Apparent discrepancy in contamination history of a sub-tropical estuary evaluated through ^{210}Pb profile and chronostratigraphical markers

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Abstract

Zn and Cd concentrations, stable lead isotopes and ^{210}Pb-derived chronology were determined in a sediment core sampled at Sepetiba Bay (South-eastern Brazil). During the last decades, the bay's watershed has been modified by the increase of industrial activities and human interventions. In particular, Zn and Cd ore treatment plants were built near the coast in 1960 and 1970, respectively, and water has been diverted from the adjacent Paraíba do Sul River watershed since 1950. The core collected at shallow depth near the industrial area exhibits four successive events: (i) at 50 cm depth, a change in the ^{206}Pb/^{207}Pb ratio from about 1.162 to more than 1.18 might be the result of the São Francisco Channel opening and water diversion from Paraíba do Sul river; (ii) at 40 cm depth, Zn concentration starts to increase (up to 0.8 mg g^{-1}) (iii) above 30 cm depth, relatively high Cd concentrations (up to 1.6 µg g^{-1}) are observed and (iv) at 16 cm depth, change in unsupported ^{210}Pb slope is probably related to a waste dam built to prevent strong metal contamination in the bay. Sediment accumulation rates evaluated by Zn and Cd profiles used as time-markers are higher than those calculated from ^{210}Pb-based chronology models. Using the constant initial concentration (CIC) model both events are supposed to date back to about 1884 and 1902, respectively, while using the constant rate of supply (CRS) model it shifts to about 1925 and 1935. Such discrepancies are probably assigned to the fact that these models do not take into account site-specific local sedimentation dynamics. In the study area, particles deposition seems to be controlled by enrichment with unsupported ^{210}Pb transported by runoff from a mangrove flat bank. Chronology derived from a model that assumes an exponential increase of the initial ^{210}Pb activity fits well with the estimated rates obtained from historical events.
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1. Introduction

The most widely used method for dating sediments deposited over the last 100 years in marine or lacustrine environments is based on the examination of ^{210}Pb profiles (Appleby et al., 1988; Appleby and Oldfield, 1983; McCall et al., 1984). The ^{210}Pb radioactive isotope has a 22.3 years half-life and belongs to the ^{238}U decay series including the noble-gas ^{222}Rn ($t_{1/2} = 3.8$ d). One fraction of the radon is released from rocks and soils to the atmosphere where it changes to ^{210}Pb through successive alpha and beta emissions. Then ^{210}Pb is quickly removed from the atmosphere

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by dry deposition and precipitation, reaching the sediment–water interface. Thus, sediments have two distinct ^{210}Pb sources: the supported one produced by the decay of the related nuclides present in the sediment, and the unsupported one (or "in excess") originating from the atmosphere. After new deposits have covered surficial sediments there will be no further unsupported ^{210}Pb input and concentration declines solely by radioactivity decay. Under some assumptions the sediment deposition date may be estimated from vertical profiles in cores (Appleby et al., 1988; Appleby and Oldfield, 1983; McCall et al., 1984; Stiller and Imboden, 1986). Theoretically the ^{210}Pb$_{exc}$ should evolve with depth following the equation:

$$^{210}Pb_{exc}(z) = {}^{210}Pb_{exc}(0)e^{-\lambda t} \qquad (1)$$

where ^{210}Pb$_{exc}(z)$ is the activity at the depth z, ^{210}Pb$_{exc}(0)$ the activity at the surface, λ is the ^{210}Pb decay constant, and t is the time elapsed since the sedimentation beginning at depth z. In the model CFCS (constant flux constant sedimentation rate), both flux and sedimentation rates are assumed to be constant. Represented in a semi-log diagram, the ^{210}Pb$_{exc}$ evolution with depth becomes a line and its slope allows the sedimentation rate to be readily calculated. In the CIC model (constant initial concentration), the unsupported ^{210}Pb initial concentration at the top layer (where no mixing should occur) is assumed constant through time because the amount of ^{210}Pb$_{exc}$ integrating the sediment is supposed to be inversely proportional to the particulate flux (Robbins and Edgington, 1975). An age can be calculated for each layer using:

$$t = (1/\lambda)\ln({}^{210}Pb_{exc}(0)/{}^{210}Pb_{exc}(z)) \qquad (2)$$

Finally, in the CRS model (constant rate of supply), only the annual ^{210}Pb$_{exc}$ flux (F_0) is supposed to be constant. It is related to the total ^{210}Pb$_{exc}$ inventory (I_0) by

