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LEAD, NITROGEN AND CARBON STABLE ISOTOPES IN THE SEDIMENTS OF BABITONGA BAY, BRAZIL: AN OIL SPILL CASE

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The hydrological complex of Babitonga Bay, Brazil, forms a vast environmental system; hosting the last great expanse of mangrove forests in the southern hemisphere. Mangroves are among the most productive ecosystems on earth. Effects of an oil spill on the Babitonga Bay ecosystem was studied using lead and carbon isotopes. Samples of the spilled oil, as well as sediment and water samples, were obtained nine months after the accident, at the time of the salvage operation. Isotopic composition of the oil was utilized to trace the extent of the environmental pollution. In addition, isotopes of lead and carbon allowed for the identification of areas where oil was present. Contaminated sediments exhibited an isotopic composition ($^{206}Pb/^{207}Pb$ *and* $^{208}Pb/^{206}Pb$*) close to that of the oil spilled.* $\delta 13C$ *data confirmed these results. The results of this investigation suggest that lead isotope ratios can be very useful in the field of environmental forensics.*

INTRODUCTION

Brazil is experiencing fast economic growth. This growth includes an increase in both production and transportation of raw materials and finished products. Brazilian harbors are located in estuaries, which are highly susceptible to changes in the ecosystem caused by increased economic production. Estuaries and bays are very important ecosystems both as a source of food production, and for recreational, aesthetic and cultural purposes (Barros et al., 2010). Despite their importance, these areas are heavily impacted by contaminants from many different sources. Estuaries and bays constitute natural reaction zones in which heterogeneous processes may affect the ecological equilibrium due to local changes in the biogeochemical conditions. In addition to natural sources, anthropogenic inputs provide significant contributions to these areas. In Babitonga Bay (BB), Brazil, several factors cause sediment pollution (CREMER et al., 2006); the major players being: (i) activities at São Francisco do Sul Harbour, (ii) inadequately treated domestic sewage, (iii) industrial activity at Joinville, and (iv) other contamination transport from tributaries (Barros Grace et al., 2008, Barros et al., 2010, Vaz et al., 2010). Estuarine systems are characterized by large amounts of organic matter, therefore the composition of stable carbon and nitrogen isotopes is useful in estuarine studies as a technique for understanding processes (Barros et al., 2010, Dehairs et al., 2000, Carreira et al., 2002, Graham et al., 2001, Goñi et al., 2003). The composition of stable carbon isotope is a useful tracer in estuarine studies as terrestrially derived material is isotopically lighter than marine materials when not under influence of C4 plants. Terrestrial material has $\delta^{13}C$ values between -30 and -24‰, while material of marine origin has values between -22 and -18‰. Meanwhile, $\delta^{13}C$ values of sewage effluents overlap both terrestrial and marine sources varying from -26‰ to -22‰. Due to this overlap, an additional tracer is needed to correctly separate sewage inputs from material of terrestrial or marine sources (Carreira et al., 2002). One possibility is $\delta^{15}N$, which may be able to distinguish between sewage inputs and other sources (e.g. Hansson et al., 1997).

The interpretation of isotope ratios can be complicated by the fact that material, especially bulk material, often represents mixtures of carbon from several different sources, and thus the isotope signatures reject integration from these different sources. Moreover, systems have variable inputs in space and time and it is difficult to separate the signal of multiple end-members from the effects of matter alteration and transport (Kendall and McDonnell, 1998; Dittmar et al., 2001; Gonneea et al., 2004).

In order to distinguish between anthropogenic and natural inputs, radiogenic isotopes of lead represent a potential indicator. Lead (Pb) is a natural constituent of the Earth's crust, which is commonly found in soils, plants, and water at trace levels. However, occurrence of metallic lead in nature is rare. It is a toxic heavy metal that can enter the human body through inhalation and ingestion of contaminated air and water, soil, and food (Cheng and Hu, 2010). It is also fairly immobile in the environment. This study was conducted within an environmental investigation. Especially in a forensic environmental investigation, it is important to determine the source of pollution and/or to characterize the transport history of the pollutants. Recognizing the sources of lead pollution can be difficult because of the large number of potential sources in typical urban settings. These include emissions from industries, exhaust from fuel combustion, sewage, atmospheric deposition, and even natural geological materials (bedrocks and soils). While the sources of Pb and the contribution from each source cannot be inferred from the total Pb concentrations measured in environmental media (e.g., air, water, and soil), it is possible to distinguish between natural and anthropogenic sources using Pb isotope ratios.

