largely on the management and future impact of the Dublin Port reclamation project.

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Three decades of Cd and Zn contamination in Sepetiba Bay, SE Brazil: Evidence from the mangrove oyster *Crassostraea rhizophorae*

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The past 30 years have witnessed drastic changes in heavy metal pollution sources to the Brazilian environment, mostly due to the reduction of point source emissions as a result of strengthening control policies and changing industrial technology. However, little has been achieved in controlling non-point source emissions, and in many areas pollution has increased rather than decreased. In addition, changes in land use have affected heavy metal sinks and remobilized large amounts of pollutants even though many years have passed since the closure of the original sources. In Sepetiba Bay, SE Brazil, emission control policies have resulted in a decrease of about 55% and 13% of the Cd and Zn annual emissions to soils and waters, respectively (Lacerda et al., 2004; Molisani et al., 2004).

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Table 1
Estimated annual Cd and Zn emissions (ton.yr^{-1}) from anthropogenic sources to Sepetiba Bay (only emissions to soils and rivers are accounted for)

Source	1980s		2005	
	Cd	Zn	Cd	Zn
Zn smelting	1	60	0[a]	0[a]
Other smelters	0.11	17	0.3	46
Wastewaters	0.05	12	0.07	20
Solid urban waste disposal	0.02	2	0.1	7
Urban runoff	0.03	0.06	0.05	1
Power generation	0.01	0.6	0.01	0.6
Agriculture	0.001	0.01	0	0
Harbor & Navigation	0.05	10	0.09	18
Manufactures (chemical paper, plastic and rubber)	0.02	4	0.02	4
Total	1.28	105	0.63	96

Numbers are rounded. *Source*: Barcellos and Lacerda (1994); Lacerda et al. (2004); Molisani et al. (2004).
[a] Runoff from tailings occurs but has not been quantified to date.

Many studies have been carried on Sepetiba Bay due to its ecological and economic importance to the metropolitan area of Rio de Janeiro in southeastern Brazil. These studies date back to the late 1970s, which make possible an evaluation of historical changes in metal concentrations in the bay region. Unfortunately, water and sediment data, although abundant, have been generated using different methodologies, which do not necessarily allow temporal comparisons. However, many studies have utilized biological monitors, in particular molluscs, which have been analyzed using the same methodology (i.e., total acidic digestion and conventional flame atomic absorption spectrophotometry). In this paper we review the existing data on the concentrations of Cd and Zn in the mangrove oyster *Crassostraea rhizophorae* Guilding, 1828 (in some studies known as *C. brasiliana*) during the past three decades when major changes in the pollution profile of Sepetiba Bay occurred.

Sepetiba Bay is a semi-closed coastal lagoon about 60 km south of Rio de Janeiro city, SE Brazil. The bay has been historically contaminated by Cd and Zn from a large Zn smelting plant, which was closed in 1996, as well as from approximately 400 other industries, mostly metallurgical plants (Lacerda et al., 1987). This industrial park remained the same throughout the period due to the country's economic stagnation during the 1980s and part of the 1990s, with the exception of the iron and steel industry, which increased production by a factor of 3. These industries however, had to adapt to new emission control measures, which became tighter during this same period. Presently, new industries are being developed, and are expected to start operations by the end of the present decade.

Major changes in pollutant sources have been due to increasing urbanization and transport infrastructure. The population inhabiting the Sepetiba basin has increased from about 600,000 in 1980 to nearly 2 million in 2000 and *per capita* urban waste production also increased from 0.5 kg inhab^{-1} day^{-1} in the 1980s to 1.2 kg inhab^{-1} day^{-1} in 2004 (Silva Filho et al., 2006). Navigation, another important potential pollutant source to the bay, has also