$$I = F_0/\lambda \qquad (3)$$

and at level z, the partial inventory below the layer z (I_z) is related to I by

$$I_z = (1/\lambda)(F_0 e^{-\lambda t z}) \qquad (4)$$

Hence, an age is calculated for a layer at depth z:

$$t_z = (1/\lambda)\ln(I/I_z) \qquad (5)$$

Although the last model is generally well adapted to date a particular layer or to provide a sedimentation rate over a given time interval, a combination with other and independent time-markers is often required to understand and to constraint sedimentary processes which may be sometimes very complex (San Miguel et al., 2004; Smith, 2001). ^{137}Cs fallout integrated to the sediments subsequently to atmospheric nuclear weapon tests is often used as complementary chronostratigraphical markers (McCall et al., 1984). Alternatively, in coastal areas, chemical compositions of sediments are directly influenced by industrial activities and by urban development. If the history of the latter is well documented, changes in environmental prox-

ies recorded in sediments (e.g., heavy metal concentrations, isotopic ratios, etc.) may also provide good time-markers allowing sedimentation rates to be evaluated.

The region of the Sepetiba Bay is particularly suitable for a comparison between the model approaches. It has experienced fast growth rates of urbanisation and industrialisation in the last decades. Agriculture has been replaced by industrial development since the 1960s. Freshwater input into the bay has been changed by transposition of waters from an external watershed into the bay (the Paraíba do Sul River), and a large harbour was constructed in the early 1970s. Population flows to the region became high, increasing from 600,000 to 1.2 million inhabitants during the last three decades, and the bay has suffered serious damage due to high pollutant discharge from the industrial park (Barcellos and Lacerda, 1994; Mendes and Moreira, 1976; Watts, 1990).

In the present study, we aim to validate the ^{210}Pb-derived chronology with stable lead isotopes and heavy metals profiles recorded in sediments of the Sepetiba Bay. A particular attention will be given to Zn and Cd, since the history of their emissions into the bay is well established. Eventual discrepancies between the ^{210}Pb-dating and other chronostratigraphical markers will be evaluated in terms of possible changes in the sedimentation pattern.

2. Methods

2.1. Study area

Sepetiba Bay is a semi-enclosed body of water separated from the ocean by a beach barrier and is located approximately 60 km W from Rio de Janeiro City (23°S, 44°W) (Fig. 1). The area has a hot and humid tropical climate with an annual precipitation varying between 1500 and 2500 mm. The geology is characterised by Precambrian granitic and metamorphic rocks and the north-eastern shore is a quaternary plain. Nine rivers desembouching at the northern sector coast of the bay drain the 447 km^2 large watershed (Mendes and Moreira, 1976; Lima et al., 1997). Mean depth is about 6 m and annual freshwater input by the rivers to the bay is 7.6 million m^3, of which the São Francisco Channel contributes to about 86%. Since 1950, the São Francisco Channel transports water from the upper part of the Paraíba do Sul River to Sepetiba Bay (Watts, 1990). Water circulation in the bay is controlled by tides and hydrodynamics features engender a preferential deposition area along the northern coast, that characterises this area as a strong geochemical barrier for continental contaminants (Sugio et al., 1979; Waserman et al., 1991). There are about 400 industries in Sepetiba Bay that can be grouped into pyrometallurgic (including two large steel plants and a Cd–Zn smelter), aluminium plants, and thermal power plants (FEEMA, 1980; FEEMA-FUNDREM, 1977). This industrial park is responsible for the input of large amounts of heavy metals into the surrounding environments, reaching the coast by
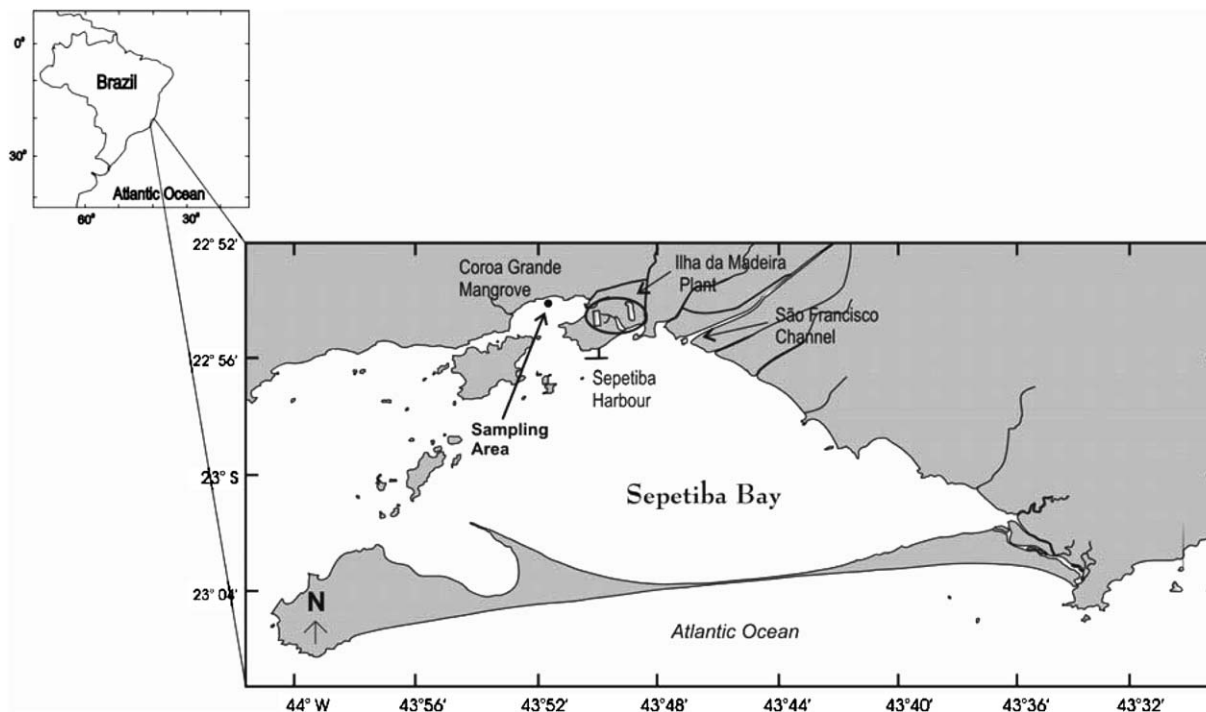
Fig. 1. Sepetiba Bay area and sampling site at Coroa Grande mangrove.

