CHROMIUM IN WATER, SUSPENDED PARTICLES, SEDIMENTS AND BIOTA IN THE IRAJÁ RIVER ESTUARY

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ABSTRACT

Analyses of chromium concentrations in waters, suspended particles, bottom sediments, fish (Poecilia reticulata), plants (Paspalum vaginatum, Sesuvium portulacastrum, Philoxeros vermicularis), soils and barnacles (Balanus sp.) were performed from August 1976 to September 1980 in samples collected from the Irajá River and inside its estuary in Guanabara Bay (Rio de Janeiro, Brazil).

Sediments and water from the Irajá River showed chromium concentrations of 17.536 and 23.39 ppm—a thousand times higher than the published data for freshwater systems.

Chromium removed from solution by bottom sediments reaches Guanabara Bay linked to particulate matter. Fish and emergent grass inside the river concentrate chromium from water and/or sediment, returning the metal to the system as detritus.

Soil and plants inside the estuary concentrate chromium thirty and ten times higher than in the control area. The vegetal community exhibits a concentration factor smaller than that related to soil and prevents the return of chromium to the estuarine waters.

Inside the Guanabara Bay, Balanus sp. appears to be an effective biological monitor as it concentrates chromium in soft tissues 10³ times higher than values found in suspended particles (0.012 μg ml⁻¹).

INTRODUCTION

Guanabara Bay, located on the southeastern coast of Rio de Janeiro State, is being subjected to increasing pollution problems, mainly due to the city of Rio de Janeiro

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on the west shore; a population of 5 million inhabitants and 4000 industries have been discharging sewage and industrial wastes through rivers and channels into the Bay for several decades. Nowadays, commercial fishing is not of great significance in the Bay but constitutes the source of income for small fishing colonies. The waters of the Bay are mainly used for recreation and tourism (Hydroscience Inc., New Jersey, 1977).

Although the greatest sanitary problem of the Bay is the discharge of organic matter, the importance of other pollutants such as oils and heavy metals from industrial complexes has also to be considered. Many industrial wastes contain salts of chromium as a byproduct of three major industrial activities—leather, paints and metal plating (FEEMA, pers. comm.).

The Irajá River, a tributary of Guanabara Bay, was selected for the present work as it has been receiving about 500 kg of total chromium monthly, released without any treatment in the effluent from the electroplating industry. As well as preventing biological life from developing, the most serious effect of this kind of discharge into an aquatic environment is the possibility of chromium accumulation in aquatic life far downstream from the source. The industrial discharge of chromium into the Irajá River takes place only 2 km upstream from its outfall into the Bay so that, if chromium were to reach the Guanabara Bay, it could be concentrated in biological systems and thereafter in estuarine food chains (Pfeiffer et al., 1980).

This paper presents the results of total chromium concentrations in water, suspended particles, bottom sediments and biological samples collected in the Irajá River and in its outfall into Guanabara Bay in order to evaluate the extent of chromium contamination in the Estuary compared with other polluted and unpolluted estuaries, and to assess concentration factors from the environment into biological systems.

DESCRIPTION OF STUDY AREA

The Irajá River flows through the middle of a highly residential and industrialised area but only the metal-plating industry discharges chromium into the river. Eight sampling stations were selected along the river and the outfall into the Guanabara Bay estuary (Fig. 1).

The industry releases chromium, mainly as chromate, between stations 2 and 3 and the pH of the water, therefore, decreases sharply at this point. As far as station 3 the waters are clean without any sewage input and the dissolved oxygen shows a normal concentration. On the other hand, from stations 4 to 6 there is a heavy input of raw domestic discharge, lowering the dissolved oxygen to levels below the detection limit, with hydrogen sulphide production (Pfeiffer et al., 1980). The heavy input of chromium and the changes in the pH in the river due to the industrial discharge, together with the sewage input, prevent the development of any
Fig. 1. Location of the sampling stations. †: domestic waste inputs; ●, electroplating industry.

biological life in most parts of the river. *Paspalum vaginatum*, an emergent grass, and *Poecilia reticulata*, a small fish, were only recorded at station 1.

Along the south margin of the estuary (station 7), the beach is completely covered by a halophyte community of two perennial plants, *Sesuvium portulacastrum* (L.) and *Philoxeros (Iresine) vermicularis* Mog. The site is not reached by normal tides but occasionally, during exceptionally high tides of equinox or storms, estuarine waters can cover part of it.
Station 8, 2 km from the south margin, shows no biological life except for a natural community of Balanus sp. which had colonised concrete piles localised within the estuary.

