiro State.

Location	Summer	Fall	Winter	Spring	Total
Iguaba	238	223	166	310	937
Serra do Mato Grosso	332	416	472	473	1.693
Maricá	281	254	221	299	1.055
Rio de Janeiro City (Aterro do Flamengo)	346	253	187	342	1.128
Floresta da Tijuca	749	510	457	718	2.434
Ilha Guaíba	547	348	256	450	1.650

Sources: Barbiére. This volume.

Table 3 - Comparison of Concentration Values for Nutrients, Trace Metals and Sulfate

Local / Element	Fe	Zn	Mn	Na	K	Ca	Mg	SO4
B. Sepetiba-Sepetiba (1)	510	7,0	40	4,8	0,61	3,5	0,89	3,28
Ilha Grande (1)	23	350	10	3,8	0,51	0,42	0,41	9,38
Ilha do Fundão (1)	370	140	40	2,2	0,32	0,45	1,04	2,94
Maricá (1)	69	46	17	3	0,34	0,37	0,38	1,69
Iguaba (1)	370	64	40	2,2	0,32	0,45	1,04	2,94
North Atlantic (2)	135	26	5					
Delaware - USA (3)	15,4	6,5	1,5					
Minnesota - USA (4)	165	147	22			2,08	0,33	1,98
Hubbard Brook - USA (5)				0,12	0,07	0,17	0,05	2,87
São Paulo - SP (6)				0,48	0,31	2,48	0,36	1,48
S.J. dos Campos - (7)				0,11	0,14	0,31	0,05	
Campos do Jordão - (7)				0.04	0,08	0,08	0,02	
Ubatuba -SP (7)				0,97	0,12	0,13	0,11	
Salvador - BA (8)				2,0-6,2	0,24-1,80	0,92-10,2	0,21-0,78	
England (9)	135-570	26-260	<5-23	1,7-25,0				
Sweden (10)	32,5	11,6	5					
Rural Areas (11)		36	5,7					
Sepetiba Bay-Itacuruça (12)	65,6	84,1	9,6	2,2	0,25	0,5	0,35	
Sepetiba Bay-Sepetiba (12)	115	117,4	18,3	14,7	1,0	2,8	2,3	
Floresta da Tijuca-RJ (13)				0,02-8,60	0,01-2,40	0,02-1,40	0,02-1,30	

(1) This study, (2) Waldichuk (1988), (3) Church et al. (1984), (4) Thornton and Eisenreich (1982), (5) Likens et al. (1977), (6) Forti et al. (1990), (7) Vieira et al. (1988), (8) Ferreira and Moreira-Nordemann (1985), (9) Peirson et al. (1974), (10) Ross (1986), (11) Galloway et al. (1982); (12) Pedlowski (1990); (13) Silva Filho (1985).

east (Maricá e Iguaba) and west (Ilha Grande). These results show a higher concentrations of trace metalsrelated to urban and industrial sites. The exceptions found in Ilha Grande seem to be related to long and short-range atmospheric transport (Silva Filho, 1996).

Comparing the results of the present study for nutrients (i.e., Na, Ca, K, Mg) with those obtained in Sepetiba and Itacuruçá (Pedlowski, 1990), it is possible to observe that element concentrations are in the same order of magnitude, with a single exception being observed for the concentrations of Na in Sepetiba. Meanwhile, values found by Silva Filho (1985) for nutrients in Floresta da Tijuca are in the same order of magnitude of the present study. For sulfate, the only exception is found in Ilha Grande where the average concentration is amongst the highest values found in the literature (Table 3).

The concentration of Fe and Mn are in the same order of magnitude found in literature. However, Zn shows concentration values up to 10 times smaller than those found by Pedlowski (1991) in Sepetiba, but Zn values are comparable to concentrations measured by Ross (1986) in Sweden. In the remaining sites, concentration values of Zn are within the range usually found in the literature.