riverine transport (Watts, 1990), industrial waste runoff (Barcellos et al., 1991a; Marins et al., 1996) and atmospheric deposition (Pedlowski et al., 1991; Silva Filho, 1997). Among these metals, cadmium and zinc represents the most serious contaminants of the bay. The metallurgical industry contributes with 24 t y^{-1} of Cd and 3360 t y^{-1} Zn; whose magnitude is about three times of pre-industrial fluxes (Barcellos and Lacerda, 1994; Barcellos et al., 1991a), so that sediments and biota have been highly contaminated (Carvalho et al., 1991, 1993; Lacerda et al., 1987b; Wasserman et al., 2001). The industrial park is concentrated near São Francisco Channel and releases its effluents 3 km upstream of the channel mouth, providing therefore a single-point source discharge (Lacerda et al., 1987a). One of the principal sources is the Ilha da Madeira plant (Fig. 1), which started operating in 1960 with zinc and later, during the early 70s, with cadmium. The treated ore is mostly calamine—$(ZnOH)_2SiO_3$—and willemite—$(ZnMn)_2SiO_4$. Since 1980, when the dam was completed, the contaminated waste release reduced, but occasional storm events may still wash out some material to the bay.

2.2. Sampling

Sediment sampling was carried out during 1995 in the Coroa Grande mangrove, located in the vicinity of Ilha da Madeira plant (Fig. 1). Samples were collected at 0.1 m in water depth during low tide with a 1 m PVC tube (inside diameter 10 cm) in the tidal flat in front of the mangrove. Special care was taken during sampling in order to keep undisturbed upper sediment layer. The sediment core was immediately sliced in thin sections (3 cm each) with a plastic cutter. Sub-samples were transported to the laboratory in polyethylene bags and stored in a freezer.

2.3. Sample extraction and analysis

Sediments were dried at 40–50 °C to minimise loss of volatile elements and then crushed in an agate mortar. 0.5 g of dried sediments were digested with an acid mixture (2 ml HNO_3 + 6 ml HCl + 2 ml HF) heated during 6 h under pressure. Then, a mixture of 1 ml HNO_3 and 3 ml HCl was added and heated for 3 h. Blanks and sediment reference material (Estuarine sediment—NIST 1646a) were included to each five batch of samples. The extracts were made up to 25 ml with distilled water and heavy metal concentrations were determined using a Varian Espectra AA-300 Atomic Absorption Spectrophotometer. Precision of this analysis, as indicated by relative standard deviations of replicates, was less than 8% for both Zn and Cd. Detection limits were about 0.05 µg g^{-1} for Cd and 0.03 µg g^{-1} for Zn. Measurements of NIST 1646a did not differ from certified values for more than ±18% for Cd and about ±1% for Zn.

