CADMIUM AND ZINC SOURCE ASSESSMENT IN THE SEPETIBA BAY AND BASIN REGION

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(Received: January 1993; revised: September 1993)

Abstract. Industrial and weathering inputs of Cd and Zn to the Sepetiba Bay and basin were assessed, based on production parameters obtained from local environment and industry authorities, and literature data. The results are compared with similar evaluations from other coastal regions and field data obtained in measuring Zn and Cd transport by rivers, direct run-off and atmospheric deposition in the region. Cadmium and zinc inputs to the bay increased by three orders of magnitude relative to pre-industrial fluxes and presently reach up to 1.6 and 180 tonnes per year for Cd and Zn, respectively, which represents a large input-to-area ratio, and explains the high concentration of these metals previously reported in the estuarine biota and sediments of Sepetiba Bay. Industrial activities, mainly metallurgical and chemical, comprise 94% and 84% of the total Cd and Zn inputs to the Bay. This figure identifies the point sources as being responsible for the environmental contamination and for regional poisoning risks.

1. Introduction

A knowledge of industrial emissions of trace metals at the regional scale are useful in the design of environmental monitoring programmes and the identification of sources of risk to human health due to such pollutants (Nriagu and Pacyna, 1988; Hutton and Symon, 1986a).

Among the trace metals of environmental significance, cadmium and zinc are particularly important due to their considerable anthropogenic mobilization. Of the total global input of Cd and Zn to the environment, estimated as 30000 ty^{-1} and 2000000 ty^{-1}, respectively (Nriagu, 1990), 84% of Cd and 72% of Zn are supposed to be of anthropogenic origin, i.e. to result from human activities. In the United Kingdom, for example, Cd is scarcely recovered. Of 1311 tons consumed per year, only 10% is recycled, and 1184 ty^{-1} are released into the environment (Hutton and Symon, 1986a). Worse conditions are expected in low income and highly industrialized regions. Cadmium and zinc contamination have been observed in almost all industrial regions of the world. Surficial sediments are enriched by Cd in the North and Baltic Seas, and West U.S. coast by a factor of 3–10 fold (Yeats and Bewers, 1987), and at least 2–fold for Zn in the North Sea (Araújo *et al.*, 1988). These metals are generally found associated in soils, sediments, ores and water, because of their similar behaviour and sources to the environment.

Sepetiba Bay is a semienclosed lagoon, 447 km^2 in area, located about 60 km West of Rio de Janeiro City (Figure 1). Its drainage basin comprises the western Rio de Janeiro Metropolitan Region, with 1.2 million inhabitants (Mendes

Environmental Monitoring and Assessment **29:** 183–199, 1994.

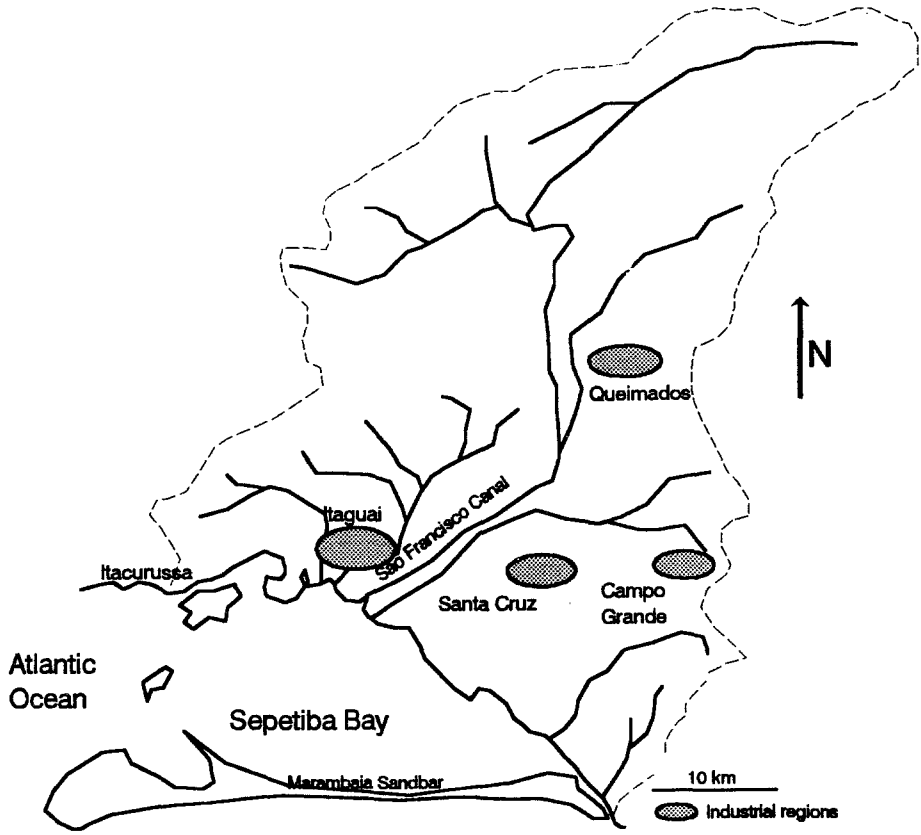

Fig. 1. Sepetiba Bay and drainage basin, main rivers and industrial regions.