Skartveit (1982) has shown that annual deposition of elements via rain is subject to strong fluctuations and that a significant percentage of teh deposition occurs within a short period of time. Different studies have shown that atmospheric deposition of elements is a non-continuous process marked by long dry periods and short periods of high humid deposition (Silva Filho 1985, Pedlowski, 1990). In tropical regions, high percentages of rain occur during very intense storms. In 1983, for example, 50% of the rain occurred during 5% of the days in the Tijuca Forest. As a result, 25% of total annual deposition of elements entered the ecosystem in only 8% of the weeks (Silva Filho, 1985). Pedlowski (1990) observed in Itacuruça-Sepetiba, that 6% of the precipitation events were responsible for 27% of the annual input of $N\text{-}NO_3 + N\text{-}NH_4^+$ and 13 to 29% for the elements studied in the Tijuca Forest (i.e., Na, K, Ca, Mg e Cl). Both reports point out to the great variability in atmospheric deposition of elements and also to the significance of cold fronts to the non-continuous nature of the deposition process on coastal ecosystems of Rio de Janeiro state.

The origin of dissolved elements in the rain

Different studies have indicated that three major sources are responsible for the elements present in the precipitation along the coast of Rio de Janeiro (Pedlowski, 1990; Silva Filho 1985; De Mello and Motta, 1988). First, there is a strong presence of marine salts as reflected by Na concentration levels and its correlation with Mg and Cl. Second, there is a strong influence of soils and roads on the concentration levels of Ca and Fe. Third, there is an important influence of plants as sources of K, P and Zn to the atmosphere (Stallard and Edmond, 1981; Artaxo et al., 1990). Other authors have indicated that elements such as Zn and Sulfate are indicators of anthropic influence in atmospheric chemistry (Nriagu and Pacyna, 1988; Irwin and Williams, 1988; Moreira-Nordemann, 1988). Wedepohl (1978) suggests that K feldspars can have Sr concentrations up to 471 $\mu g\ g^{-1}$, while these concentrations can reach 906 $\mu g\ g^{-1}$ in plagioclases, and Wasserman (1991) established that the association among Ca, Sr, Al, Fe, Mn and Ti is mainly related to weathering of FeMg and feldspar minerals.

The behavior and origin of elements present in the rain water along the coast of Rio de Janeiro was studied using the cluster analysis technique. The results indicate that sources can be grouped into three major sets (Figure 3). The larger group includes 7 elements: Mn, Ti, Fe, Si, Al, Sr e Ca. The major source

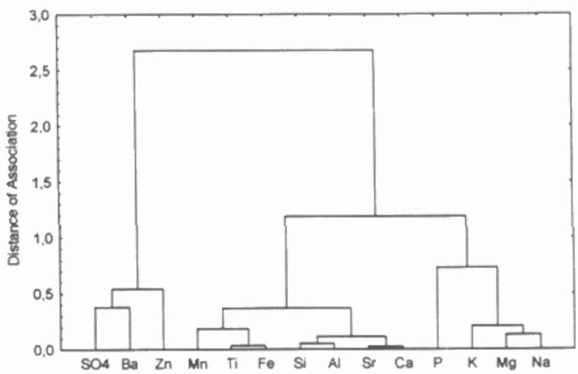

Fig. 3 - Identification phenogram of dissolved elements association in the rain water using Ward amalgamation and mean distance Pearson methods.