A shipping accident occurred in the summer of 2008 leading to a large oil spill, which impacted the BB ecosystem. A salvage operation was conducted eight months after the spill to recover the shipwreck. This operation caused further loss of oil yet provided an opportunity to collect samples of oil remaining in the holds of the ship. One month after the salvage operation, a sampling campaign was performed in order to search for residues of this spill. The major objectives of the present study, therefore, are to characterize the different isotopic compositions of carbon, nitrogen and lead in BB, and to elucidate on the origin of Pb, N and C in the sediments. Lead, nitrogen and carbon isotopic compositions were determined for bulk sediments and residues, in order to identify the different (natural or anthropogenic) inputs. Many studies have shown correlations between lead and sediments in estuarine areas, but using different approaches from those presented here. In the current case, lead was chosen as an additional tracer to identify the origin of the oil, as the isotopic composition of Pb is not significantly affected by physico-chemical fractionation processes (Komárek et al., 2008).

SITE DESCRIPTION

The hydrological complex of Babitonga Bay (BB) is located 45 km northeast from the city of Joinville, which is the principal (capital) city of Santa Catarina State (Southern Brazil), Figure 1. The drainage basin of the bay consists of a vast environmental complex, where agriculture and shellfish farming as well as a variety of industries, coexist with a unique natural area of Brazilian rain forest. Babitonga Bay, which houses the largest expanse of mangrove forests left in the southern hemisphere, is connected to the Atlantic Ocean via an inlet with a width of 1850 m and is characterized as a salt-wedge estuary. Tides are mixed, semidiurnal with a mean range of 1,80 m (Schettini and Carvalho, 1996). This oscillation is very important for the flushing of the entire system. The region is characterized by a humid subtropical climate with an average rainfall of 2000 mm/year. There are two seasons: summer (from November to April) and winter (from May to October). During summer the weather is characterized by high temperature and humidity, with intense precipitation caused by local convection processes strictly controlled by the regional orography. During winter the influence of polar air-masses leads to a decrease in both temperature and precipitation.

The complex encompasses two main basins: Cubatão and Cachoeira. The largest stream discharging into the BB is the Cubatão River, which has a drainage basin of 483.8 km^2 and a length of more than 75 km. Its source is located in the Serra do Mar at an altitude of 1300 m. The mean discharge at the mouth of the river is 17.7 m^3/s but is marked by rapid fluctuations due to intense precipitation events on the steep slopes of the Serra do Mar. In addition to being used as a public water supply, Cubatão waters are also withdrawn for industrial and agricultural purposes (IBAMA, 1998). The Cachoeira River basin (84.82 km^2) is located entirely within the urbanized area of Joinville, and flows into the Saguaçu Lagoon. Its hydraulic head is located at an altitude of 40 m, with a mean riverbed elevation of about 10 m. The mouth is characterized by estuarine circulation and is home to residual mangrove forests. There are little data concerning the Cachoeira River discharge; however it is believed to range from 3 to 5 m^3/s. Water quality is very poor, mainly due to the input of mostly untreated domestic and industrial effluents. Heavy loading of untreated wastes leads to very low concentrations of dissolved oxygen observed in this river. Two other relatively pristine rivers discharge into BB. The Palmital River basin drains an area of 357.60 km^2 and the Parati River drains an area of 72.20 km^2: their estuaries receive contributions from several streams, all of which are influenced by tides and heavily forested with mangroves.