and Moreira, 1976) and some of the main regional industrial activities, within a total area of 2065 km^2. Urbanization and industrialization are recent trends in the region. Agriculture has been replaced by industrial development since the 1960s and expanded during the 1970s, with the definition of three 'exclusive' industrial sites for chemical, siderurgical and metallurgical factories and some sites of 'predominant' industrial use (Figure 1).

Recent studies have reported moderate metal contamination and focused on the main pathways of heavy metals inputs to the Bay, either by atmospheric deposition (Pedlowski, 1990), riverine transport (Watts, 1990) or industrial waste disposal (Barcellos, 1991). Sepetiba Bay sediments and biota have also been reported to be highly contaminated by Cd and Zn (Pfeiffer *et al.*, 1985; Lacerda *et al.*, 1987; Carvalho *et al.*, 1992). The detailed origin of these two metals, however, is mostly unknown.

The aim of this work is to gather and compare different anthropogenic and natural (weathering) sources which may contribute to the regional contamination by Cd

and Zn in Sepetiba Bay. This inventory allows the quantification and qualification of the Cd and Zn inputs to the Bay, and is a key step for risk assessment of the regional contamination.

2. Major Sources of Cd and Zn to Sepetiba Bay

The main economical activities in the Sepetiba Bay basin are summarized in Table I.

Most of the employees in the Sepetiba basin work in industrial activities, mainly in metallurgical, chemical and paper factories. Paper and graphic industries have the higher concentration of workers, followed by metal (Fe, Al and Zn) primary production and plastics manufacturing. As all these activities include metal handling, use, or production, this indicates a concentration of metal poisoning risk among few industries in the region.

Other important economic activities are linked to fisheries and tourism which play an important role in the total income and occupation. They comprise 60 tourist boats and 200 shrimp trawlers. Harbour movement reaches a total of 200 carrier ships per year (IFIAS, 1988). These activities need for an aesthetic and seafood quality environmental control.

Production features were obtained from the state environmental and health agencies, and detailed production data on feedstocks and production rates (ABIQUIM, 1987; Química and Derivados, 1988). Production data were used to calculate Cd and Zn emissions using 'waste factors' (the quantity of solid and particulate waste and liquid effluents generated per produced or consumed units) or 'pollution factors' (the quantity of a pollutant released per unit produced or consumed) (WHO, 1982). These factors are not easily discovered in the literature, and regional or national data are more appropriate in this calculation step. It is known that technological and cultural features make large differences in the pollutant emissions in developing countries (Nriagu, 1988).

Tables II and III show the results of Cd and Zn emissions to soil, air and water, followed by the respective calculation data.

The primary metal production industry is the major source of Cd and Zn to the Sepetiba Bay and basin. It is responsible for a total of 24 ty^{-1} of Cd, and 3660 ty^{-1} of Zn, introduced into the Sepetiba Bay basin. This figure is comparable to the Cd input in the whole U.K. environment by the same activity (Hutton and Symon, 1986a). The low production efficiency is most probably largely responsible for these high emission factors, which is partially due to the singularity of the technological process (hydrometallurgy using silicate zinc ore). Recovery efficiency has been improved from 75% to 90% since the 1960s (Barcellos *et al.*, 1991), which is still far below the present ratios, up to 98%, achieved by other technologies (Hopkin, 1991).

The total European emissions of Zn and Cd were calculated to be around 81000 ty^{-1} and 1270 ty^{-1}, respectively. The primary metal production (Cu, Ni, Pb and Zn)

TABLE I

Main economic activities in the Sepetiba Bay basin; number of facilities, production and employes.

	facilities[a]	production[a] (ty^{-1})	employes[b]
Metal smelting			
Fe	3	1102000	4053
Al	2	98500	925
Zn	1	36000	438
Manufacturings			
Paper/graphics	5	534000	4041
Chemicals	16	176900	3887
Metallurgic/Mechanics	19	33370	4372
Plastics/Tires	3	30900	1722
Foods and beverage	8	16700	1645
Others[c]	13	7200	1996
Electric plants	1	160 MW[d]	250[g]
Agriculture and fishing	–	10500[e]	14000
Harbour and navigation	1	19000000[f]	300[g]
Total	72	–	37879

References and remarks

[a] FEEMA, unpublished data.