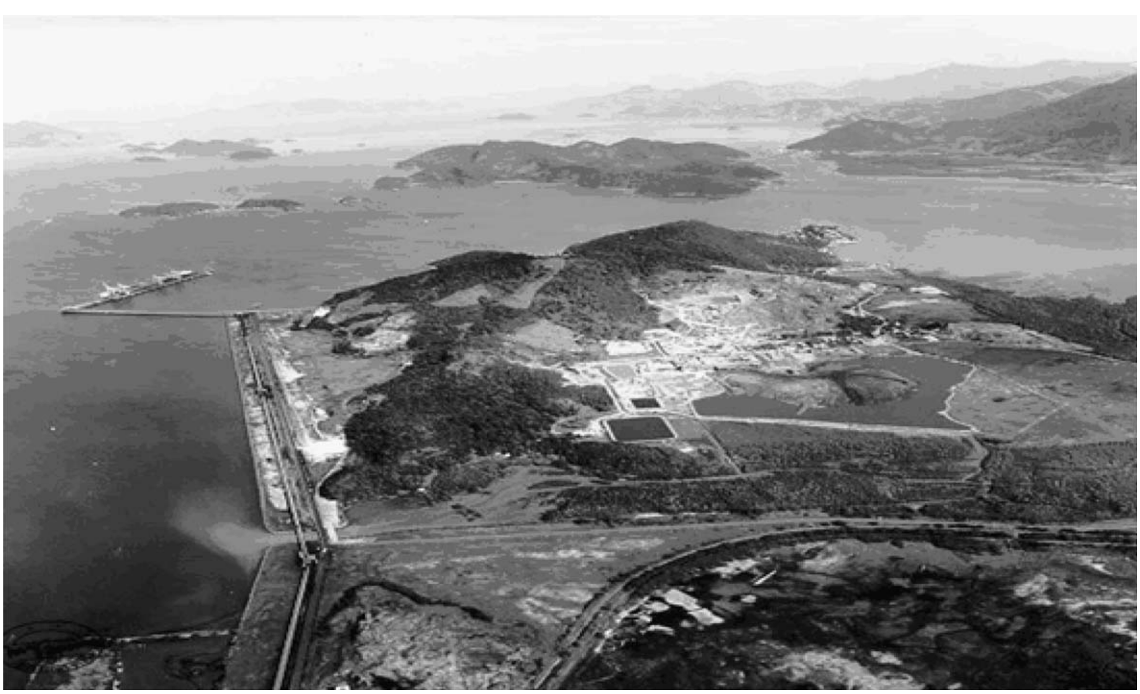

Fig. 1. Tailings of the Zn and Cd smelter at Sepetiba Bay, Rio de Janeiro, SE Brazil in 1996. Note the spill of contaminated material entering the bay after heavy rains. Photo courtesy of *C. barcellos*.

increased; Sepetiba harbor, the major port facility in southern Rio de Janeiro has doubled its original capacity of 20 million t yr^{-1}. However, agriculture, which was an important economic sector in the 1970s, has virtually disappeared and the remaining areas of natural vegetation on the coastal plain have been deforested (FEEMA, 1997).

Table 1 shows the estimated annual emissions of Zn and Cd to Sepetiba Bay based on a 1986 pollutant emission database inventory (Barcellos and Lacerda, 1994) and updated to present conditions (Lacerda et al., 2004; Molisani et al., 2004). Changes in Cd and Zn emissions during the period were mostly due to the closure of the Zn smelting plant, which not only cut Cd emissions by half but also resulted in a significant reduction in Zn emissions. However, increasing iron and steel production capacity and urbanization resulted in an increase in Zn emissions, which nearly equals the reduction due to the closure of the Zn smelting plant. A legacy of the Zn smelting plant is the 20×10^6 tons of tailings deposited beside the Bay. These tailings contain about 380 tons of Cd and 210,000 tons of Zn (Barcellos et al., 1991, 1992). During heavy rains in summer months, runoff waters enriched in Zn and Cd reaches the bay (Fig. 1). For example, Amado Filho et al. (1999) and Rebelo et al. (2003a) reported sudden increases in Cd and Zn concentrations in brown seaweeds and oysters, respectively, after a large spill of tailings material in 1996. However, this input has not been adequately quantified (Lacerda et al., 2004).

The mangrove oyster *Crassostrea rhizophora* has been used as a biomonitor all along the Brazilian coast (Lima et al., 1986; Silva et al., 2001; Curtius et al., 2003; Vaisman et al., 2005, among others). This mollusk has many ecological and biological characteristics which make it a suitable biological monitor for heavy metals contamination. In Sepetiba Bay, *C. rhizophorae* has been analyzed in metal pollution studies since 1978, allowing a long-term temporal comparison of the evolution of heavy metals contamination in the Bay. At least 12 studies between 1980 and 2005 have been published on Cd and Zn concentrations; we selected those results obtained from the inner part of the bay close to the old smelter site. Most of these studies used an adjacent area to Sepetiba Bay, Angra dos Reis Bay, as a control site, and these results are also presented for comparison. In addition, the studies focused on adult animals of similar size and were undertaken over a period of at least 6-months, thus minimising the possible effects of size and season on Cd and Zn concentrations.