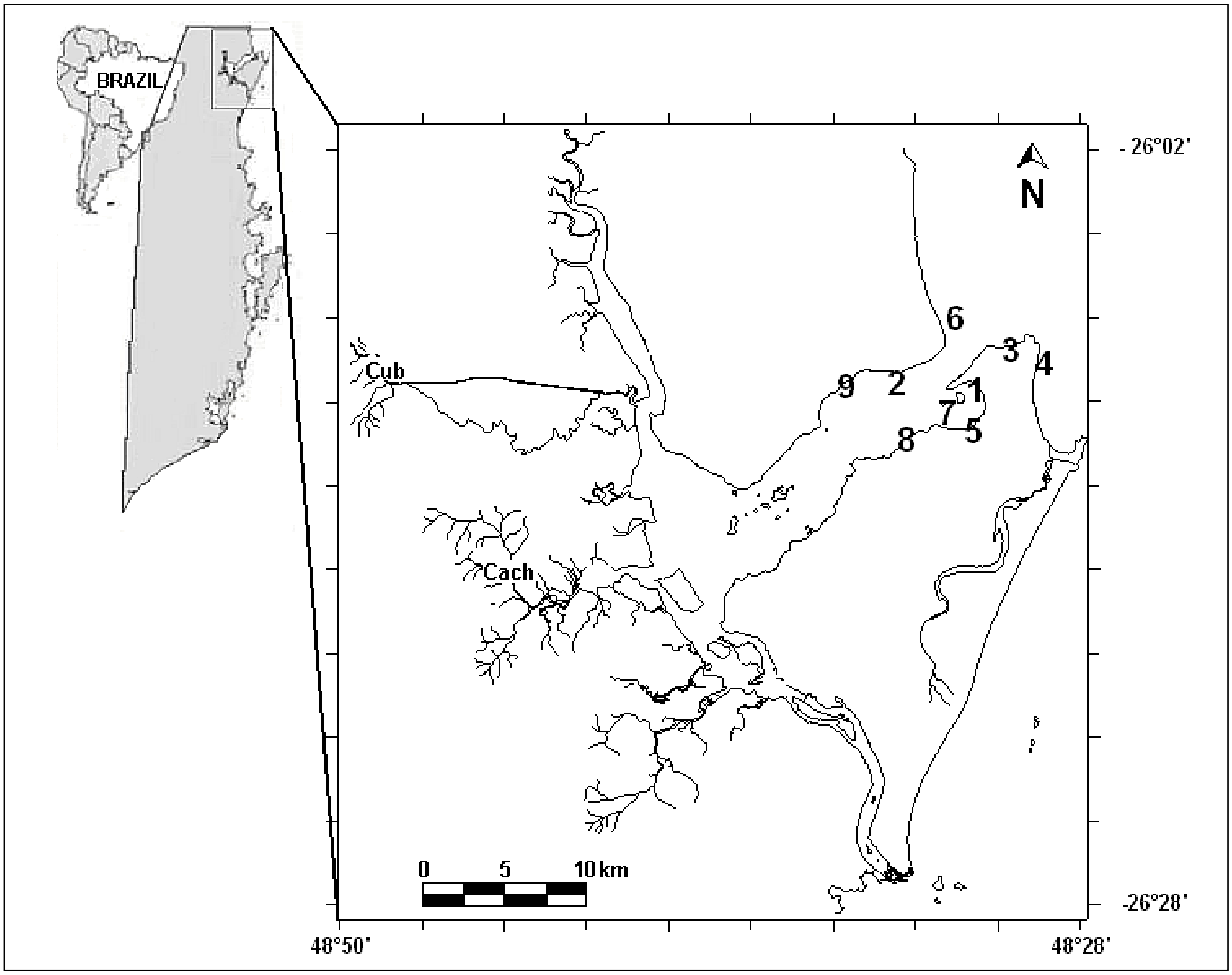

Figure 1. Babitonga Bay respect to Brazil and sample points.

GEOLOGICAL CONTEXT

Santa Catarina Granulite Complex - SCGC

The high-grade terranes in Southern Brazil are most visible in the SCGC, with an exposed area of about 6,000 km^2 (Hartmann et al., 1979). The complex is unique in that it was not internally impacted by thermal effects or by ductile deformations during the orogenesis of the Neoproterozoic Brasiliano cycle. However, it was impacted by the intrusion of Brasiliano granites. The Santa Catarina Granulite Complex is the oldest tectonic unit in the Catarinense Shield (Guadagnin et al., 2010). This complex is composed of tonalitic, granodioritic, and trondhjemitic orthogneisses interspersed with mafic and ultramafic rocks. Metasedimentary rocks such as quartzites and banded iron formations are also present, albeit to a lesser extent. The first mantle–crust differentiation of the Santa Catarina Granulite Complex is of Archean age (2.8 Ga (TDM model age)). Meanwhile, tectonic stabilization occurred in the Paleoproterozoic (1.9 Ga (K-Ar in biotite)). The Santa Catarina Granulite Complex metamorphosed into a granulite facies during two events. The first event occurred at 2675±12 Ma, and the second event occurred at 2168±18Ma (U-Pb SHRIMP) when the magmatic protoliths crystallized at 2716±17Ma (Hartmann, et al. 2000). Hartman et al. 2000, interpreted the Santa Catarina Granulite Complex as a stable craton after 1.9 Ga, and the complex remained an undeformed block during the orogenesis of the Brasiliano/Pan-African Cycle (Luis Alves Microplate).

MATERIALS AND METHODS

Sampling was authorized by public prosecutor (PP) nine months after the oil spill. A preliminary campaign, also authorized by the PP, was performed one month before the main investigation. This initial campaign took place when the salvage operation was conducted, in order to collect three samples of the oil, which remained trapped for 8 months inside the hull of the capsized ship. The salvage operation led to further loss of oil inside the bay. Sample sites were chosen as a function of the oil slicks that were formed after the spill. Samples collected at these sites were analyzed by Centro de Pesquisas Geocronológicas - University of São Paulo – USP (Pb isotopes) and Centro de Energia Nuclear na Agricultura – University of São Paulo – USP (C isotopes). BB bottom sediment samples were collected from the upper 15 cm of the benthic layer with a Petit Ponar sediment grab and sealed immediately. Beach sands from the upper 15 cm were collected with a plastic grab and sealed immediately. Within BB organic matter and mud are the dominant sediment fractions, while beaches were mainly composed of sand.