[b] Only industries with more than 60 employes (FIRJAN, 1986).

[c] Includes electric, nonmetallic and construction.

[d] Nominal capacity, actually working in peak demand periods.

[e] Banana, manioc and potato production, Censo Agropecuário (IBGE, 1980a).

[f] Import and export of coal, iron ore and steel (FEEMA-FUNDREM, 1977).

[g] Data obtained from the respective trade union.

corresponds to 67% and 65% of this total. These industries have also the highest emission factors for these metals (Pacyna and Munch, 1987). Its distribution in the environment is in agreement with the calculations made in this study: 77% to soil, 13% to the atmosphere and 10% to water systems.

Agricultural inputs of heavy metals are negligible due to its low technological state (extensive production, with low use of chemicals). P_2O_5 fertilizer, which often contains Cd and Zn, is imported by Rio de Janeiro harbours at a rate of about

TABLE II

Cadmium inputs to Sepetiba Bay and basin (tonnes per year) from the major local economical activities.

Activities	Soil		Air		Water	
Metal smelting						
Al	0.03	[1]	0.01	[2]	0.001	[3]
Zn	14	[4]	9	[5]	1	[6]
Fe	1.0	[7]	0.33	[8]	0.1	[9]
Electric plants	0.05	[10]	0.02	[11]	0.01	[12]
Sewage discharge	–		–		0.05	[13]
Waste disposal	0.4	[14]	–		0.02	[15]
Agriculture	0.01	[16]	0.001	[17]	0.001	[18]
Urban drainage	0.3	[19]	–		0.03	[20]
Harbour and nav.	0.5	[21]	–		0.05	[22]
Manufacturings						
Paper	0.3	[23]	0.001	[24]	0.012	[25]
Chemicals	0.4	[26]	0.004	[27]	0.004	[28]
Plastics/Tires	0.04	[29]	0.9	[30]	0.001	[31]
Total	17.3		10.25		1.28	

Remarks and references.

[1] 25% input to atmosphere and 75% input to soil (Hutton and Symon, 1986a).

[2] 0.1 gt^{-1} . 98500 ty^{-1} (Nriagu and Pacyna, 1988).

[3] 3% of soil losses (Fleisher *et al.*, 1974).

[4] Based on waste and production data (Barcellos *et al.*, 1991).

[5] 20% of Cd production (Fleisher *et al.*, 1974; Simpson, 1981) and based on production mass balance (Barcellos, 1991).

[6] Directly released to the bay. Based on tidal exchange in the adjacent basin (Barcellos and Pfeiffer, 1991), or 9 ty^{-1} before control measures (FEEMA, 1980).

[7] 25% input to atmosphere and 75% input to soil (Hutton and Symon, 1986a).

[8] 0.3 gt^{-1} . 1100000 ty^{-1} (Fleisher *et al.*, 1974).

[9] 10% of soil losses (Fleisher *et al.*, 1974).

[10] 0.1 g Cd t^{-1} oil (Fleisher *et al.*, 1974).

[11] 100 $MW5hd^{-1}$. 365 dy^{-1} . 0.3t oil MWh^{-1} . 0.3g Cd t^{-1} oil, or 15 $\mu g\ MJ^{-1}$ ((Fleisher *et al.*, 1974; Nriagu and Pacyna, 1988).