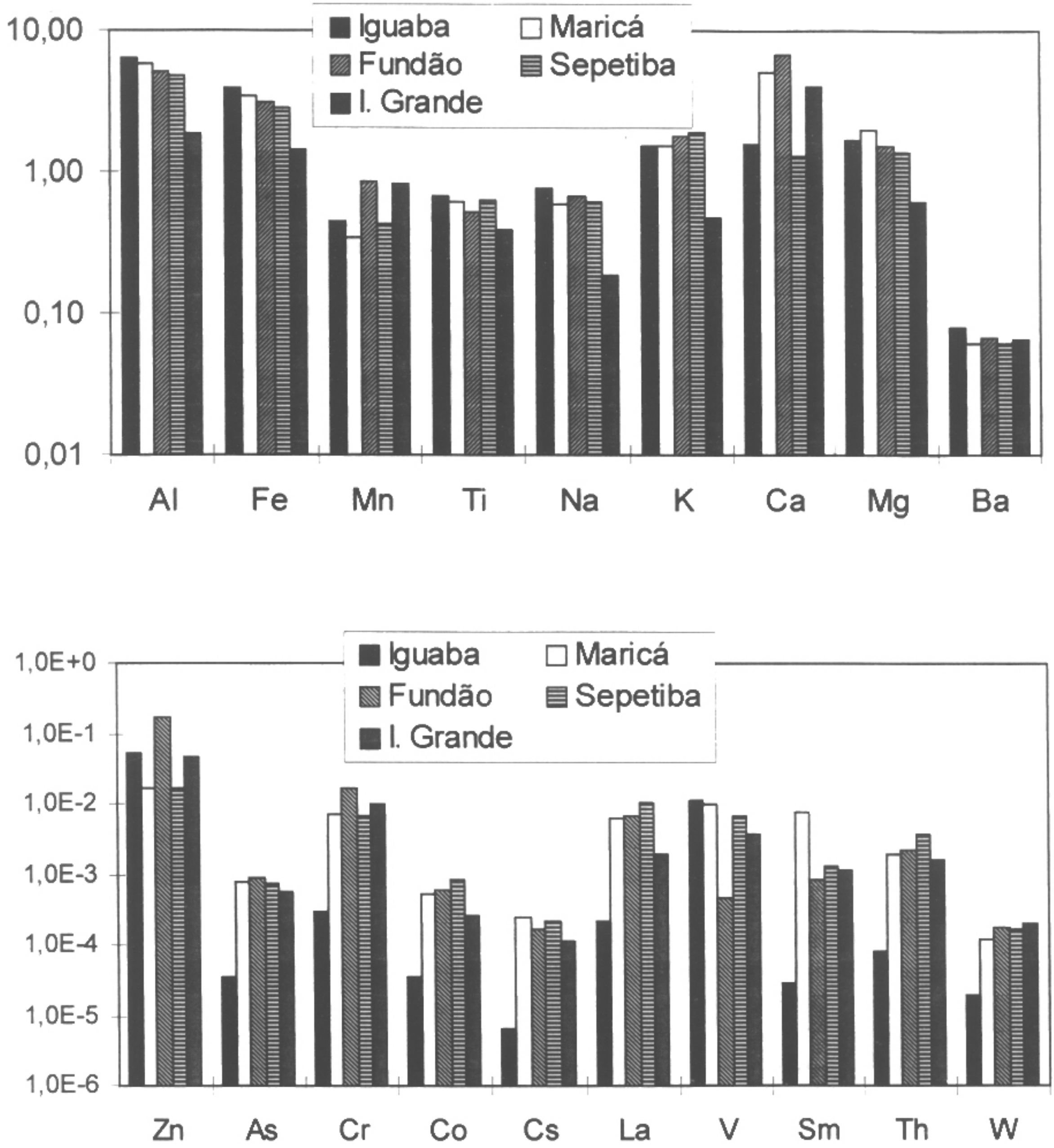

Fig. 4 - Histogram of nutrients and trace metals concentrations relative to total particulate matter.

of all these elements is the crust and associated with major minerals found on regions formed by granitic-gnaises, such as feldspars ($KAlSi_3O_8$), plagioclases ($(Na,Ca)AlSi_3O_8$), FeMg mica-silicates ($\{K(Mg,Fe)_3,KAl2\}(AlSi_3O_{10})(OH_2)$) and silica ($SiO_2$) (Souza, 1992; Bidone and Silva Filho, 1991). In fact, podsoils are dominant in the saltmarshes close to the station of Sepetiba, hydromorphic podsoils are found at 200 m heigth, and cambisoils and latisoils are usually encountered above 500 m height at the slopes of the mountain range.