In order to complete the Pb isotopic analysis, each sample was washed ultrasonically in triple distilled water before chemical degradation. The sediment was completely dissolved using 3 ml of 6 N HCl plus 2ml of HNO_3 with a Parr® Teflon® bomb and then further dissolved in 2 ml of 0.7 N HBr. The sample was then passed through an ion exchange column filled with Dowex 1X8 AG anion exchange resin. After treatment within the column, the solutions were evaporated and the remaining residues were further dissolved in 0.7 N HBr and passed again through the same (Dowex 1X8 AG) ion exchange column as described above. Pb was separated using HBr+HCl chemistry in Dowex 1X8 AG ion exchange resin. Lead was loaded onto a Re ribbon, using silica gel plus H_3PO_4 and analyzed by a fully automated VG 354 Micromass multicollector thermal ionization mass spectrometer. Analyses using the "National Bureau of Standards" standard NBS 981 yielded mass discrimination and fractionation corrections of 1.0024 ($^{206}Pb/^{204}Pb$), 1.0038 ($^{207}Pb/^{204}Pb$) and 1.0051 ($^{208}Pb/^{204}Pb$); the combination of these uncertainties and within-run uncertainties are typically 0.15%–0.48% for $^{206}Pb/^{204}Pb$, 0.13%–1.07% for $^{207}Pb/^{204}Pb$ and 0.10%–0.45% for $^{208}Pb/^{204}Pb$, all at the 2ó (95%) confidence level. The total Pb blank contribution, <1 ng, is negligible. Classical Pb concentration in sediments and sands were performed using inductively coupled plasma - atomic emission spectrometry (ICP-AES), following USEPA 6010C.

Samples for carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotopic compositions in sediments and sands were initially washed with 0.1 N HCl to eliminate carbonates or shell fragments. Isotope ratios were determined in organic samples by the combustion of a known mass of the glass fiber filters in an Elemental Analyser (Carlo Erba EA 1400) in line with the mass spectrometer (Finnigan Mat Delta Plus). Results are expressed in ‰V-PDB and Atmospheric Nitrogen standards (Gonfiantini, 1978, 1995). Analytical errors are: 0.3‰ for $\delta^{13}C$ and 0.5‰ for $\delta^{15}N$. The analytical precision values were obtained based on duplicate measurements of internal calibrated standards used at the laboratory as well as samples from the present study (Gonfiantini et al., 1995).

RESULTS AND DISCUSSION

The samples analyzed represent the surface layer of the sedimentary pile at the sites (Figure 1). Pb, N and C isotopic composition was determined in nine samples chosen by the public prosecutor, and are presented in Table 1. Pb concentration is presented in Table 2.

Lead

BB has a history of contamination by heavy metals (Cremer et al., 2006, Vaz et al., 2010, de Oliveira et al., 2010), previous work found lead concentrations to be high in BB sediments (Cremer et al., 2006, Ahmed and Häder, 2010). Table 1 presents Pb concentration at the sites sampled.

Table 1. Lead concentration (mg/kg) in BB sediments.

Site	Pb (mg/kg)
1	1.28
2	2.32
3	1.9
4	1.2
5	1.98
6	1.94
7	0.99
8	1.35
9	1.89

Differences between Pb from the oil spill and other sources of Pb were determined through the investigation of Pb isotope composition. Important isotopic differences are observed between samples from the ships' hold and the natural background (Figure 2). Pb isotopic composition tends to be more radiogenic (high ^{206}Pb/^{207}Pb ratio) in BB sediments, which mimics the composition of the oil collected inside the ship. It is important to note that BB is strongly impacted by the disposal of raw sewage, but the impact of this effluent is only apparent in the inner part of the bay (Barros et al., 2010). Samples in this investigation were collected towards the mouth and therefore should not be influenced by raw sewage. The system indicates a simple binary mixing of geogenic with anthropogenic Pb.