After total dissolution with a mixture of HCl, HNO_3 and HF, lead was purified using anion exchange resins Bio-Rad AG-1X4 following the conventional technique. Lead isotopic abundances were then measured using a Thermal Ionisation Mass Spectrometer VG SECTOR (Monna et al., 2000). Results were corrected for mass fractionation by systematic NBS 981 measurements before each series of analyses, yielding a value of 1.2‰/amu. Blank corrections were never required. Most of the isotopic

ratios are measured with a precision better than 1.4‰ for $^{206}Pb/^{204}Pb$ and better than 0.8‰ for $^{206}Pb/^{207}Pb$.

^{210}Pb activity was evaluated by measuring the activity of ^{210}Po ($t_{1/2} = 138$ d) assumed to be at secular radioactive equilibrium. It has also been assumed that the supported ^{210}Pb (in situ produced) was in equilibrium with its antecedent ^{230}Th. About 500 mg of dried sediment were therefore spiked with 0.25 Bq of ^{208}Po ($t_{1/2} = 2.93$ years) and 0.25 Bq of ^{229}Th ($t_{1/2} = 7340$ years), heated with $HNO_3:HCl$ (conc.) at 70 °C, and then digested during 5 h by heating with $HNO_3:HF:HClO_4$ (conc.) under pressure (Bojanowski et al., 1983). After this, HCl 8 N:$HClO_4$ (conc.) was added, and samples were carefully heated to almost dryness. This operation was made twice. The residue was redissolved with 10–15 ml of HCl 2 N, 2 ml of 20% (w/v) sodium citrate solution was added and pH was adjusted to 1.5–2.0 with drops of ammonia solution (33% w/w). Thereafter, the solution was heated (60 °C) and 1 g of solid ascorbic acid and water were added to obtain a final volume of 25–30 ml. Polonium was spontaneously deposited on silver disks (2 cm diameter) with a holder developed to fit 40 ml glass tubes. Plating was carried out in 70–75 °C during 150 min. At the end, the disc was removed, rinsed with water and ethanol and left to dry in a dessicator (Flynn, 1980; Smith and Hamilton, 1984). The remaining solution was heated to almost dryness, dissolved with $HNO_3:HClO_4$, heated again to almost dryness and finally redissolved with HNO_3 8 N. Thorium was separated from this solution by ion chromatography, using the anion exchange resin Dowex AG-1X8 (200–400 mesh resin), previously conditioned with HNO_3 8 N, and HCl 6 N was used for elution (Bojanowski et al., 1983; Marques Jr., 1996). Thorium isotopes were electrodeposited onto a disk of stainless steel (2 cm diameter) with 2 A current during 1 h and using sulphuric acid as an electrolyte at pH 2.1–2.4 (Hallstadius, 1984; Tomé and Sánchez, 1990). Polonium and thorium isotope activities were counted in a EG&G-ORTEC α-spectrometer 576 A with silicon barrier detectors coupled to a multichannel analyser. Detection efficiency of the system was about 30% and backgrounds were 3.1×10^{-4} and 1.4×10^{-4} counts/s, respectively for the regions of Po and Th spikes. Polonium activities were calculated taking into account decay corrections for ^{210}Po and ^{208}Po. Overall chemical yields of ^{210}Po and ^{230}Th were >90% and >70% as determined by ^{208}Po and ^{229}Th recovery checks. The propagated counting errors for ^{210}Po and ^{230}Th was approximately <7% and 6%, respectively.