SAMPLE COLLECTION AND TREATMENT

Irajá River

From August 1976 to May 1979, water, bottom sediments, plants (Paspalum vaginatum) and fish (Poecilia reticulata) samples were collected along the Irajá River. At station 6 there was no bottom sediment available for analyses of total chromium.

Bottom sediments and water samples were prepared as described elsewhere (Pfeiffer et al., 1980).

Samples of plants were collected from 25 x 25 cm quadrats, brought to the laboratory, washed thoroughly with tap water and sorted into leaves, stems and roots. The samples were then dried at 100 °C for 24 h.

Fish were washed with deionised water and sorted into two kinds of sample—whole fish and soft tissues. The samples were then dried at 100 °C for 24 h.

Estuary

From October 1978 to December 1979, surface soils, plants and water samples were collected monthly from station 7, and from October 1978 to September 1980, barnacle and water samples were collected from station 8.

Plant material (halophyte community) was collected from 25 x 25 cm quadrats for each species. After the clear cutting of all living material the litter inside the quadrat was removed by hand. At the same time soil surface samples were collected (0-0-5-0 cm depth). Both the vegetation and the soil samples were transported in plastic bags to the laboratory. Plant material was washed in tap water and sorted into leaves, stems and litter. Both soil samples and plants were dried for 24 h at 100 °C.

The barnacles were removed from the concrete piles with a spatula, transported in ice pockets and stored at 5 °C in the laboratory until analysis could be carried out. The samples were then washed with tap water and the soft tissues separated from the shells. Both soft tissues and shells were transferred to porcelain dishes and dried at 100 °C for 24 h.

Water samples were treated in the same way as the Irajá River water samples, but the filtrate was discarded as the levels of dissolved chromium were below the detection limit of the method employed.

ANALYTICAL PROCEDURES

Irajá River

Water samples, dried particulate matter and sediment samples were prepared as described elsewhere (Mathis & Cummings, 1973; Pfeiffer et al., 1980). Samples of
dried plants and fish were weighed and ashed at 450 °C in a muffle furnace overnight. The ashes were digested in a hydrochloric/perchloric acid solution (1:3) until the solution became clear; it was then dried, diluted with a hydrochloric acid solution and filtered through a Whatman No. 44 filter paper to retain any insoluble material.

**Estuary**

*Soil samples:* Exchangeable chromium in dried soil samples was determined by extraction with 1 N ammonium acetate (pH 7) for 24 h. The mixture was then filtered through a Whatman No. 44 filter paper. The non-exchangeable chromium was determined by extraction of the previously leached soil in 30 ml of diluted hydrochloric acid (1:3).

*Plant samples:* Known amounts of dry plants were ashed overnight at 450 °C. The ashes were digested with an acid mixture (HClO₄: HNO₃, 1:3) until the solution became clear. After being brought to dryness the samples were diluted with 20% hydrochloric acid.

*Barnacles:* Dried samples of soft tissues and shells were weighed and ashed overnight in a muffle furnace at 450 °C. The ashes were digested in concentrated nitric acid until the solution became faint yellow or clear. The solution was then brought to dryness and diluted to 50 ml with 20% hydrochloric acid. The solution was filtered through a Whatman No. 44 filter paper to remove any insoluble material left from the digestion.

The particulate material retained on the filters was digested with HClO₄: HNO₃, 1:3 until the solution turned faint yellow or clear. After evaporating to dryness, the samples were dissolved in 20% hydrochloric acid.

All chromium analyses were performed using a Varian Model AA-120 atomic absorption spectrophotometer, following the recommended standard operating procedures. Matrix interferences were determined in all samples and corrected for instrumental measurements. The detection limit of 0.05 ppm was assessed experimentally and linear calibration curves were obtained in the range 0.05–8.00 ppm of chromium.

Whenever necessary, reagent blanks were prepared with the same amounts of reagents used in the digestion procedures. The results were expressed in µg ml⁻¹ or µg g⁻¹ dry weight.

**RESULTS**

*Irajá River*

Chromium concentrations in sediments, suspended particles, water and biological samples from the Irajá River are presented in Tables 1 and 2.