A different behavior can be observed among leachate and the residual phase of samples. Leachate presents a Pb isotopic composition, which is, in general, more radiogenic (^{206}Pb/^{207}Pb ratio between 1.1465 and 1.1824) than the residual phase (^{206}Pb/^{207}Pb ratio between 1.1052 and

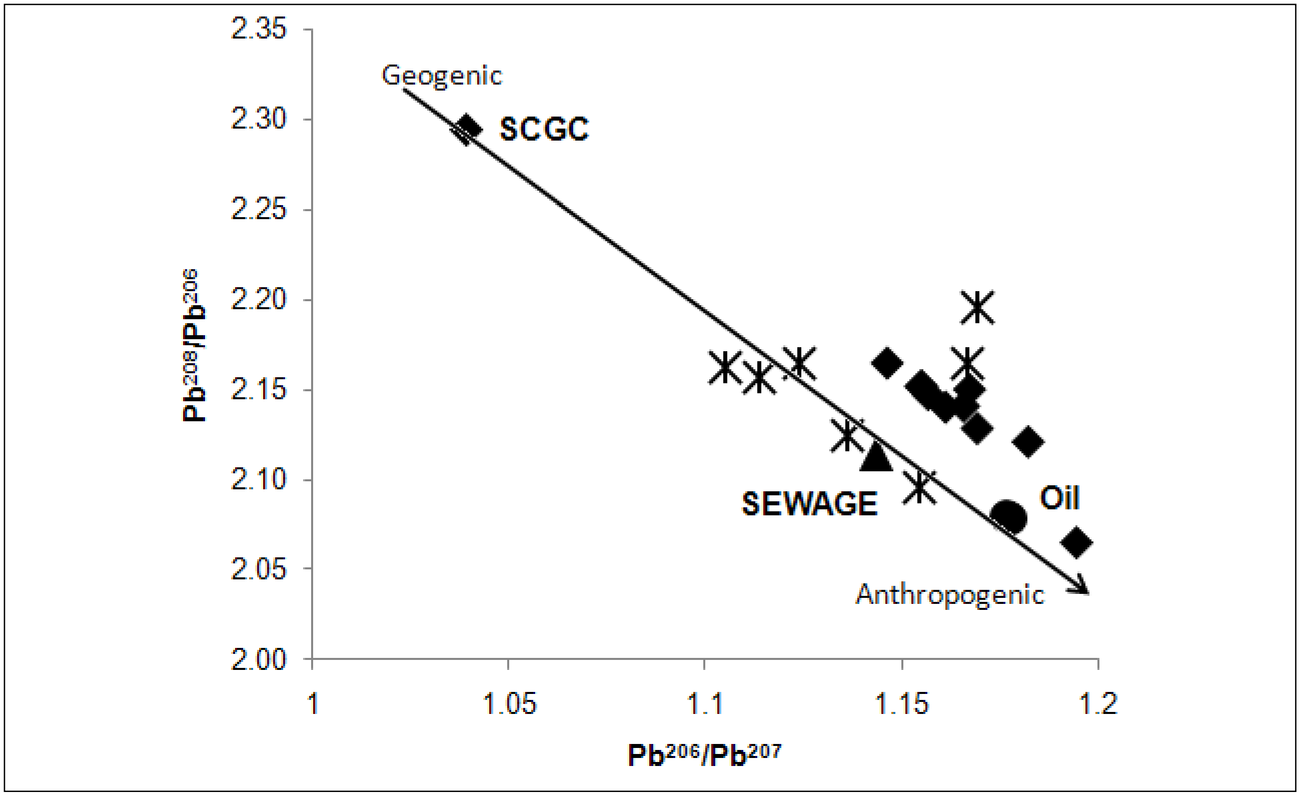

Figure 2. Isotopic differences between samples from the ships' hold and the natural background showing a mixing line.

1.1546). This shows that sediments at sample points are affected by an important anthropogenic input (oil sample presented ^{206}Pb/^{207}Pb ratio 1.1766). Meanwhile, in the leachate, no important anthropogenic contribution, such as sewage, was observed. A large amount of the anthropogenic lead added to sediment is most likely leached from the residue by dilute acid (Chow et al., 1973, Shirahata et al., 1980, Kober et al., 1999). The influence of organic matter (OM) and the iron oxyhydroxide surface can originate from reasonable differences between residual and leachate (Gioia et al. 2006). Lead released from the structures of silicate minerals is isotopically distinct from lead released from other sources, demonstrating distinct lead reservoirs. BB mangrove sediments have a great amount of OM. Another area of important anthropogenic contribution is in the vicinity of the Capri Iate Club; here the ^{206}Pb/^{207}Pb value is as low as 1.1362 from the residue. In the vicinity of the Sao Francisco do Sul Harbor, it is expected that the Pb isotopic composition would be close to that of the oil.