Table 2 summarizes the reported Cd and Zn concentrations from 1978 to 2002 in *C. rhizophorae* from Sepetiba and Angra dos Reis Bays. The results show different temporal trends for Cd and Zn concentrations in oysters. Average Cd concentrations decreased from 1.4 to 8.6 $\mu g\ g^{-1}$ d w during the late 1970s and the 1980s, to 0.9 to 2.9 $\mu g\ g^{-1}$ d w during the late 1990s; average Zn concentrations increased continuously from 2244 $\mu g\ g^{-1}$ d w in 1978 to about 11,984 $\mu g\ g^{-1}$ d w at present. Zn concentrations are amongst the highest reported for oyster tissues worldwide (Rebelo et al., 2003a,b). Peak concentrations of both metals, however, were reported after the 1996 spill (Fig. 1). As expected, the non-contaminated site at Angra dos Reis showed much lower concentrations of both metals (in particular Zn; 1706–2022 $\mu g\ g^{-1}$ d w) and no detectable changes occurred during this period.

The results for Cd and Zn concentrations in oyster tissues are in agreement with the estimated changes in metal emissions (Table 1), showing that whereas the closing of the Zn smelter resulted in a drastic decrease in Cd emissions, it had little effect on the concentrations of Zn. Increasing urbanization, resulting in rising solid waste and waste water production, increasing harbor activities and, to a lesser extent, recent industrialization has apparently maintained Zn emissions at earlier levels.

Other studies covering relatively long periods found contrasting results depending on the type of samples analyzed. Amado Filho et al. (1999) compared Cd and Zn concentrations in two brown algae (*Padina gymnospermae* and

Table 2
Concentrations (range and average) of Cd and Zn in *C. rhizophora* from Sepetiba and Angra dos Reis Bays between 1978 and 2002

Year/Reference	Sepetiba Bay		Angra dos reis	
	Cd	Zn	Cd	Zn
1978 – Lacerda (1983)	3.9–10.9 (6.9)	237–4151 (2244)	–	–
1980 – Pfeiffer et al. (1985)	0.8–1.9 (1.4)	1209–1854 (1533)	–	–
1983 – Lima et al. (1986)	1.6–20.5 (8.6)	3477–16,130 (8073)	3.0–3.4 (3.2)	1675–1871 (1773)
1989 – Carvalho et al. (1991, 1993)	3.3–4.6 (3.9)	4686–5016 (4950)	0.9	1650–1782 (1706)
1996 – Rebelo et al. (2003a)[a]	29	80,724	–	–
1997 – FEEMA (1997)	0.3–4.9 (2.6)	3630–14,718 (9174)	–	–
1999 – Rebelo et al. (2003a)	1.3–5.4 (2.9)	8058–28,523 (14,849)	2.8	1627
2001 – Amaral et al. (2005)	0.4–1.3 (0.9)	2100–17,350 (9770)	–	–
2002 – Rebelo et al. (2003b)	1.6–2.0 (1.7)	10,963–17,420 (11,984)	1.2–2.2 (1.7)	1100–2859 (2022)

Values are expressed in $\mu g\ g^{-1}$ dry weight.
[a] After a tailings spill following heavy rains in 1996.

Sargassum stenophylum) from Sepetiba Bay between 1990 and 1997. They reported peak concentrations following the 1996 spill, but failed to show any overall trends during this period. Rezende et al. (1991) compared the concentrations of Mn, Cr, Pb and Zn in intertidal sands from 7 beaches along the Sepetiba Bay coastline between 1980 and 1990. Their results indicated few differences between the concentrations of Pb, Mn and Cr, but showed increasing Zn concentrations in the 1990 sampling at all beaches studied when compared with the concentrations reported in 1980 (Lacerda et al., 1985).

This long-term analysis of Sepetiba Bay contamination using oyster tissues illustrates the present state of local metal pollution control policies. Although point source control has been relatively successful during the past three decades, the increasing magnitude of diffuse sources, such as those associated with urbanization and newer industries, appears to have maintained high contamination levels (at least for some elements such as Zn), ensuring that metal exposure may continue to provide a permanent risk to the environment.

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