The highest values for water and bottom sediments (80 ppm and 54,300 ppm) were found at station 3 near the point of release. From stations 3 to 5 chromium concentration decreased four hundred times in water, thirty times in bottom
TABLE 1
CONCENTRATIONS OF CHROMIUM IN COMPARTMENTS OF THE IRAJÁ RIVER

<table>
<thead>
<tr>
<th>Stations</th>
<th>N</th>
<th>Water (µg ml⁻¹)</th>
<th>Suspended particles (µg ml⁻¹)</th>
<th>Bottom sediments (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7</td>
<td>0.05-0.35ᵃ</td>
<td>0.007-0.646</td>
<td>210-2920</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.14)</td>
<td>(0.16)</td>
<td>(1420)</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>0.07-1.92</td>
<td>0.014-2.19</td>
<td>11400-70000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(54)</td>
<td>(0.72)</td>
<td>(24820)</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0.371</td>
<td>0.422-5.67</td>
<td>10070-69700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(80)</td>
<td>(1.53)</td>
<td>(54300)</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>0.04-38</td>
<td>0.066-6.22</td>
<td>1780-11020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6-0)</td>
<td>(2.24)</td>
<td>(5440)</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0.03-0.73</td>
<td>0.058-3.69</td>
<td>230-4870</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.20)</td>
<td>(1.30)</td>
<td>(1700)</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>0.007-0.022</td>
<td>0.016-0.25</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.012)</td>
<td>(0.12)</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Related to the corresponding water volume.
ᵇ Range.
ᶜ Mean.
NA Not available.
N Number of samples analysed.

...sediments but was similar for suspended particles. At station 6, 1 km from the point of release, the river's volume is increased at least twenty times since it receives a heavy input of sewage discharge from the surrounded populated area (Fig. 1). The chromium concentration in water fell to 0.012 ppm, six thousand times less than the value found at station 3; on the other hand, chromium levels in suspended particles were only ten times less than the value found at station 3.

Upstream of the point of release (station 1), concentrations of chromium were still higher than those found in other freshwater systems (Mathis & Cummings, 1973; Namminga & Wilhm, 1977) and the only available species of fish in this area has its feeding habits related to suspended particles in shallow water. Both whole fish and tissues (Table 2) showed metal concentrations two orders of magnitude higher than the value of 0.3 µg ml⁻¹ found in the water (solution plus suspended particles—Table 1).

TABLE 2
MEAN CHROMIUM CONCENTRATIONS IN PLANTS AND FISH AT STATION 1 OF THE IRAJÁ RIVER (µg g⁻¹ DRY WEIGHT)

<table>
<thead>
<tr>
<th>PASPALUM VAGINATUM</th>
<th>N*</th>
<th>LEAVES</th>
<th>STEMS</th>
<th>ROOTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td>16.98</td>
<td>7.57</td>
<td>49.79</td>
</tr>
<tr>
<td>P. reticulata</td>
<td>N*</td>
<td>WHOLE FISH</td>
<td>SOFT TISSUES AND BONES</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>39.97</td>
<td>23.31</td>
<td></td>
</tr>
</tbody>
</table>

* N = Number of samples analysed.
CHROMIUM IN IRAJÁ RIVER ESTUARY

The emergent grass *Paspalum vaginatum* may absorb chromium from water and/or sediments. Total chromium concentrations found in all organs analysed were higher than the values found in the water but lower compared with the mean concentration in bottom sediments at station 1.

Data for mean chromium concentration in sediments, water and biological samples compared with results for other freshwater systems reported in the literature are shown in Table 3. Mean chromium concentrations in sediments and water from the Irajá River were 17,536 ppm and 23.39, respectively—three and four orders of magnitude higher than the results found in other polluted areas. The highest value of 17 ppm found in sediments of the Illinois River was roughly three times higher than the mean concentrations of 6.0 ppm and 5.7 ppm reported for unpolluted areas. Aquatic life, fish and emergent plants in the Irajá River have chromium concentrations ten times higher than other polluted areas (Mathis & Cummings, 1973; Mudroch & Capobianco, 1978; Namminga & Wilhm, 1977; Taylor, 1976).