Carbon and Nitrogen

Carbon and nitrogen were analyzed following the same method previously presented for Pb. Unfortunately, sand beaches do not have sufficient OM, and, therefore, it was not possible to detect the carbon isotopic composition due to its low concentration. However, mangrove sediments were analyzed and the results are presented in Table 2. Elemental and stable isotope analyses were used in a large number of studies to determine the spatial and temporal distribution of different sources of organic matter (allochthonous detritus and local phytoplankton) in suspended matter and sediments of estuarine systems – including BB (e.g. Cifuentes et al., 1996, Barros et al., 2010). This approach utilizes the fact that different biochemical pathways, and the degree to which carbon and nitrogen are reworked, will lead to different isotopic ratios of δ^{13}C and δ^{15}N. When the resulting stable isotope signatures of the sources are sufficiently different, it is possible to locate the sources of organic matter (Barros, 2005) found in BB sediments. δ^{13}C values range from -22.58‰ to -24.94‰. Heavier δ^{13}C values are observed at seaward sampling sites, suggesting a large contribution of marine organic matter, which is characterized by a typical mean value -21.0‰ (Fisher et al. 1998). δ^{15}N values of BB sediments range from 3.56 to 6.43‰, with enriched values observed towards the ocean. Oil isotopic composition ranges from 8.24 to 8.64‰ for δ^{15}N and from -26.31 to -24.15‰ for δ^{13}C. Sediment samples collected after the accident were marked by an isotopic composition varying from -24.69 to -2.07‰ for δ^{13}C, and from 4.22 to 10.57‰ for δ^{15}N. Just one organic matter sample matches with the oil sample. This discrepancy could be due to the time elapsed (nine months) between the accident and the fieldwork campaign. In addition several factors including tidal action alternatively exposing and submerging sample sites, two seasons (summer and autumn), and biogeochemical processes contributed to the isotopic fractionation.

CONCLUSION

Estuaries around the world are experiencing a strong loss of natural features due to recurrent acute and chronic impacts from human activities. In BB this is not different. In this case, a forensic study was conducted to point a source in an area that is undergoing constant impacts from different sources. Here, various elements have contributed to an answer in this case: previous δ^{13}C data were available, samples of the spilled oil itself were collected for analysis (after 8 months) and the ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratio variations between geogenic (natural) and oil samples were large. The use of isotopes, like Pb isotopes, which undergo little fractionation when exposed to weathering and biogeochemical processes is important and can be a valuable alternative, or

Table 2. Isotopic compositions of BB sediments and oil samples. L is for leachate and R for residue. Numbers in samples S1, S2, etc are sample points, Figure 1.

Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	Error % (1σ)	$^{207}\text{Pb}/^{204}\text{Pb}$	Error % (1σ)	$^{208}\text{Pb}/^{204}\text{Pb}$	Error % (1σ)	$^{206}\text{Pb}/^{207}\text{Pb}$	Error % (1σ)	$^{208}\text{Pb}/^{206}\text{Pb}$	Error % (1σ)	^{15}N	^{13}C
Oil1	18.654	0.056	15.613	0.058	38.507	0.058	1.195	0.009	2.065	0.008	8.24	-24.57
Oil2	18.347	0.225	15.595	0.223	38.152	0.226	1.177	0.021	2.080	0.013	8.59	-24.15
Oil+seaw	18.416	0.006	15.638	0.006	38.269	0.006	1.178	0.001	2.078	0.002	8.64	-26.31
S1 - L	18.345	0.007	15.688	0.007	39.040	0.007	1.169	0.002	2.128	0.002	nd	nd
S1 - Res	17.783	0.023	15.650	0.025	37.762	0.024	1.136	0.004	2.124	0.002		
S2 - L	17.981	0.008	15.684	0.009	38.918	0.011	1.147	0.002	2.165	0.004	4.22	-24.69
S2 - Res	17.475	0.006	15.544	0.006	37.835	0.006	1.124	0.001	2.165	0.002		
S3 - L	18.333	0.016	15.704	0.017	39.411	0.02	1.167	0.005	2.150	0.009	nd	nd
S3 - Res	22.893	0.004	16.284	0.005	42.810	0.005	1.406	0.001	1.870	0.002		
S4 - L	18.225	0.01	15.692	0.011	38.996	0.012	1.161	0.002	2.140	0.003	nd	nd
S4 - Res	17.468	0.006	15.685	0.005	37.673	0.006	1.114	0.001	2.157	0.001		
S5 - L	18.102	0.006	15.672	0.006	38.942	0.007	1.155	0.001	2.151	0.001	4.92	-21.71
S5 - Res	18.312	0.005	15.695	0.005	39.620	0.005	1.167	0.001	2.164	0.001		
S6 - L	18.566	0.016	15.702	0.015	39.370	0.017	1.182	0.003	2.121	0.002	nd	nd
S6 - Res	18.343	0.01	15.688	0.01	40.276	0.01	1.169	0.002	2.196	0.001		
S7 - L	18.132	0.054	15.696	0.05	39.023	0.053	1.155	0.006	2.152	0.007	10.57	-10.73
S7 - Res	17.310	0.056	15.662	0.056	37.414	0.057	1.105	0.006	2.162	0.005		
S8 - L	18.276	0.056	15.674	0.056	39.115	0.057	1.166	0.004	2.141	0.005	nd	nd
S8 - Res	18.113	0.025	15.686	0.024	37.954	0.024	1.155	0.004	2.096	0.003		
S9 - L	18.163	0.088	15.706	0.096	39.009	0.101	1.157	0.009	2.147	0.012	9.95	-2.07
S9 - Res	19.230	0.023	15.797	0.025	38.369	0.025	1.217	0.005	1.995	0.004		