The high variability in atmospheric particulate concentrations of trace elements also reflects the influence of constant changes in the atmospheric conditions. This variability can be minimized by the use of concentration histograms, normalized to the total particulate mass (Orsini et al., 1984). This normalization prevents significant variations in concentration values (Figure 4). A qualitative examination reveals that for industrial areas (e.g., Ilha do Fundão and Sepetiba) trace elements such as As, Zn, Cr, Sm, La, Co, W, Cs and Th can reach one order of magnitude above the values observed at Iguaba. On the other hand, the high vanadium concentrations in Iguaba (a non-industrialized area) contrasts with the antrophogenic character of this element. Therefore, the lithological background in Iguaba can not be ruled out as the cause of V anomalies in atmospheric particulates at the area.

Three conclusions can be drawn from analyzing the concentration of trace metals (Figure 4). First, there is a significant uniformity of concentrations among crustal elements (e.g., Al and Fe) in all areas. Second, there are higher concentrations of industrial elements at Ilha do Fundão and Sepetiba (e.g., Zn, Cr, Ca) as compared to other areas. Finally, the in general significantly higher concentrations of Al and Fe are consistent with the well-known dominance of these elements in tropical environments.

Origin of elements in the rain water particulates

For analytical purposes, this study utilized cluster analysis using logarithmic data, combining the Ward Amalgamation Method and the Euclidean mean square distance method (Figure 5). The resulting phenogram divides 19 elements into three major groups. The first group distributes V, Ba, Zn and Mn into two sub-groups. In the first sub-group, only V is present. This fact is probably associated with burning of oil (Cooper, 1981). The significantly high concentrations of V in Iguaba (a tourist region) are possibly associated with biogenic emissions during periods of upwelling (Valentin et al. 1987). Biggs and Swinehart (1976) have shown that *Thalia Democratica* (an invertebrate marine zooplancton, of the tunicates group) can accumulate V up to 10^5 a 10^6 times above normal marine levels (1 a 30 µg/L) (Van Zinderen Bakker and Jaworski, 1980). Despite the fact that Upwelling is more intense in the Cabo Frio region, it certainly influences the entire Rio de Janeiro coastline. In Sepetiba Bay, the combination of Upwelling with

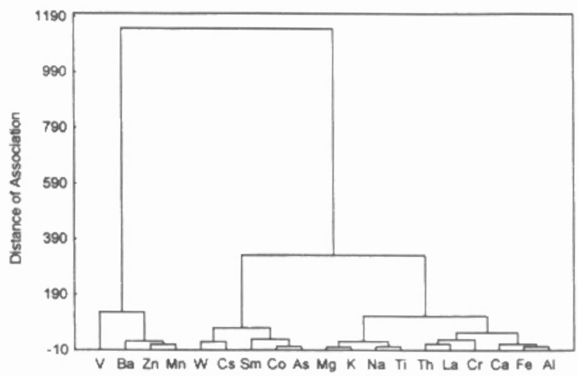

Fig. 5 - Phenogram of Cluster Analysis for all Sampling Stations.

a marked activity of cold fronts could be a possible source of Vanadium in the atmospheric particulates. Sub-group 2 includes Ba, Zn and Mn and seems to reflect a mixture of natural and anthropic sources of emission. First, all three elements are found in the main minerals constituting the most abundant rocks in the region (biotites and plagioclases). Second, Ba is known as to be used as smoke supressor in diesel vehicles while Mn and Zn can be emitted by metallurgical plants during their production cycles. Finally, burning trash can release Zn (Gordon et al., 1981; Nriagu and Pacyna, 1988).

Group 2 identifies two associated sub-groups that include W, Cs, Sm, Co and As. W and Cs are included in the first sub-group. The geochemistry of cesium is very similar to that shown by potassium (ionic radium of 1,33 e 1,63 A respectively) which indicates soil and rocks as the most probable sources of Cs in the atmospheric particulates. In agreement with the above, the Department of Mineral Resources (DRM, 1982) described the existence of 152 pegmatites in 31 municipalities of Rio de Janeiro state with most of them under commercial exploitation. On the other hand, both Cs and W presented their highest average concentration in Sepetiba, Fundão and Maricá. While Sepetiba and Fundão are heavily urbanized and industrialized, Maricá is a more remote location and has only a small airport, agricultural activities, and commercial exploration of pegmatites. These different environments seem to confirm that different sources can be responsible for the presence of these trace metals in the atmosphere. In the second sub-group Sm, Co and As are included. As is an element with a similar geochemistry and chrystallochemistry of P in