**Estuary**

Total chromium concentrations in the physical and biological components in the estuary in Guanabara Bay, compared with the control area, Sepetiba Bay, are shown in Tables 4 and 5.
<table>
<thead>
<tr>
<th>Area studied</th>
<th>Suspended particles</th>
<th>N</th>
<th>Total soil ($\mu g , g^{-1} , dry , weight$)</th>
<th>Exchangeable soil ($\mu g , g^{-1} , dry , weight$)</th>
<th>Sesuvium portulacastrum</th>
<th>Philoxeros vermiculares ($\mu g , g^{-1} , dry , weight$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station 7</td>
<td></td>
<td>3</td>
<td>$0.012-0.065^a$ (0.0325)$^b$</td>
<td>$25.5-353.0$ (88.0)</td>
<td>$&lt;0.2-1.80$ (0.93)</td>
<td>$&lt;2.0-30$ (10)</td>
</tr>
<tr>
<td>Sepetiba Bay</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Lacerda, 1980)</td>
<td>12</td>
<td></td>
<td>$2.1-6.4$ (3.6)</td>
<td>$&lt;0.0025$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(M. van Weerelt, pers. comm.)</td>
<td>3</td>
<td></td>
<td>$&lt;0.0025$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Ranges.

^b Means.

\(N\) Number of samples analysed.
**TABLE 5**
CHROMIUM CONCENTRATION (ppm) IN SUSPENDED PARTICLES AND BARNACLES IN THE IRAJÁ ESTUARY AND IN SEPETIBA BAY (CONTROL AREA)

<table>
<thead>
<tr>
<th>Area studied</th>
<th>N</th>
<th>Suspended particles (µg ml&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Balanus sp. soft tissues (µg g&lt;sup&gt;-1&lt;/sup&gt; dry weight)</th>
<th>Balanus sp. shells (µg g&lt;sup&gt;-1&lt;/sup&gt; dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Station 8</td>
<td>8</td>
<td>&lt;0.003–0.028&lt;sup&gt;a&lt;/sup&gt; (0.0123)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.5–53.05 (20.95)</td>
<td>2.13–15.15 (6.20)</td>
</tr>
<tr>
<td>1 km from the shore</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sepetiba Bay (M. van Weerelt, pers. comm.)</td>
<td>3</td>
<td>&lt;0.0025</td>
<td>(2.41)</td>
<td>(3.43)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Ranges.
<sup>b</sup> Means.

N Number of samples analysed.

Mean chromium concentrations in suspended particles range from 0.0123 µg ml<sup>-1</sup> (station 8) to 0.0325 µg ml<sup>-1</sup> (station 7), one order of magnitude lower than station 6 (Table 1), 1 km above the estuary. The control area in the less industrialised area, Sepetiba Bay, shows chromium concentration in plants and soft tissues of barnacles (Lacerda, 1980; M. van Weerelt, pers. comm.), one order of magnitude lower than the results found in Guanabara Bay, whereas chromium in the soils of Sepetiba Bay are twenty-five times lower than that found in Guanabara Bay. Chromium concentrations in soft tissues of the barnacles (Table 5) are three orders of magnitude higher than the values found in suspended particles (0.012 µg ml<sup>-1</sup>). Mean chromium concentration in the soil surface shows a value for total soil of 88 ppm compared with only 0.93 ppm for exchangeable soil (Table 4). With the exception of *Sesuvium portulacastrum* litter, the mean chromium concentrations for leaves and stems in the two species analysed are of the same order of magnitude.

Although the mean values for shells (Table 5) are of the same order of magnitude as those found in Guanabara Bay, chromium in suspended particles in Sepetiba Bay is below the detection limit of the method used.

Chromium concentrations in suspended particles and barnacles were compared with other contaminated estuarine waters (Table 6).

In suspended particles the range of 12.3 µg litre<sup>-1</sup> to 32.3 µg litre<sup>-1</sup> of chromium found in the estuary is at least one order of magnitude higher than the value reported by Barbaro *et al.* (1978) in the North Adriatic industrial zone and the same order of magnitude as the value reported in polluted Narragansett Bay (Phelps *et al*., 1973). The chromium concentrations in soft tissues of barnacles in Guanabara Bay are again of the same level as reported by Phelps *et al.* (1973) in Narragansett Bay—nine times higher in *Mercenaria mercenaria* than the values found by Barbaro *et al.* (1978) for *Balanus amphitrite*, and fifteen times higher than the values reported for the bivalve *Scrobicularia* in the Gannel Estuary (Brian & Hummerstone, 1978).
TABLE 6
MEANS AND RANGES OF CHROMIUM CONCENTRATIONS IN SUSPENDED PARTICLES AND SHELLFISH IN THE
ESTUARY OF THE IRAJÁ RIVER COMPARED WITH OTHER POLLUTED ESTUARIES