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[12] 20% of soil losses (Fleisher *et al.*, 1974).
[13] 1.2 millions of inhabitants . 10 $\mu g\ l^{-1}$ of sewage . 200 $l\ inhab^{-1}\ day^{-1}$. 70% (Metcalf-Eddy, 1981; Macnnicol and Beckett, 1989) or 100 $\mu g\ inhab^{-1}\ d^{-1}$ (Moriyama *et al.*, 1989).
[14] 850000 of inhabitants (users) . 0.45 $kg\ inhab^{-1}\ day^{-1}$. 3 $mg\ kg^{-1}$ (ABES, 1983; Philippi Junior, 1988; Rousseaux *et al.*, 1989) (wet weight base).
[15] 5% of Cd subject to leaching, linked to plastics and batteries (Rousseaux *et al.*, 1989).
[16] 15 gt^{-1} . 500 kg $P_2O_5\ ha^{-1}y^{-1}$. 1000 ha (Nriagu and Pacyna, 1988; Hutton and Symon, 1986a; IBGE, 1980a).
[17] For fertilizers $1gt^{-1}$ to the atmosphere . 500 kg $ha^{-1}y^{-1}$. 1000 ha (Nriagu and Pacyna, 1988). For slash and burns, considering 0.2 gt^{-1} of burned vegetation (Pacyna and Munch, 1987) primary and secondary forest: 50 $m^3\ ha^{-1}$. 2 $km^2\ year^{-1}$, pasture areas: 0.3 $m^3\ ha^{-1}$. 10 $km^2\ year^{-1}$ (Uhl and Buschbacher, 1988).
[18] 10% of Cd in fertilizers application (Hutton and Symon, 1986a).
[19] 100 ha . 3 $kg\ ha^{-1}\ y^{-1}$ (Randall and Grizzard, 1983; Hewitt and Rashed, 1988).
[20] 100 ha . 0.3 $kg\ ha^{-1}\ y^{-1}$ (Hewitt and Rashed, 1988; Luca *et al.*, 1990).
[21] 0.5 gt^{-1} . 19000000 ty^{-1} . 5% of coal and iron ore lost in storage and transportation (Fleisher *et al.*, 1974).
[22] Directly released to the bay. 10% of storage and transportation losses.
[23] 54 m^3 of waste t^{-1} of paper produced . 0.01 gm^{-3} . 534000 ty^{-1} (WHO, 1982).
[24] 123 g of particulate t^{-1} of paper produced . 534000 ty^{-1} . 2 $\mu g\ g^{-1}$ (WHO, 1982).
[25] 23 kg of suspended solids t^{-1} of paper . 1 $mg\ kg^{-1}$. 534000 (WHO, 1982).
[26] 2 m^3 of waste t^{-1} of produce . 177000 ty^{-1} . 5 gm^{-3} (WHO, 1982).
[27] Equal to water losses (Fleisher *et al.*, 1974).
[28] 2.2 kg of suspended solids t^{-1} . 177000 ty^{-1} . 2 $mg\ kg^{-1}$ (WHO, 1982) or less than 0.036 ty^{-1} (FEEMA, 1980).
[29] 12.5 $m^3\ t^{-1}$. 30900 ty^{-1} . 0.1 gm^{-3} (WHO, 1982).
[30] 1846000 tires y^{-1} . 0.5 g $tire^{-1}$ (Nriagu and Pacyna, 1988).
[31] 12 kg of suspended solids t^{-1} 30900 ty^{-1} . 3 $mg\ kg^{-1}$ (WHO, 1982).

TABLE III

Zinc inputs to Sepetiba Bay and basin (tonnes per year) from the major local economical activities.

Activities	Soil		Air		Water	
Metal smelting						
Al	1.6	[1]	1.1	[2]	0.03	[3]
Zn	3000	[4]	600	[5]	60	[6]
Fe	168	[7]	30	[8]	17	[9]
Electric plants	3.0	[10]	0.5	[11]	0.6	[12]
Sewage discharge	–		–		12	[13]
Waste disposal	42	[14]	–		2.1	[15]
Agriculture	0.15	[16]	0.01	[17]	0.01	[18]
Urban drainage	6.0	[19]	–		0.6	[20]
Port and nav.	95	[21]	–		10	[22]
Manufacturings						
Paper	58	[23]	0.03	[24]	2.4	[25]
Chemicals	35	[26]	0.2	[27]	0.2	[28]
Plastics/Tires	3.9	[29]	8.3	[30]	0.26	[31]
Metallurgical	10	[32]	1.0	[33]	1.1	[34]
Total	3423		641		106	

Remarks and references.

[1] 16 gt^{-1} . 98500 ty^{-1} (WHO, 1982).

[2] 11 gt^{-1} . 98500 ty^{-1} (Nriagu and Davidson, 1986).

[3] 2% of soil losses.

[4] 10% of total production (Barcellos *et al.*, 1991).

[5] Barcellos (1991) or 2% of Zn production (Wilber *et al.*, 1980).

[6] Directly released to the bay. Based on Barcellos and Pfeiffer (1991) calculations, or 923 ty^{-1} before control measures (FEEMA, 1980).

[7] 15% input to atmosphere, 85% input to soil (Hutton and Symon, 1986a).

[8] 27 gt^{-1} . 1100000 ty^{-1} (Nriagu and Davidson, 1986).

[9] 10% of soil losses leachate or 35 ty^{-1} (FEEMA, 1980).

[10] 15% to atmosphere, 85% to soil (Hutton and Symon, 1986a).

[11] 100 MW . 5hd^{-1} . 365 dy^{-1} . 0.3 t oil MWh^{-1} . 10 g Zn t^{-1} oil, or 100 μg MJ^{-1} (Nriagu and Pacyna, 1988).