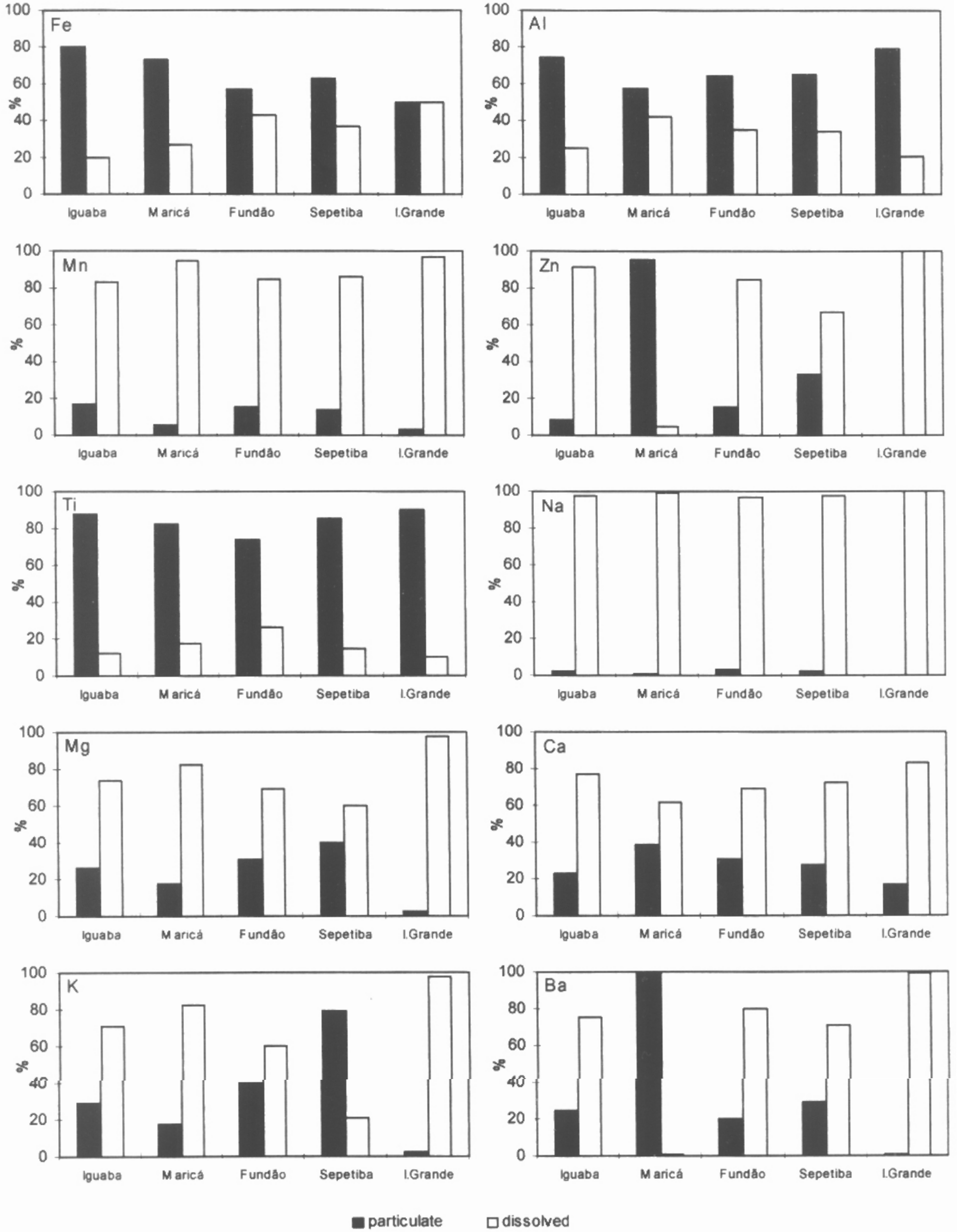

Fig. 6 - Relative contribution of dissolved and particulate phases in the atmospheric deposition of metals (%).