3. Results and discussion

3.1. Heavy metals and stable lead isotopes

Zn and Cd concentration profiles in the Coroa Grande core are marked by a downward decrease (Fig. 2). Similar pattern have already been reported for these elements in other areas of the bay, with enrichments reaching up to 26 times for Zn, and 6 times for Cd with respect to pre-
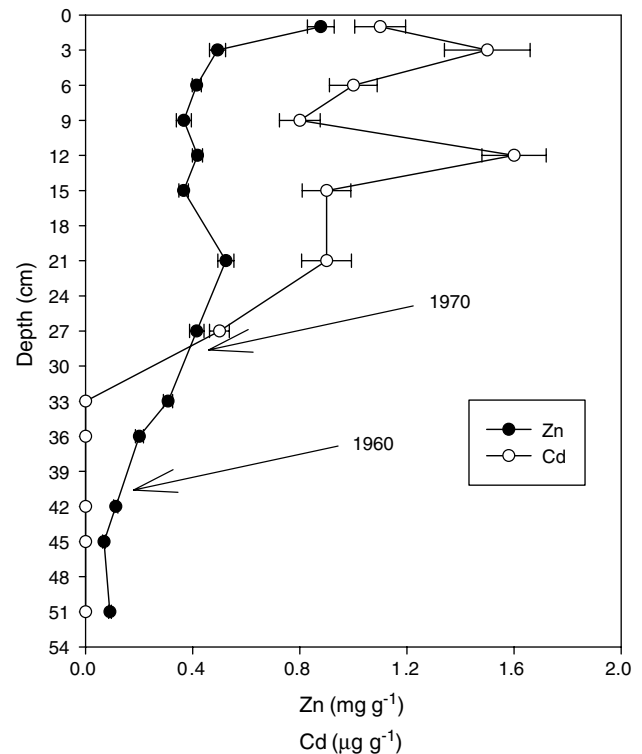

Fig. 2. Vertical profiles of Zn and Cd in the Coroa Grande core (note the values of pre-industrial levels). Values are means (±SD) of triplicate analysis.

industrial values (Barcellos et al., 1991b; Lima et al., 1997; Wasserman et al., 2001). In the present core, industrial inputs are clearly observed from 40 cm and 30 cm depth upwards for Zn and Cd, respectively. Metal averages were significantly (t, $p < 0.05$) lower below these layers, distinguishing two different phases of contamination history, i.e., pre-industrial and industrial periods recorded in the core (Table 1).

Under pristine conditions, lead isotopic ratios of lagoon sediments are supposed to reflect the isotopic compositions of the drainage basin rocks, but if lead inputs originating from anthropogenic activities (industrial lead or alkyl lead additives to gasoline) occur, they tend to disturb these "natural signatures" (Ferrand et al., 1999; Monna et al., 1995; Veron et al., 1999; Walraven et al., 1997). Our results revealed a remarkable change in the $^{206}Pb/^{207}Pb$ ratios

Table 1
Average concentrations of zinc and cadmium in Coroa Grande profile showing significant differences (t, $p < 0.05$) between pre- and post-industrial values

Coroa Grande profile	Zn (µg g^{-1})	Cd (µg g^{-1})
Full core (0–51 cm depth)	358	0.64
	69–878	<0.2–1.6
Post-industrial levels (0–33 cm depth)	438	1.0
	201–878	0.5–1.5
Pre-industrial levels (33–51 cm depth)	91	<0.2
	69–103	

Table 2
Lead isotopic ratios in the sediments of the Coroa Grande core

Depth (cm)	$^{206}Pb/^{204}Pb$	2σ	$^{206}Pb/^{207}Pb$	2σ
0	18.547	0.004	1.1838	0.0001
3	18.459	0.009	1.1780	0.0001
6	18.433	0.004	1.1774	0.0001
9	18.464	0.004	1.1787	0.0002
12	18.451	0.005	1.1765	0.0001
15	18.504	0.007	1.1818	0.0001
21	18.651	0.004	1.1898	0.0001
27	18.543	0.007	1.1836	0.0001
30	18.496	0.008	1.1802	0.0001
36	18.504	0.007	1.1805	0.0001
39	18.709	0.004	1.1927	0.0001
42	18.491	0.004	1.1803	0.0001
45	18.380	0.003	1.1735	0.0001
51	18.203	0.003	1.1616	0.0001

The errors represent the 95% confidence level.