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[12] 20% of soil losses.
[13] 1.2 million inhabitants. 200 μg l^{-1} of sewage . 200 l $inhab^{-1}$ day^{-1} . 70% (Metcalf-Eddy, 1981; Macnicol and Beckett, 1989) or 40 mg $inhab^{-1}$ day^{-1} (Moriyama *et al.*, 1989).
[14] 850000 inhabitants (users at Santa Cruz and Campo Grande). 0.45 kg $inhab^{-1}$ day^{-1} . 300 mg kg^{-1} (ABES, 1983; Philippi Junior, 1988; Rousseaux *et al.*, 1989) (wet weight base).
[15] 5% of Zn subject to leaching, Zn is linked to organic matter and plastics (Rousseaux *et al.*, 1989).
[16] 300 gt^{-1} of P_2O_5 . 500 kg ha^{-1} y^{-1} . 1000 ha (Hutton and Symon, 1986a; IBGE, 1980a).
[17] For fertilizers: 15 gt^{-1} to the atmosphere . 50 kg ha^{-1} . 1000 ha (Nriagu and Davidson, 1986). For slash and burns: 5 gt^{-1} of burned vegetation (Nriagu and Pacyna, 1988) primary and secondary forest: 50 m^3 ha^{-1} 2 km^2 y^{-1} ,pasture areas: 0.3 m^3 ha^{-1} . 10 km^2 y^{-1} (Uhl and Buschbacher, 1988).
[18] 7% of Zn in fertilizers soil application (Hutton and Symon, 1986a).
[19] 100 ha . 6 kg ha^{-1} y^{-1} (Randall and Grizzard, 1983).
[20] 100 ha . 062 kg ha^{-1} y^{-1} (Randall and Grizzard, 1983; Luca *et al.*,, 1990).
[21] 100 gt^{-1} . 19000000 ty^{-1} . 5% of coal and iron ore lost during storage and transportation (Nriagu and Pacyna, 1988).
[22] Directly released to the bay. 10% of storage and transportation losses.
[23] 54 m^3 of waste. t^{-1} of produced paper . 2 gm^{-3} . 534000 ty^{-1} (WHO, 1982).
[24] 123 g of particulate t^{-1} of produced paper . 534000 ty^{-1} . 500 μg g^{-1} (WHO, 1982).
[25] 23 kg of suspended solids t^{-1} of paper . 200 mg kg^{-1} . 534000 ty^{-1} (WHO, 1982).
[26] 2 m^3 of waste t^{-1} of produce . 177000 ty^{-1} . 100 gm^{-3} (WHO, 1982).
[27] Equal to water losses (Fleisher *et al.*, 1974).
[28] 2.2 kg of suspended solids t^{-1} . 177000 ty^{-1} . 500 mg kg^{-1} (WHO, 1982) or 0.7 ty^{-1} (FEEMA, 1980).
[29] 12.5 m^3 t^{-1} . 30900 ty^{-1} . 10 gm^{-3} (WHO, 1982).
[30] 4.5 g $tire^{-1}$. 1846000 tires y^{-1} (Nriagu and Pacyna, 1988).
[31] 12 kg of suspended solids t^{-1} . 30900 ty^{-1} . 700 mg kg^{-1} (WHO, 1982) or 200 mg Zn l^{-1} of effluents (Wilber *et al.*, 1980) or 0.7 ty^{-1} (FEEMA, 1980).
[32] 5000 ty^{-1} of electroplating . 2 kg t^{-1} (Nriagu and Pacyna, 1988).
[33] 5000 ty^{-1} . 0.2 kg t^{-1} (Nriagu and Pacyna, 1988).
[34] 5000 ty^{-1} of zinc electroplating . 0.224 kg t^{-1} (WHO, 1982; Nriagu and Pacyna, 1988).

13000 tons annually (CDRJ, 1988) and its use in the Sepetiba Bay catchment is estimated to be around 500 ty^{-1}. This activity has a small participation in the whole regional economical income and employs 14000 workers among a total of 30000 rural population (Mendes and Moreira, 1976).

