Geochemical Characterization of Rain Water Particulate Material on a Coastal Sub-Tropical Region in SE - Brazil

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Airborne contamination has been of concern for a number of scientist in temperate regions. In the tropics, a very small amount of data is available. In this work, rain water particulate material was monitored in two sites in Rio de Janeiro State (Brazil): the first (Sepetiba), subjected to high inputs of metals from industrial activities and the second (Iguaba), subjected to very mild contamination. Particulate material was obtained by filtration of rain water samples. The filters were analysed by instrumental neutron activation analysis. The results show three important features: 1) the element enrichment patterns could be split into two groups, crustal and anthropogenic derived; 2) uniformity of element loads in rain water particles is observed; 3) enrichment of certain trace elements in airborne particles is probably an important source of contaminants to soils, sediments and the marine environment.

Keywords: rain water particulate matter, trace metals, coastal region, SE Brazil

Introduction

Atmospheric inputs of trace metals in coastal areas have been the subject of a number of recent investigations, particularly in temperate regions\textsuperscript{1} and to a lesser extent, in tropical areas\textsuperscript{2,3,4}.

The State of Rio de Janeiro is the second most important industrial and urban area in Brazil, with about 14 million inhabitants living within the metropolitan region of Rio de Janeiro. In the last three decades industrial, tourism and urban expansion have been very intensive, leading to a series of environmental impacts. The southern most part of the metropolitan area, which includes the Sepetiba basin, shows the fastest growing rates of industrialization and urbanization, due to transportation facilities (roads and railways), cheap and extensive available land and good freshwater supply. Large population flows and the construction of a large harbour in the early 70’s made the area more attractive for industrial development. Currently, there are over 400 industries, mostly: pyrometallurgic, including two large steel plants, an aluminum plant and thermal
oil-fired power plant. This industrial park is responsible for the input of large amounts of heavy metals into the surrounding environment, reaching the coastal region by rivers or through atmospheric deposition.\(^4\,5\) The Iguaba Municipality is located approximately 100 km north of Rio de Janeiro city, it has developed into an important tourist area where natural beaches and lagoons represent an attraction for summer vacations. The population of this area doubles during the summer season. No industrial activities are present in this area except salt extraction from the lagoons. The main trace metal sources in this area are domestic wastes and urban runoff, although significant inputs of Pb were recorded from the atmospheric deposition.\(^6\)

Although the chemistry of rain water has been the subject of a number of studies, the associated particulate material has been virtually ignored, for example, this fraction of the atmospheric deposition, can be significant, in particular in coastal regions.\(^7\) Duce and Hoffman\(^8\) concluded that the rainfall deposition of particles is about twice as great as the dry deposition whereas Keeler et al.\(^9\), suggested that at least for some trace metals, the particulate phase may dominate the bulk atmospheric deposition. Also, atmospheric particle deposition is responsible for a considerable scavenging of trace metals, resulting in their deposition relatively close (< 100 km) to their sources.\(^10\) Due to the importance of particulate material in rain water chemistry, two regions (Sepetiba, 60 km to the south and Iguaba 100 km to the north of the Rio de Janeiro city) were chosen to investigate trace element contents in particulate material. Collectors from rain sample sites are shown in Fig. 1.

**Materials and Methods**

Both stations of rain water sampling were located close to shore, the rain water samplers were equipped with an acrylic funnel (collection area of 0.0625 m\(^2\)) and a polyethylene plastic bucket attached to a narrow end. The samplers were fixed at a height of 1.5 m above the ground. The collector provides bulk samples (wet and dry deposition). All devices used for sampling were pre-cleaned with metal-free acids and distilled water (Milli-Q) and the samples were collected using the standard procedures (National Atmospheric Deposition Program).\(^11\)

Rain water samples were collected monthly during a period of one year, from August 1993 to August 1994. Except in February at Iguaba, since atipically, no rain was recorded during that month.

After the measurement of the total volume, rain samples were filtered through acid pre-washed and pre-weighed 0.45 µm Millipore\(^\circ\) membranes (47 mm diameter), dried for 1 week at room temperature in a laminar flow hood and weighed.