from about 1.16 to about 1.18 between 40 and 50 cm depth, and the ratio remained steady up to the surface of the core (Table 2 and Fig. 3). Such lead isotopic signatures can be compared to those measured in another core collected in Maricá Lagoon (Fig. 4), an area devoid of industrial pollution sources located 30 km East of Rio de Janeiro (Fernex et al., 1992), with similarities in the drainage basin geological matrix. In a $^{206}Pb/^{204}Pb$ vs. $^{206}Pb/^{207}Pb$ diagram, a first group, including almost all Maricá's sediments and the deepest Sepetiba sample, appears to be rather homogeneous and characterised by low $^{206}Pb/^{204}Pb$ and $^{206}Pb/^{207}Pb$ ratios. These signatures should represent sediments resulting only from the erosion of coastal mountains (Serra do Mar), carried to the bay before the São Francisco Channel was built and the industrial park developed. The
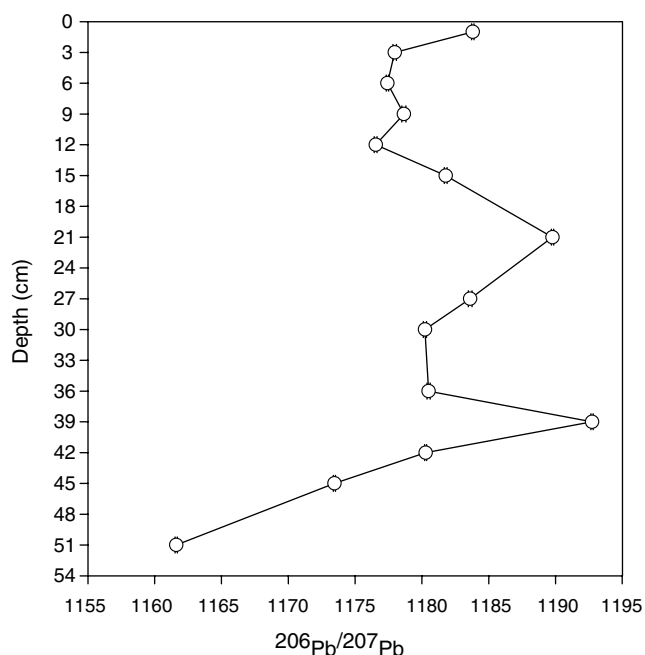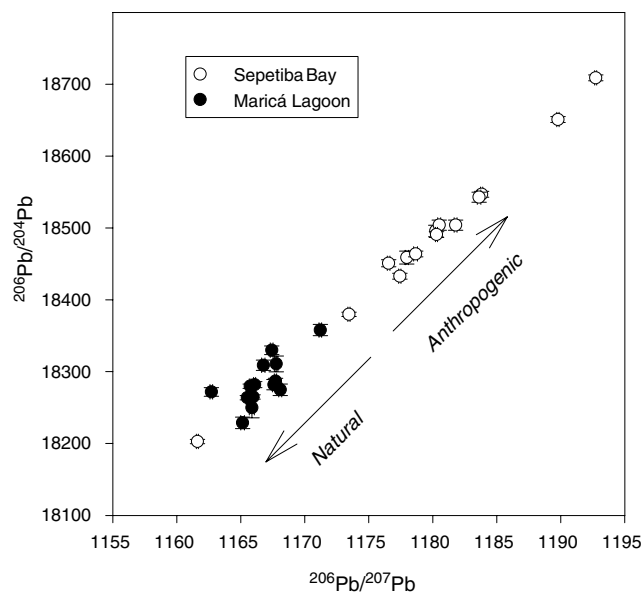

Fig. 4. Relationship between lead isotopic ratios in sediments from Sepetiba Bay and Maricá Lagoon core (a non-polluted site), showing signatures from natural to anthropogenic sources.

other samples corresponds to the most recent sediments of the Sepetiba's core. These sediments present higher $^{206}Pb/^{204}Pb$ and $^{206}Pb/^{207}Pb$ ratios. Such more radiogenic values are possibly due to anthropogenic lead inputs associated with waste effluents from metallurgic industry and/or to "allochtonous" natural sediments carried by the channel after 1950.