complement, to carbon isotopes. Despite a relatively complex process, the use of combined isotopes tracers allowed for the possibility to spot areas where the spilled oil could be identified.

Pb isotopic compositions in Pb-containing products (e.g., gasoline, leaded pesticides, and leaded paints) depend only on the source ores; ores from different parts of the world often have their own Pb isotope signatures, which are preserved during transport over vast distances and transfer processes. Therefore, from the ratios of the isotope concentrations of ^{208}Pb, ^{207}Pb, and ^{206}Pb detected in a sample, it is possible to pinpoint the source of Pb by matching the Pb isotopic composition found at the contamination site with those of the potential sources. It is also possible to apportion the contributions of the major sources based on their Pb isotopic compositions in cases where lead pollution has resulted from multiple sources (Cheng and Hu, 2010). This study is just an example of the possibility of using Pb isotopes to trace those responsible for environmental damage.

REFERENCES

Barros G.V., Martinelli L.A., Oliveira N.T.M., Ometto J.P., Zuppi G.M. 2010. Stable isotopes of bulk organic matter to trace carbon and nitrogen dynamics in an estuarine ecosystem in Babitonga Bay (Santa Catarina, Brazil) Science of The Total Environm;408:2226-2232.

Barros V.G., Study and monitoring of biogeochemical process of Babitonga Bay catchment—Brazil, using chemical and isotopes approaches. 2005. PhD Thesis, University of Ca' Foscari di Venezia, Venice, Italy.

Barros V.G., Mas-Pla J., Oliveira T.M.N., Sacchi E, Zuppi GM. 2008. Hydrological mixing and geochemical processes characterization in na estuarine/mangrove system using environmental tracers in Babitonga Bay (Santa Catarina, Brazil). Cont Shelf Research 28:682-695.

Carreira R.S., Wagener A.R., Fileman T., Readman J., Macko S.A., Veiga A. 2002. Changes in sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay, Brazil: an elemental, isotopic and molecular marker approach. Mar Chem.79:207–227.

Chow T.J., Bruland K.W., Bertine K., Soutar A., Koide M., Goldberg E.D. 1973. Records in Southern California coastal sediments. Science 81:551–552.

Cifuentes L.A., Coffin R.B., Solorzano L., Cardenas W., Espinoza J., Tilley R.R. 1996. Isotopic and elemental variations of carbon and nitrogen in a mangrove estuary. Estuar Coast-Shelf Sci. 43:781–800.

Cremer M. (Org). 2006. Diagnóstico ambiental da Baía da Babitonga. Joinville, SC: UNIVILLE

Dehairs F., Rao R.G., Chandra Mohan P., Raman A.V., Marguillier S., Hellings L. 2000. Tracing mangrove carbon in suspended matter and aquatic fauna of the Gautami-Godavari Delta, Bay of Bengal (India). Hydrobiologia 431:225–241.

Dittmar T., Lara R.J., Kattner G. River or mangrove? 2001. Tracing major organic matter sources in tropical Brazilian coastal waters. Mar Chem. 73: 253-271.

Fisher T.R., Hagy J.D., Rochelle-Newall E. 1998. Dissolved and particulate organic carbon in Chesapeake Bay. Estuaries 21: 215-229.

Gioia S.M.C.L., Pimentel M.M., Tessler M., Dantas E.L., Campos J.E., Guimarães E.M., Maruoka M.T., Nascimento E.L. 2006. Sources of anthropogenic lead in sediments from an artificial lake in Brasília-central Brazil Science of The Total Environ 356: 125-142.

Gonfiantini R., Stichler W., Rozanski K. 1995. Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements. Reference and Intercomparison Materials for Stable Isotopes of Light Elements, IAEA-TECDOC-825. Vienna. IAEA.

Gonfiantini R. 1978. Standard for stable isotope measurement in natural compounds. Nature 217:534-536.

Goñi M.A., Teixeira M.J., Perkeya D.W. 2003. Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). Estuar Coast Shelf Sci . 57:1023–1048.