The impact of domestic waste landfill must be considered due to its close proximity to water courses and the potential mobility of Cd and Zn in those materials. In English domestic waste, for example, 74% of Cd is contained in pigments, 19% in stabilizers, and 7% in Ni/Cd batteries (Hutton and Symon, 1986a). In France, the contribution of batteries to total Cd in wastes was estimated as 45% due to the absence of recycling education or programmes (Rousseaux *et al.*, 1989). The only waste landfill in the Sepetiba Bay region started in 1978 and in 1983 comprised an area of approximately 105000 m^2, disposing 300 t day^{-1} (ABES, 1983). This landfill may contribute 0.4 and 42 t y^{-1} of Cd and Zn, respectively, to soil, and the weakly bound fraction of metals can reach ground and surficial waters through leaching, seepage and percolation processes. Other final disposal alternatives are avoided since garbage incineration was prohibited by Federal law in 1977. This measure resulted in a decline of Cd (but not of Zn) emissions in the 1970s in Rio de Janeiro City (Trindade *et al.*, 1981).

Municipal sewage systems have a low impact on Cd pollution of Sepetiba Bay, being responsible for 4% of total input to the bay. It is well known that even primary treatment processes are able to remove heavy metals from sewage waters (Metcalf-Eddy, 1981). The absence of sewage treatment plants in the region implies the discharge of the original metal content of sewage into the rivers, but ironically eliminates the sludge disposal problem, which constitutes a secondary source of metals to soil in Europe (Davis, 1984; Macnicol and Beckett, 1989).

For the North Sea, sewage contribution reaches 8.6% of the total Cd input (Hutton and Symon, 1986b). The different weights of sewage contributions in the two regions are possibly related to the diversification of pollution activities in U.K., and the absence of sewer networks in the majority of urban areas of Sepetiba Bay basin (IBGE, 1980b). Sewage derived zinc represents 11% of total Zn inputs to Sepetiba Bay through liquid pathways. Zinc is largely used in detergents and its distribution in other coastal areas of Rio de Janeiro State, such as in Jacarepaguá river basin is also explained by sewage discharge (Azevedo *et al.*, 1988).

3. Pathways of Cd and Zn to the Sepetiba Bay

Table IV sumarizes the total Cd and Zn inputs to the rivers and to the Bay itself.

Primary Zn production and harbour activities are responsible for the direct discharge of Cd and Zn to the Bay, which represents 80% and 62% of the total input. The direct impact of navigation on the input of heavy metals is unknown. The chemical protection of vessel hulls is responsible for 160–200 ty^{-1} of Zn released to the South California waters (Young *et al.*, 1980). However, in Sepetiba

TABLE IV

Natural and industrial inputs of Cd and Zn to the rivers and Sepetiba Bay (in tonnes per year).

	Industrial Discharges		Weathering Inputs*
	to rivers	to the Bay	
Cd	0.23	1.05	0.10
Zn	36	70	21

* Calculation parameters in the text.

Bay, this source may be negligible due to the low movement and residence times of ships in the bay.

Weathering products have a negligible weight in Cd and Zn input (6% and 16% respectively) to the bay, as summarized in Table IV. Diffuse sources (agriculture, sewage discharge, soil erosion and leaching) are of secondary importance compared to industrial ones. By contrast, in the Rhine River, industrial sources represent 22% of total Cd load (8.5 tonnes per year) and non-point anthropogenic sources play an important role in total input. The same situation was reported for zinc, with a total load of 2800 tonnes per year (Malle, 1990). Rather than for Europe and other developed regions (Novotny, 1988), point industrial sources in Sepetiba Bay (identified from Table II), are of major importance, and are presently underrepresented in the existing environmental control and monitoring programmes.

Sediment transport is often considered as a 'natural' or 'non-anthropogenic' input of trace metals to coastal waters. In this region, because of the changes in the water resources management, these expressions should be avoided. In Sepetiba Bay the present particulate input (3105 ty^{-1}) (IFIAS, 1988) is a result of the increase, from 10 $m^3 s^{-1}$ in 1903 to 180 $m^3 s^{-1}$ in 1953, in the Guandú River discharge. This was caused by the basin water transposition from the Paraíba do Sul River, used for hydropower generation (CNEC, 1987). Assuming a power function between the suspended sediment load and the water flow, with an exponent around 2 (Linsley *et al.*, 1975), the preindustrial sediment input to the Bay must have been 300 times lower than the present. In fact, the northeastern region of Sepetiba Bay presents a high sedimentation rate up to 6 cm y^{-1} (Barcellos *et al.*, 1991) and accelerated coastline transgression due to the excavation of the Guandú River bed (Ponçano *et al.*, 1976). The present metal input linked to river sediment transport (Table IV) was calculated based on background sediment concentrations of 0.3 and 70 mg kg^{-1} for Cd and Zn, respectively (Salomons and Forstner, 1984). It can therefore be assumed that preindustrial particulate Cd and Zn inputs to the Bay from natural weathering were around 0.3 and 70 kg y^{-1}, respectively.