3.2. ^{210}Pb geochronology

Unsupported ^{210}Pb activities (^{230}Th–^{210}Po) measured in Coroa Grande core are plotted in a semi-logarithmic scatter graph (Fig. 5). ^{210}Pb profile activities decline downward into two strokes, with distinct slopes, disrupted at 16.5 cm depth. Moreover, ^{210}Pb data from the upper levels of the core (until 7.5 cm depth) do not show the expected decrease with depth and so this layer cannot be used to define a valid slope (7.5–16.5 cm depth). These upper level results are lower than profile data usually reported for estuarine sediments (Fernex et al., 1992; San Miguel et al., 2004) and may be due to mixing processes of underlying layers by bioturbation, which has already been observed in this area (Forte, 1996; Smoak and Patchineelam, 1999). Since these upper values did not correspond to the real initial concentration, they were disregarded for evaluation of the sedimentation rates. Thus, we assigned the depth of 7.5 cm to represent the $^{210}Pb_{exc}(0)$ of the core and assumed activity decline only due to radioactivity decay for layers below this depth, allowing the determination of sedimentation rate. In a similar way, we must keep in mind that as soon as particulates contaminated by Cd or Zn reached the bottom, bioturbation led underlying layers to be contaminated till the depth of 7.5 cm. This mixing zone was taken into account
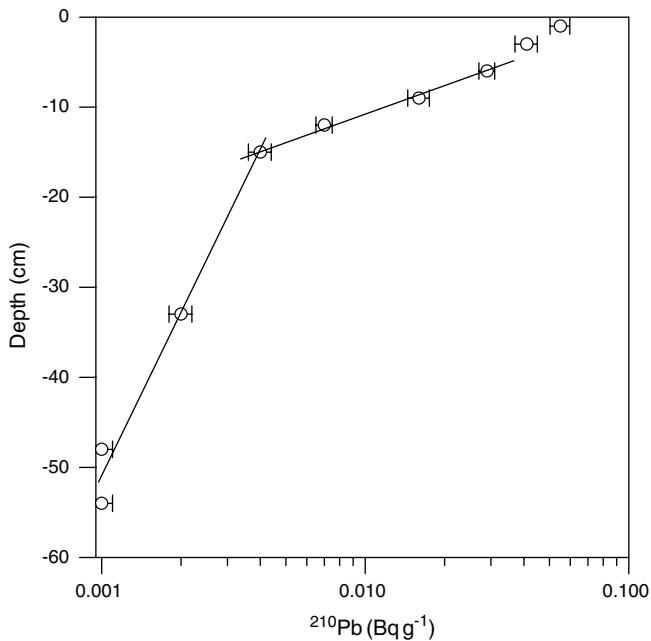

Fig. 3. Vertical profile of the $^{206}Pb/^{207}Pb$ ratio in Coroa Grande core.

Fig. 5. Vertical profile of the unsupported ^{210}Pb (^{210}Pb–^{230}Th activities) in Coroa Grande sediments.

to correct the contamination beginning date and determine pollutant inventories.

Using the CIC model with these assumptions, the average sedimentation rate in the upper part of the core calculated from the ^{210}Pb activity values between 7.5 and 16.5 cm is 0.13 cm year^{-1}. The deposition of the layer at 16.5 cm would therefore have occurred 82 years before the sampling, i.e., during 1913. Downward in the core, the sedimentation rate would have been approximately 0.7 cm year^{-1}. Assuming the mixing zone of 7 cm below the interface, Cd contamination beginning corresponds to 24.5 cm depth (31.5–7 cm), and the interval between 24.5 cm and 16.5 cm (=8 cm) lasted 11 years (8/0.7). The age derived from the model for the Cd contamination beginning is (82 + 11) 93 years, corresponding to 1902. Using the same approach for Zn (43.5–7 cm = 36.5 cm), we determine the age of Zn contamination beginning would be 29 + 82 years = 111 years, i.e., 1884.

The calculation with CRS model needs ^{210}Pb inventory I to be known, as well as the inventory I_z below the considered level. Taken into account the water content, the inventory is $I = 0.16$ Bq/cm^2. The partial inventory for I_{Cd} (at 24.5 cm) is 0.14 Bq/cm^2, and for I_{Zn} (at 36.5 cm) is 0.15 Bq/cm^2. In such a way, the Zn contamination would have started in 1925, while Cd contamination beginning would have started in 1935.

Neither the CIC nor the CRS models resulted in dating estimations that correspond to the history of industrialisation in the area. The Zn ore treatment plant was installed in 1960 and the Cd in the early 70s. The discrepancies between the sedimentation rates obtained by dating models and the assessment of the metal profiles deserves a discussion. It is rather common to see published articles that use ^{210}Pb as a geochronometer with little regard if dating assumptions are really met. Besides, interpretation of contaminant profiles without the previous knowledge of the deposition dynamics often become impossible to establish a definitive chronology. A single protocol for acceptance of papers using ^{210}Pb geochronology was proposed in recent years, i.e., the validation with at least one independent tracer providing unambiguous time horizon (Smith, 2001). In the case of Sepetiba Bay, we consider that contaminant historical records, like channel and dam building as well as the beginning of industrial activities, provided independent time-marks. These time-marks can be associated with changes in sedimentation conditions at the Coroa Grande site that has also local depositional constraints.