<table>
<thead>
<tr>
<th>Area studied</th>
<th>Suspended particles (µg g⁻¹ dry weight)</th>
<th>Shell fish (µg g⁻¹ dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(µg litre⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Narragansett Bay</td>
<td>186–211</td>
<td>10·5–25·0*</td>
</tr>
<tr>
<td>(Phelps et al., 1973)</td>
<td></td>
<td>(17·3)c</td>
</tr>
<tr>
<td>Lagoon of Venice</td>
<td>—</td>
<td>2·10–2·79</td>
</tr>
<tr>
<td>(Barbaro et al., 1978)</td>
<td></td>
<td>(2·4)</td>
</tr>
<tr>
<td>Gannel Estuary</td>
<td>—</td>
<td>1·5–2·2</td>
</tr>
<tr>
<td>(Bryan &amp; Hummerstone, 1978)</td>
<td></td>
<td>(1·73)</td>
</tr>
<tr>
<td>Irajá River Estuary</td>
<td>163–535</td>
<td>3·51–53·00</td>
</tr>
<tr>
<td></td>
<td>12·3–32·3</td>
<td>(20·95)</td>
</tr>
</tbody>
</table>

* Related to the corresponding water volume.

b Range.
c Mean.

TABLE 7
CONCENTRATION FACTORS FOR BIOLOGICAL SAMPLES IN THE IRAJÁ RIVER AND IN ITS
ESTUARY IN GUANABARA BAY

<table>
<thead>
<tr>
<th>Concentration factor</th>
<th>µg Cr g⁻¹ dry weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µg Cr ml⁻¹ of water*</td>
</tr>
<tr>
<td>Poecilia reticulata</td>
<td>Whole fish</td>
</tr>
<tr>
<td></td>
<td>133</td>
</tr>
<tr>
<td>Paspalum vaginatum</td>
<td>Leaves</td>
</tr>
<tr>
<td></td>
<td>56·6</td>
</tr>
<tr>
<td></td>
<td>Stems</td>
</tr>
<tr>
<td></td>
<td>25·6</td>
</tr>
<tr>
<td></td>
<td>Roots</td>
</tr>
<tr>
<td></td>
<td>167</td>
</tr>
<tr>
<td>Balanus sp.</td>
<td>Tissues</td>
</tr>
<tr>
<td></td>
<td>1700b</td>
</tr>
</tbody>
</table>

* Chromium available in solution plus suspended particles.

b Value only related to chromium in suspended particles.

Concentration factors for biological samples shown in Table 7 were calculated from data in Tables 1, 2 and 5.

DISCUSSION

Irajá River
Chromium released by the electroplating industry is distributed in the biological and physical components, either in the Irajá River or inside the estuary (Tables 1, 2, 4 and 5).

Some of the values reported in this paper for chromium concentration are the highest ever recorded in the literature for freshwater systems (Table 3). Although
near the point of release (station 3), the chromium concentration of 80 ppm in water (Table 1) is $10^3$ times higher than the maximum levels allowed for freshwater systems (Mearns et al., 1976), the metal is quickly removed from the solution. This can be observed either upstream at station 1 or downstream at station 6, where the level in the water drops as much as six thousand times. Hexavalent chromium in solution reduced to the trivalent state in an anaerobic environment precipitates and is, in consequence, attached to bottom sediments and suspended particles (Pfeiffer et al., 1980). This mechanism, which is associated with large water inputs into the Irajá River on its way to the estuary, appears to be the main reason for the self-cleaning process of chromium in solution.

Bottom sediments at station 1, with the lowest values for chromium in the Irajá River, are still a hundred times more contaminated than sediments in rivers elsewhere (Mathis & Cummings, 1973; Mudroch & Capobianco, 1978). Chromium in bottom sediments is only available to biological life at station 1 or as a source for suspended particles when resuspension occurs.