Gonneea M.E., Paytan A., Herrera-Silveira J.A. 2004. Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years. Estuar Coast Shelf Sci. 61:211-227.

Gordon E.S., Goñi M.A. 2004. Controls on the distribution and accumulation of terrigenous organic matter in sediments from the Mississippi and Atchafalaya river margin. Mar Chem. 92:331-352.

Graham M.C., Eaves M.A., Farmer J.G., Dobson J., Fallick A.E. 2001. A study of carbon and nitrogen stable isotope and elemental ratios as potential indicators of source and fate of organic matter in sediments of the Forth Estuary, Scotland. Estuar Coast Shelf Sci. 51:375–380.

Guadagnin F., Chemale Jr. F., Dussina I.A., Jelineka A.R., Santos M.N., Borba M.L., Justino D., Bertotti A.L., Alessandretti L. 2010. Depositional age and provenance of the Itajaí Basin, Santa Catarina State, Brazil: Implications for SW Gondwana correlation. Precambrian Res. 180:156-182.

Guo L.,Tanaka T.,Wang D.,Tanaka N., Murata A. 2004. Distributions, speciation and stable isotope composition of organic matter in the southeastern Bering Sea. Mar Chem. 91: 211–226.

Hansson S., Hobbie J.E., Elmgren R., Larsson U., Fry B., Johansson S. 1997. The stable nitrogen isotope ratio as a marker of food-web interactions and fish migration. Ecology 78:2249-2257.

Hartmann L.A., Santos J.O.S., Mcnaughton N.J., Vasconcellos, M.A.Z., Silva, L.C. 2000. Ion Microprobe (SHRIMP) dates complex granulite from Santa Catarina, southern Brazil. Anais da Acad Bras de Ciênc. 72:559–572.

Hartmann L.A., Silva L.C., Orlandi Filho V. 1979. O Complexo Granulitico de Santa Catarina. Descrição e implicações genéticas. Acta Geol. Leopoldensia 3: 93-112.

Hefa C., Yuanan H. 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review. Environ Poll 158: 1134–1146.

Hoda A., Häder D. 2010. Rapid ecotoxicological bioassay of nickel and cadmium using motility and photosynthetic parameters of Euglena gracilis. Environ and Exper Botany 69:68-75.

Hu J., Peng P., Jia G., Mai B., Zhang G. 2006. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. Mar Chem. 98:274–285.

IBAMA (Instituto Brasileiro do Meio Ambiente). 1998. Proteção e controle de ecossistemas costeiros: manguezal da Baia de Babitonga. Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis. Coleção meio ambiente. Série estudos – pesca. Brazil.

Kendall C., McDonnell, J.J. 1998. Isotope Tracers in Catchment Hydrology. Amsterdam: Elsevier Science.

Kober B., Wessels M., Bollho A., Mangini A. 1999. Pb isotopes in sediments of Lake Constance, central Europe constrain the heavy metal pathways and the pollution history of the catchment, the lake and the regional atmosphere. Geochim Cosmochim Acta 63(9):1293–1303.

Komárek M., Ettler V., Chrastný V., Mihaljeviè M. 2008. Lead isotopes in environmental sciences: A review. Environ Intern. 34:562–577.

Maksymowska D., Richard P., Piekarek-Jankowska H., Riera P. 2000. Chemical and Isotopic Composition of the Organic Matter Sources in the Gulf of Gdansk (Southern Baltic Sea). Estuar Coast Shelf Sci. 51:585-598.

Oliveira C. R. Speciation of butyltin derivatives in surface sediments of three southern Brazilian harbours. 2010. Journal of Hazardous Materials 81:851-856.

Schettini C.A.F., Carvalho J.L.B., Jabor P. 1996. Comparative hydrology and suspended matter distribution of four estuaries in Santa Catarina State – Southern Brazil. Proceedings of Workshop on Comparative Studies of Temperate Coast Estuaries 29-32.

Shirahata H., Elias R.W., Patterson C.C., Koide M. 1980. Chronological variations in concentrations and isotope compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond. Geochim Cosmochim Acta 44:149–162.

Thornton S.F., McManus J. 1994. Applications of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. Estuar Coast Shelf Sci 38:219–233.

Vaz C., Oliveira T.M.N., Böhm R.F.S., Spitzner EC, Simm M., Barros V.G. 2010. Use of Artemia salina to identify sites with risk of contamination in the waters of Babitonga Bay. Toxicology Letters 196:S120.

Voss M., Liskowa I., Pastuszak M., Rüâ D., Schultec U., Dippnera J.W. 2005. Riverine discharge into a coastal bay: A stable isotope study in the Gulf of Gdan´sk, Baltic Sea. J Mar Syst. 57:127–145.

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