The core was sampled at low tide, at 10 cm below the sea level and near the Zn–Cd industrial plant. When contamination started in the area, the ancient layers (from 43.5 to 31.5 cm) were at the water–sediment interface and probably covered by a water column of 30–40 cm. During this period, sedimentation should have been largely controlled by lateral transport of material from neighbouring littoral zones. It would be expected that, more recently, sediment accretion, with the progressive evolution of the system, in particular the water depth decline, has been more and more controlled by settling particles brought by smooth runoff from the mangrove flat bank. We suppose that these particles originating from the bank surface have been relatively rich in atmospheric ^{210}Pb. This should have resulted in progressive increase of ^{210}Pb concentration in the near shore sediments.

Applying this principle for ^{210}Pb supply, we stated an alternative approach to calculate sedimentation rate. In such modelling, the ^{210}Pb distribution is characterised by initial concentration increase, and a constant sedimentation rate is assumed. In the studied core, the profile displays two very different sediment accumulation rates (upon and below 16.5 cm), and therefore we have to consider the upper and lower parts separately. We assume that initial activity ($A_{0,t}$) increases exponentially in the course of time (t). The relationship between the initial concentration at the top level and that at a layer deposited t years before is

$$A_{0,t} = A_{0,0} \mathrm{e}^{-kt} \qquad (6)$$

where $A_{0,0}$ = initial ^{210}Pb$_{exc}$ activity (Bq g^{-1}) in the top level (to be determined by least-square fitting); k = standardisation coefficient allowing the calculated exponential curve to be fitted to the experimental profile.

The ^{210}Pb$_{exc}$ activity at a defined time interval (A_{tz}) is determined as

$$A_{tz} = (A_{0,0}\mathrm{e}^{-kt})\mathrm{e}^{-\lambda t} = (A_{0,0}\mathrm{e}^{-(k+\lambda)t}) \qquad (7)$$

where λ = ^{210}Pb decay constant (0.0311 year^{-1}).

Using this model for the layers between 7.5 and 16.5 cm, i.e., for 9 cm, we can approximate the value at 7.5 cm to be 0.03 Bq g^{-1}, which corresponds to $A_{0,0}$. A very low value (3 10^{-4} Bq g^{-1}) can be assumed for greater depth (25 cm).

The exponential curve that best fits the measured profile gives $(k + \lambda) = 0.17$, and 11.6 years for 9 cm. Thus, the sedimentation rate in the upper part of the profile is approximately 0.8 cm y^{-1}. The great modification in the sediment accumulation rate, at 16.5 cm, would have occurred 12 or 14 years before sampling, that is 1981–1983. In fact we ascertain a slight discrepancy, since it was in 1980 that the dam was built to prevent most of the ore wastes to be released to the bay.

The same procedure was used for the deeper part of the core, the "new top" level is at 16.5 cm. Taking into account the unsupported ^{210}Pb activity at 34.5 cm ($2 \ 10^{-3}$ Bq g^{-1}), we obtained $A_{0,0} = 0.24$; $K = 0.05$, and 17.5 years for (34.5–16.5) cm. The sedimentation rate for the deeper part was 1.03 cm y^{-1}.

By this way, referring to the metal profiles and taking into account 7 cm sediment as a mixing layer, we obtained the following contaminant chronologies: (a) Cd pollution starts in 24–26 cm, reaching an age of 19–22 years that corresponds to 1973–1976; (b) Zn pollution starts in 35–39 cm with an age of 32–36 years that corresponds to 1959–1963. These age estimations are in agreement with the historical industrial phases at the Ilha da Madeira plant.

4. Conclusions

Four successive historical events are marked in the sediment core at Coroa Grande. The first one at about 50 cm, indicated by Pb isotopic signature changes, probably corresponds to São Francisco Channel opening (1950) that allowed input of material from geological systems outcropping in the Northwest of the Rio de Janeiro State. The second and the third events, recorded in slices approximately at 40 and 30 cm depth, showed increases of Zn and Cd concentrations, respectively. Finally, we observed a change in the unsupported ^{210}Pb slope, which would be associated to building of the dam that prevents industrial waste input to the Bay.

Both "classical" models, CIC or CRS, did not allow time evaluations for the beginning of the Zn and Cd contamination to the sediment layers that corresponds to the starting dates of Zn and Cd ore treatment operations in Coroa Grande. Moreover, the use of these models assign ages for the change of Pb isotopic ratios that are pretty older than the date of São Francisco Channel opening. As the sampling site is very shallow, bordering on a large mangrove flat bank, it has been assumed that the ^{210}Pb initial concentration has exponentially increased in the course of time. This approach allowed a good age estimation of four successive events, as they were recorded in the near shore sediment profile.

Acknowledgements

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