The fish Poecilia reticulata from station 1 accumulates chromium in its tissues (Table 7) by a concentration factor of 133 related to the total chromium available ($0.3 \mu g ml^{-1}$ in surface water: solution plus suspended particles—Table 1). The emergent plant Paspalum vaginatum also has a concentration factor higher than that related to the water in all organs analysed and lower than that related to the sediments. Similar findings have been reported for fish and chironomids, not only for chromium but for other metals as well (Mathis & Cummings, 1973; Namminga & Wilhm, 1977). The ability of the biological material analysed in the Irajá River to remove chromium from the environment, plus the fact that the ratio between chromium in dead and living plant material has been found to be higher than 1 (Lacerda et al., 1979), indicates the importance of these living systems in returning chromium in the form of detritus to the aquatic system, which can then be transported to other less, or unpolluted, environments.

The results in the Irajá River (Table 1), as has been reported previously (Pfeiffer et al., 1980), show that suspended particles are the main source of the transport of chromium through the water column, thus enabling chromium to reach Guanabara Bay. This transport mechanism has also been indicated by Phelps et al. (1973) in his study of the distribution of chromium in Narragansett Bay and by Bloom & Ayling (1977) in their work on heavy metals in the Derwent Estuary. The highest concentration of chromium in suspended particles within the estuary in Guanabara Bay was found at station 7 where the halophyte community is densely distributed over an area of 700 m². At this site total chromium concentration in the total surface soil was almost thirty times higher than the values found in the control area of Sepetiba Bay (Lacerda, 1980), but in a non-exchangeable form.

Although there is no accumulation of chromium from soil to plant, the concentration of this element in the organs of the two plant species studied and in soils seems to reflect the contamination of the local area, as the values of chromium
in plants and soils from Guanabara Bay are ten and twenty-five times higher than those found in the control area of Sepetiba Bay. On the other hand, chromium associated with plants, and returning to the soil as dead material, is retained by the system, mainly associated with litter (Table 4) and is prevented from reaching the water again. This was demonstrated by Lacerda (1980) in his study of the mineral cycle in the halophyte community in Guanabara Bay.

Barnacles, as a filter-feeder organism, seem to accumulate chromium in soft tissues, as shown by the concentration factor of $1.7 \times 10^3$ related to chromium available in suspended particles. A similar result was found for *Balanus amphitrite* in the North Adriatic Sea (Barbaro *et al.*, 1978) and an even higher concentration factor was reported for chromium in molluscs at Punta Higueiro, Puerto Rico (Stevenson *et al.*, 1965).

Chromium concentrations in shells of *Balanus* sp. are higher than the levels found in suspended particles (Table 5) but are of the same order of magnitude as those found in shells of the control area, where the chromium in suspended particles is below the detection limit of the method. This may indicate that the levels of chromium found in shells of *Balanus* sp., unlike the results found in tissues, are independent of the levels of this element available in suspended particles.

On the other hand, this ability of the barnacles to concentrate chromium can be a potential risk to the estuarine food chain, as they could either be consumed by other marine animals or return the metal in the form of biological detritus into the aquatic system. Therefore more research is required to discover whether this metal accumulation is a mechanical or a biological process and the importance of the chemical form of chromium in the metabolic behaviour of this filter-feeder organism.

CONCLUSIONS

(1) The Irajá River presents some of the highest values of chromium contamination ever reported in the literature for freshwater systems, mainly in sediments and water.
(2) The system presents a self-cleaning process of chromium in solution, mainly due to the reduction of the hexavalent form to a trivalent one, and thereafter retention by bottom sediments and suspended particles. The metal attached to particulate matter is the main source of transport through the Irajá River to Guanabara Bay, 2 km downstream from the point of release by the electroplating industry.
(3) Fish and emergent plants in the Irajá River show the ability to concentrate chromium from the environment and are able to return it in the form of detritus as a source of particulate matter.
(4) In the estuary of the Irajá River chromium levels in soils and plants (halophyte association) are thirty and ten times higher, respectively, than the levels found in the control area (Sepetiba Bay). Although the plant organs analysed (leaves and stems)
show no accumulation from soil concentrations, they seem to reflect the contamination of the area. Chromium concentration in the vegetation is mainly retained by the litter.

(5) Soft tissues of Balanus sp. present a concentration factor of $10^3$ for chromium, confirming results of studies performed elsewhere. On the other hand, adsorption of chromium by the shells of Balanus sp., does not seem to be significant and is relatively uniform. Thus, barnacles could be used as a biological monitor for chromium contamination in polluted environments.

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REFERENCES