The particles elemental concentration was determined by instrumental neutron activation analysis (INAA). Membranes, folded into precleaned polyethylene bags, and elemental standards were irradiated for 5 min (to determine Al, Mn, Na, Ti and V) and for 8 h (to determine As, Ba, Ca, Co, Cr, Fe, K, La, Sm, Th and Zn) under a thermal neutron flux of 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 an hyperpure Ge detector after different decay times. Spectra analysis were carried out using the VISPECT software developed at IPEN-CNEN/SP. Two reference materials: Coal Fly Ash (ICHTJ-CTA-FFA-1) and Urban Particulate Matter (NBS-SRM-1648), were analysed in order to check the precision and accuracy of the method. Results obtained and certified values are presented in Table 1. The accuracy and precision are higher than 90% for most of the elements. Membrane blanks were treated as particulate samples and routinely run during the analysis in order to check sample contamination.

**Results and Discussion**

Table 2 shows the annual precipitation and the result of the gravimetric measurements of the particulate mass at the two sites. The results show that the total particulate mass deposition in Sepetiba is three times higher than those in Iguaba.

Figure 2 shows the fluxes of trace elements in the particulate material. A qualitative examination reveals that in the industrial region (Sepetiba) the concentrations of Fe, Al, Mn, Zn, Ti, Na, K, Ca, Mg, As, Ba, Co, W, Cs and Th are higher than those observed at Iguaba. For the elements (Fig. 2a) Fe, Al, Mn, Zn, Ti, Na, Mg, Ca, K and Ba deposition fluxes in Sepetiba were 2 to 3 times higher than in Iguaba, suggesting that the increase in total particulate mass deposition (Table 2), is responsible for the observed increase. For the elements, As, Cr, Co, Sm, Th, La, Cs and W (Fig. 2b) deposition fluxes in Sepetiba were one to two orders of magnitude higher. On the other hand, vanadium fluxes in Iguaba are three orders of magnitude higher than in Sepetiba. These large differences may be explained by

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**Figure 1.** Location of sampling stations.
different concentrations between particles from the two areas (Fig. 3).

The high variability in the atmospheric particulate concentrations of trace elements reflects the influence of constant changes in the atmospheric circulation conditions. This characteristic can be minimized by the use of histograms of these concentrations, normalized to the total particulate mass\(^{13}\). This normalization prevents significant variations in concentrations (Fig. 3). Four conclusions can be drawn from Figure 3: 1) significant uniformity of concentration of the crustal elements (e.g.: Al, Fe and marine aerosol derived elements; e.g. Na and Mg) (Fig. 3a) in both areas; 2) the higher concentration of Al and Fe are consistent with the well-known dominance of these elements in a tropical environment\(^{14}\); 3) there is a marked increase in concentration of industrial derived elements in Sepetiba, when compared to Iguaba (Fig. 3b); 4) vanadium presented a different pattern from all other elements with concentra-

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**Table 1.** Certified values and elemental concentration obtained for Urban Particulate Matter (NBS-SRM-1648) and Coal Fly Ash (ICHTJ-CTA-FFA-1) reference materials.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration unit</th>
<th>NBS-SRM-1648</th>
<th>ICHTJ-CTA-FFA-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>%</td>
<td>3.24±0.06</td>
<td>3.42±0.11</td>
</tr>
<tr>
<td>As</td>
<td>µg g(^{-1})</td>
<td>114.5±0.7</td>
<td>115±10</td>
</tr>
<tr>
<td>Ba</td>
<td>µg g(^{-1})</td>
<td>736±74</td>
<td>737</td>
</tr>
<tr>
<td>Ca</td>
<td>%</td>
<td>5.5±0.4</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>µg g(^{-1})</td>
<td>17.4±1.1</td>
<td>18</td>
</tr>
<tr>
<td>Cr</td>
<td>µg g(^{-1})</td>
<td>370±24</td>
<td>403±12</td>
</tr>
<tr>
<td>Fe</td>
<td>%</td>
<td>3.76±0.08</td>
<td>3.91±0.10</td>
</tr>
<tr>
<td>K</td>
<td>%</td>
<td>0.92±0.11</td>
<td>1.05±0.01</td>
</tr>
<tr>
<td>La</td>
<td>µg g(^{-1})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>µg g(^{-1})</td>
<td>778±68</td>
<td>860</td>
</tr>
<tr>
<td>Na</td>
<td>%</td>
<td>0.40±0.02</td>
<td>0.425±0.002</td>
</tr>
<tr>
<td>Sm</td>
<td>µg g(^{-1})</td>
<td>3.9±0.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Th</td>
<td>µg g(^{-1})</td>
<td>6.4±0.5</td>
<td>7.4</td>
</tr>
<tr>
<td>Ti</td>
<td>µg g(^{-1})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>µg g(^{-1})</td>
<td>128±7</td>
<td>140±3</td>
</tr>
<tr>
<td>Zn</td>
<td>µg g(^{-1})</td>
<td>460±20</td>
<td>476±14</td>
</tr>
</tbody>
</table>