Tidal exchange does not represent any significant input of metals to the Bay. On the contrary, water circulation is one of the several ways (e.g. particulate deposition,

TABLE V

Comparison between industrial outputs and effective inputs to the Sepetiba Bay, by atmospheric and riverine pathways (in tonnes per year).

	Atmospheric		Riverine	
	Calculated emission in the basin	Measured deposition to the bay[a]	Potential release into rivers	Measured inputs to the bay
Cd	10.25	0.2	0.32	0.9 [b]
Zn	641	56	57	330 [c]

Ref.: [a] Pedlowski, 1990; [b] Watts, 1990; [c] Lacerda, 1983.

metal precipitation) of diluting and removing metals from the water column in Sepetiba Bay. The average ocean concentrations of Cd and Zn were measured as 20 ng l^{-1} (Boyle *et al.*, 1976) and 200 ng l^{-1} (Martin *et al.*, 1980; Yeats, 1988), respectively. These very low concentrations also enable the assumption of an insignificant contribution of ocean spray formation and deposition to the total atmospheric input to Sepetiba Bay (Waldichuk, 1982).

When comparing the calculated Cd and Zn releases to the local environment and their measured inputs to Sepetiba Bay, it is noted that for the atmospheric pathway there is a significant loss of Cd and Zn. This fact may be attributed to the deposition of large and dense particles closely around the sources. Cadmium and zinc are restricted in the atmospheric spreading process due to the size of particles formed (Nriagu, 1990). The ashes of the zinc smelter are ZnO_2 (SES, 1988) which have a small range of transport in the atmosphere because of their large average particle diameter (60 μm) (Fleisher *et al.*, 1974). Krell and Roeckner (1987) reported that approximately 12% of Cd industrial emissions are deposited locally. The total particulate emission for monitored industries in Sepetiba basin is 6956 ty^{-1} (FEEMA, 1984). Considering an average Cd concentration of 5.0 gt^{-1} in the industrial particulate (Trindade *et al.*, 1981; Nriagua and Pacyna, 1988), a particulate Cd emission of 0.035 ty^{-1} is estimated which is compared to a sixfold higher measured deposition, and a three hundred-fold higher calculated total industrial emission. Atmospheric emission is also spread in the continent more intensively than in the Bay, considering that there is an areal proportion of 50 : 1 between the drainage basin and the bay, and that the winds blow predominantly northwards (Signorini, 1980). Estimated Cd emissions in Europe represent between 4 and 12 times its deposition in the Mediterranean Sea (Martin *et al.*, 1989). Around 75% of Cd precipitation is made by humid deposition. This is dependent on rain regime (Krell and Roeckner, 1987).

TABLE VI

Main pathways of Cd and Zn to Sepetiba Bay (in tonnes per year).

	Atmosphere[1]	River and runoff[2]	Total
Cd	0.2	1.37	1.57
Zn	56	127	183

Ref.: [1] Pedlowski, 1990. [2] This work.

On the other hand, the sum of calculated industrial and weathering borne metal releasing rates is considerably lower than measured river loads, mainly for Zn (sixfold) than for Cd (threefold). The difference between the potential and actual pollutant load is likely to be caused by the use of low emission factors, obtained from developed countries. The actual release of metals can be underestimated due to the different production conditions in developing countries (Andreottola and Bressi, 1991). For instance, an industry with recovery efficiency of 90% releases five times the pollutant discharge of an industry with 95% of efficiency.

River input estimates, performed in different years using different methodologies, give one order of magnitude difference for Zn (Lacerda, 1983; Watts, 1990). Calculated industrial plus weathering input to the aquatic environment is within this range. Industrial Zn discharges, estimated in this work as 106 ty^{-1}, is within the range of previous evaluations, based on effluent monitoring data of 5.5 and 934 ty^{-1} (FEEMA, 1980). Industrial Cd input of 1.28 ty^{-1} is considerably lower than previous estimates of 35 ty^{-1} (FEEMA, 1980).

For larger areas,the atmosphere can play a more important role in Cd deposition. The global input of Cd to the oceans is around 1260 ty^{-1}. Considering that river inputs (5120 ty^{-1}) are settled nearshore (4300 ty^{-1}), atmospheric inputs to the ocean (440 ty^{-1}) play an important role in the global Cd mass balance (Yeats and Bewers, 1987). For the North Sea, 67% of Cd is transported by rivers and 8.6% is introduced from sewage systems (Hutton and Symon, 1986b). These results are in agreement with the estimated 136 ty^{-1} Cd, deposited in the North Sea by the atmosphere from a total Cd discharge of 233 ty^{-1} (Krell and Roeckner, 1987). In the northwestern Mediterranean Sea, the total input of Cd is around 100 ty^{-1}, with 85% of this total corresponding to the atmospheric input. River particles enriched by Zn and Cd are supposed to be trapped in the coastal zone (Martin *et al.*, 1989). Nearly 87% of total Cd and 69% of total Zn inputs to the Sepetiba Bay are transported through rivers and direct runoff, while the atmosphere contributes 13% and 21%, respectively.