phosphates (both in ionic radium and electronic "valence" As^{+5} 0,47 A e P^{+5} 0,34 A). The major sources of these elements in the atmosphere are: burning fossil fuels (coal and oil), metallurgic plants (Cu, Zn e Pb), and herbicides and pesticides (Servant, 1982; Nriagu and Pacyna, 1988). A study in Sepetiba Bay found high levels of As in sediments and in *Tillandsia usneoides* that was used as a indicator of atmospheric As (Magalhães, 1996).

Three sub-groups form the third group. The first sub-group is formed by Mg, Na, K and Ti; the second by Th, La and Cr; and the third by Ca, Fe and Al. The three sub-groups contain elements that are associated with sources such as sea spray and soils. Some examples of such an association is Na, Mg, Th, Fe, Al and Ti. Concentration levels in sub-group 1 seem to increase from Iguaba towards Sepetiba, but decrease drastically at Ilha Grande. The elements included in sub-group 2 (Th, La e Cr) also show a tendency to an increase of concentrations from Iguaba to Sepetiba. This behavior seems to be associated with an increasing urban and industrial density that characterizes the region. Meanwhile, Cr has the highest mean concentration at Ilha do Fundão, and the highest concentration in Ilha Grande an area near the industrial areas of Sepetiba Bay and Paraíba Valley. Finally, the elements included in the sub-group are associated with resuspension of dust from roads and soil existent in the region.

Importance of the wet and dry deposition

The diameter of particulate material can vary from < 0,02 μm to > 400 μm in coastal atmospheres. Particles with diameter > 2 μm are usually generated by mechanic processes, including crust and sea spray as major sources of aerosols. Particles with diameter < 2 μm are probably more associated with transitional processes such as condensation and with the formation of secondary aerosols (e.g., amonium sulfate). There is a strong possibility that coarse particulates dominate atmospheric deposition along coastal areas. According to Preston (1992), gravitational processes control the deposition of particles with diameters between 5 and 10 μm. On the other hand, the deposition of particles with diameters between 0.1 e 5 μm is controlled primarily by impactation and/or interception by surfaces. In summary, the processes of wet and dry deposition are highly dependent on the size of particles (sources), geographic location and weather conditions. Randall et al (1978) have shown that the wet fraction dominates the larger components of bulk deposition. In addition, Sigg and Zobrist (1989) demonstrated that if rainwater pH is below 5.0, the bigger fractions of trace metals will be in a dissolved phase. Several studies on coast of Rio de Janeiro state have shown that rainwater mean pH is about 4.7 (Silva Filho, 1985; De Mello and Motta, 1988; Pedlowski, 1990). Vieira et al (1988) observed that atmospheric deposition of Na, K, Ca, Mg and Cl is dominated by wet deposition. In addition, Georgii et al. (1983) points out that the deposition of trace metals occurs mainly through wet processes. The only exceptions being Fe and Mn (particles with diameters above 2 μm) in which dry deposition is more important than wet deposition. Preston (1992) indicates that the wet fraction represents 80% of the bulk deposition for trace elements such as Zn, Ni, and Cd. On the other hand, for Fe, Al and Si this ratio is 60:40. We also observed that most nutrients showed different ratios between the particulate and dissolved phases for different sampling areas. The only exception was Na which is found mainly in the dissolved phase (Figure 6). Ilha Grande showed the more striking differences. This fact must related to atmospheric transport of small particles and gases from other regions.

Another interesting observation is the high concentration of Zn and Ba in the particulate fraction in Maricá. This fact is probably associated with landing and take-off of airplanes at the local airport. On the other hand, Mn is mainly found in the dissolved phase, which differs directly from Fe and Al found basically in the particulate phase.