**Table 2.** Annual precipitation and total particulate mass deposition in Sepetiba and Iguaba.

<table>
<thead>
<tr>
<th></th>
<th>Sepetiba</th>
<th>Iguaba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation (mm year(^{-1}))</td>
<td>1616</td>
<td>987</td>
</tr>
<tr>
<td>Particles (µg cm(^{-2}) year(^{-1}))</td>
<td>2748</td>
<td>902</td>
</tr>
</tbody>
</table>

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![Figure 2](image-url)  
**Figure 2.** Annual deposition fluxes of trace elements associated with rain particles over Iguaba and Sepetiba, SE Brazil.

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marine aerosols with remains of planktonic tunicates (Salpa spp.) particularly abundant in the upwelling waters off Iguaba15; which characteristically present an extremely high V concentration, of the order of $10^6$ times higher than sea water concentration, reaching over 1,000 µg g$^{-1}$ of dried animal weight16. This sound hypothesis however, could not be tested here.

Enrichment factors can be used as a tool for determining the source (s) of aerosols. The enrichment factors used in this work are the ratio of the element with Fe in the particulate matter divided by the same ratio in the average crustal igneous rocks17. Most researchers agree that ratios greater than 10 are indicative of non-crustal sources, and values below 7 are indicative of soil source18. The mean enrichment factors of elements are shown in Fig. 4.

Elements such as Al, Mn, Na, Mg, Ca, V, Co and W were characterized by moderate enrichment values in both sites (enrichments between 0 and 3) (Fig. 4a).

Considering the significant element-element correlations, it is inferred that the particles originating from the earth crust and marine aerosols are the main sources for these elements in the atmosphere. In this group, V and Co could be originated from fossil fuel utilization from high-temperature combustion processes19 as in oil-fired (thermo-electric plants) such as the Santa Cruz Plant. Rubber industry can also contribute with Co20. The other of element group presented is characterized by moderate enrichment, but different between the two sites, with higher enrichments in Sepetiba (Fig. 4b). Suggesting the influence of industrial activities. Chromium, Ti naturally enriched in Brazilian coals21 are probably associated with the presence of steel plants and pigment and paint production, in the Sepetiba region.

A third group of elements (Fig. 4c) are represented by As, Zn, Th and Rare Earth Elements (REE) with extremely high enrichment factors observed in Sepetiba. Arsenic is largely used in pyrometallurgical non-ferrous metal production20,22. Barcellos et al.23 and Magalhães24 showed that a zinc and cadmium smelting plant, in Sepetiba, is also a major source of As to the environment. The source of Th and REE is probably associated with the coal combustion, which is supplied by Santa Catarina State and used in the reduction process of the Blast-furnace in the Sepetiba area.

**Conclusion**

This study has compared rain water particulate contents of elements in two sites from the Coastal region of the State of Rio de Janeiro - Brazil. First of all, Iguaba can be considered a remote region, without significant contamination from anthropogenic sources. In Sepetiba, the results show a clear separation of the studied elements into three classes, the “crustal and marine aerosol derived” ones, such as Al and Na, having enrichment factors between 2 and 7 in the two sites, a second group with medium enrichment and, consistently higher in the Sepetiba site and a third group constituted by those elements mostly originating from anthropogenic (industrial) sources, with enrichment factors greater than 10. Another feature to be underlined is a remarkable small seasonal variation in the elemental composition of the rain water particulate. Our results suggest that the aerosol particles are one of the sources respon-
sible for the element contamination of coastal areas of Rio de Janeiro State.

References


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