A comparison of Cd and Zn inputs, water and sediment concentrations between Sepetiba Bay and other coastal areas is presented in Table VII. Sepetiba Bay has

TABLE VII

Comparison between Cd and Zn inputs to Sepetiba Bay, Firth of Forth, North Sea and Western Mediterranean Sea, and their related impacts on water and sediment quality.

	Area (km^2)	Input (ty^{-1})		Water concentration ($ng.l^{-1}$)		Sediment concentration ($mg.kg^{-1}$)	
		Cd	Zn	Cd	Zn	Cd	Zn
Sepetiba Bay (ref. 1, 2, 3)	447	1.6	180	3000	40000	2.1	634
Firth of Forth (ref. 4)	800	2	–	30–250	–	3	–
North Sea (ref. 5, 6, 7, 8)	760000	200	25000	7–36	250–2000	0.47	99
Western Mediterranean (ref. 9, 10, 11, 12)	1000000	100	9500	5–10	250	0.1–2.3	80

References.

[1] Lacerda, 1983
[2] FEEMA, 1980
[3] Patchineelam *et al.*, 1989
[4] Balls and Topping, 1987
[5] Dicke *et al.*, 1987
[6] Irion and Muller, 1987
[7] Kersten *et al.*, 1988
[8] Araujo *et al.*, 1988
[9] Martin *et al.*, 1989
[10] UNEP, 1987
[11] Ruiz-Pino *et al.*, 1991
[12] Fernex *et al.*, 1986
– data unknown.

one of the highest input-to-area relations in comparison with other large coastal regions. As a result, a significant enrichment in sediment metal concentration is observed. This pattern is due to the concentration of specific industrial activities in the region, and hydrodynamical influences on the Bay's dispersal capability.

Unlike other estuaries and coastal environments, Cd and Zn are directly introduced into the Bay, mainly by industrial wastes erosion and leaching (Barcellos *et al.*, 1991), and atmospheric deposition (Pedlowski, 1990).

4. Conclusions

Industrial activities, mainly metallurgical processing, have an important role from the economical (Table I) and pollution (Tables II and III) points of view. Nearly 24000 workers are involved with industrial processes containing Cd or Zn, 8% working in highly contaminated areas, being therefore, exposed to poisoning risks. However, these exposures must be detailed.

The Zn : Cd ratio is wastes was found to range from 9–1000, with an average value of 80. In natural sediments and soil, this ratio ranges from 150–250 (Fleischer *et al.*, 1974). The larger variations in Zn : Cd ratio in wastes shows the specific

features of production processes and the rupture of the geological elemental equilibrium. Atmospheric emissions have Zn : Cd ratios of about 65, indicating the industrial enrichment of airborne Cd, as observed by Pedlowski (1990) in regional rainwater samples.

Primary zinc production is the predominant industrial source of Cd and Zn to the bay. Chemical and plastics industries must also be considered as potential sources. Weathering products are negligible when compared to industrial inputs of these metals to the bay.

Soil is the main sink (perhaps temporary) of industrial contaminated wastes. The possible transfer of Cd and Zn to surficial and ground waters as well as resuspension of Cd and Zn rich particles should be investigated. Beside, the treatment of liquid effluents and atmospheric emissions tend to enlarge soil contamination (through landfills) as a final disposal alternative, reducing aqueous and aerial inputs (Yost, 1984), at least temporarely.

Zinc was observed to have a large diversity of potential sources (chemical metallurgical industries, sewage, weathering). This is probably due to its wide use and consumption in industrial and domestic activities. On the contrary, Cd has fewer and more specific sources in the region. Besides, industrial Cd represents 94% of total aquatic input to the bay.

Some of the main Cd and Zn inputs to the bay are negligible from the contamination point of view because of the inert chemical form of contained metals and the low enrichment in relation to background levels (for instance, the losses of iron ore during transportation). On the contrary, zinc primary works produce high contaminated liquid and solid wastes in very mobile species.

Acknowledgements

The authors are grateful to FEEMA (the State Environmental Control Agency) and Secretaria de Estado de Saúde do Rio de Janeiro (the State Health Secretary) for the access to file data, and Bruno de Brito Queiroz Souza for searching some of the informations cited in this work. This project was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

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