The role of atmospheric precipitation in the total flux of elements on the Rio de Janeiro coastal areas

The respective contribution of dissolved and particulate fractions of atmospheric deposition of elements are compared to other studies done in Rio de Janeiro state (Table 4). Our deposition rates are in the same order of magnitude to those measured previously in the Tijuca National Forest and Sepetiba

Table 4 - Comparison of different studies on the bulk deposition of elements (particulate + dissolved phase) on the coast of Rio de Janeiro state ($\mu g.cm^{-2}.year^{-1}$).

Ion	[1]Floresta da Tijuca	[2,3]Sepetiba	[4]Iguaba	[4]Maricá	[4]Fundão	[4]Sepetiba	[4]I. Grande
Fe		20	38,6	32,7	64,6	127,5	5,51
Al			68,7	69,4	90,9	197,9	4,38
Mn		2,0	1,39	2,70	3,24	4,32	1,02
Zn		30	4,94	138,9	13,6	1,73	25,9
Ti			6,65	5,20	8,22	20,8	0,82
Na	220	420	248,0	509,6	272,8	552,4	354,7
Mg	50	60	50,4	75,2	61,0	98,6	54,4
Ca	60	90	48,6	96,1	123,3	143,0	44,4
K	40	50	41,9	65,2	52,4	70,6	45,5
Ba			2,40	414,5	4,06	6,11	19,4

1. Silva Filho et al (1985); 2. Pedlowski et al (1991); 3. Pedlowski et al. (1992); 4. Silva Filho (1997).

Bay. However, a few important exceptions were identified from the results of these different studies. For example, Fe and Mn are one order of magnitude smaller in relation to remaining sites and the same fact was noticed for Zn in Sepetiba.

We also compared the contribution of atmospheric and fluvial inputs of Zn, Mn and Fe to Sepetiba and Guanabara Bay (Table 5). The atmospheric flows of Zn represent 0,3% of the total Zn annual load in Guanabara Bay and 2.5% for Sepetiba. The atmospheric inputs of Mn and Fe represented 4.3% and 4.0% of the total load entering Sepetiba Bay, respectively. The present estimates are in contradiction with other studies done previously in the area. For example, Pedlowski et al. (1991) indicates that the atmospheric input of Zn represented 38,3% of the total annual load. On the other hand, the calculated flows of Fe and Mn were 4 orders of magnitude below our results. These differences may reflect the different analytical procedures adopted to conduct the respective studies.

Table 5 - Comparison of atmospheric and river inputs to Sepetiba Bay and Zn in Guanabara Bay.

	Trace Metals (Tons.year-1)	Zn	Mn	Fe
Sepetiba Bay	Atmospheric Flow (Silva Filho, 1997)	8,2	33	953
	Rivers (Lacerda (1983) and Rodrigues (1990)	330	760	24.000
Guanabara Bay	Atmospheric Flow (Silva Filho, 1997)	74	19	368
	Rivers (JICA,1992)	29.000	-	-

Conclusions

The collection of rain water by continuous gauging allows for the integration and monitoring of different process occurring in the atmosphere. The results of this study showed that the sea and the crust are the major sources of elements to the atmosphere in the coastal areas of Rio de Janeiro state. The analysis of dissolved and particulate phases indicated the presence of three groups of elements in bulk atmospheric deposition. The first group of elements were mainly associated with the particulate phase (e.g., Fe, Al and Ti), the second belonged to the dissolved phase (e.g., Na, Mg and Ca), and the third group was dependent on both their sources of emission and the physical-chemical characteristics of the receptor (e.g., Ba, Mn and Zn).

The atmospheric fluxes of the elements were in general low, when compared to other severely contaminated environments. However, in the remote areas far from major anthropogenic sources, the contribution of atmospheric deposition in comparison to other sources, gained importance and should not be neglected in future budget assertions. The enrichment of Zn and Cd in sediments of Ilha Grande show that long range atmospheric transport may also contribute to the contamination of ecosystems not being directly impacted by industrial or urban areas. The atmospheric deposition of elements is strongly influenced by cold fronts which cause most of the rain events on the Rio de Janeiro coastline.

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