



Baseline

Evaluation of metals and hydrocarbons in sediments from a tropical tidal flat estuary of Southern Brazil



Eduardo S. Costa^{a,*}, Caroline F. Grilo^a, George A. Wolff^b, Anu Thompson^b, Rubens Cesar Lopes Figueira^c, Renato Rodrigues Neto^a

^a Departamento de Oceanografia e Ecologia, Universidade Federal do Espírito Santo, Brazil

^b School of Environmental Sciences, University of Liverpool, United Kingdom

^c Instituto Oceanográfico, Universidade de São Paulo, Brazil

ARTICLE INFO

Article history:

Available online 16 December 2014

Keywords:

Transition metals

n-alkanes

Terpanes

Isotopes

Estuary

ABSTRACT

Although the Passagem Channel estuary, Espírito Santo State, Brazil, is located in an urbanized and industrialized region, it has a large mangrove system. Here we examined natural and anthropogenic inputs that may influence trace metal (Cd, Cr, Cu, Ni, Sc, Pb and Zn) and hydrocarbon (*n*-alkane and terpane) deposition in three sediment cores collected in the tidal flat zone of the estuary. The cores were also analyzed for carbonate, grain size and stable isotopic composition ($\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{total}}$). Metal enrichment and its association to petroleum hydrocarbons in the surficial sediments of one of the cores, indicate crude oil and derivative inputs, possibly from small vessels and road run-off from local heavy automobile traffic. At the landward sites, the major contributions for metals and hydrocarbons are from natural sources, but in one case, Cu may have been enriched by domestic effluent inputs.

© 2014 Elsevier Ltd. All rights reserved.

Studies of many estuarine systems have shown that the rise in human activities near these ecosystems can lead to the accumulation of contaminants in the sediment (Jones and Turki, 1997; Binning and Baird, 2001; Lee and Cundy, 2001; Bahena-Manjarrez et al., 2002; Rosales-Hoz et al., 2003). In parts of Brazil, the anthropogenic contribution of metals and oils to estuarine sediments has been reported by several authors (Carvalho et al., 1999; Carreira et al., 2002; Machado et al., 2004; Monteiro et al., 2012; Silva et al., 2013). Nevertheless, little is known about the degree of contamination of estuarine sediments in Espírito Santo state. Grilo et al. (2013) analyzed triterpenoids, $C_{\text{org}}/N_{\text{total}}$ ratios, sedimentation rates and total organic carbon (TOC) contents in sediments from Passagem Channel estuary (Espírito Santo State, Brazil) and found a strong terrestrial influence in the sedimentary organic composition and contamination by fecal compounds. Due to the intense urbanization and industrialization of this region (Grilo et al., 2013), human activities may also contribute to metal and petrogenic compounds accumulation, resulting in degradation of water quality. The present study aims to evaluating the trace metals, hydrocarbons (*n*-alkanes and hopanes) concentrations,

calcium carbonate (CaCO_3) and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ stable isotopic composition of the same sediment cores as those analyzed by Grilo et al. (2013). Furthermore, the various urban sources of contaminants inputs to the estuary are discussed.

Three hypotheses are tested in this study: (a) the study area accumulates contaminant metals and hydrocarbons. (b) The contaminants arise from activities associated with the use of oil and its derivatives. (c) Sewage is also an important source of metals.

The sediment cores sampling was performed as described in Grilo et al. (2013). Briefly, three sediment cores, each ca. 50 cm long, were collected with a push corer at Passage Channel tidal flats on March 2008 during ebb tide. All cores were frozen ($-20\text{ }^\circ\text{C}$) and then sliced at 1 cm intervals from the top to 3 cm depth, then at 2 cm down to 11 cm depth and finally at 5 cm down to 50 cm depth. Samples were then freeze-dried and stored ($-20\text{ }^\circ\text{C}$) until analysis.

For the metal analysis, the sediment samples were processed following the SW 846 US EPA 3050B (USEPA, 1996) method. Thus, dried and homogenized sediment ($\approx 1\text{ g}$) was digested with nitric acid (10 mL; 1:1, v:v) at $95\text{ }^\circ\text{C}$ for 15 min. The solution was then cooled and a further aliquot of nitric acid (5 mL) added and the mixture heated again at $95\text{ }^\circ\text{C}$ for 30 min. Another aliquot (5 mL) of nitric acid was then added to ensure that the sample was oxidized. The solution was then evaporated (to 5 mL) and cooled; ultrapure water ($\text{Milli-Q; } 18.2\text{ M}\Omega\text{ cm}^{-1}$) and 30% hydrogen

* Corresponding author.

E-mail addresses: eduoceano@gmail.com (E.S. Costa), carolinegrilo@gmail.com (C.F. Grilo), wolff@liverpool.ac.uk (G.A. Wolff), anu@liverpool.ac.uk (A. Thompson), rfigueira@usp.br (R.C.L. Figueira), rrneto@gmail.com (R.R. Neto).

Table 1
CRM SS-2 metal concentration and standard deviation.

Metal	Consensus value (ppm)	Confidence interval (ppm)	Tolerance interval (ppm)	Analyzed value (ppm)	SD %
Zn	467	444–490	337–597	438.04	0
Cd	2	–	–	2.07	0.34
Sc	–	–	–	4.87	0.10
Ni	54	50–58	33–75	46.45	0.36
Cu	191	182–200	139–243	170.00	0.27
Cr	34	30–38	14–54	33.19	0.42
Pb	126	116–136	68–184	98.10	0.59

– Not analyzed.

peroxide (3 mL) was then added with heating. The procedure was repeated by adding further hydrogen peroxide (1 mL) to remove all organic matter. The final solution was filtered using a qualitative filter paper followed by the dilution with 100 mL ultrapure water (Milli-Q; $18.2 \text{ M}\Omega \text{ cm}^{-1}$) in a volumetric flask. The solution was analyzed by Optical Emission Spectrometry with Inductively Plasma Coupled (ICP-OES) according SW 846 US EPA 6010C methodology (USEPA, 2013). The following metals were analyzed: cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), scandium (Sc) and zinc (Zn). The method was certified using the SS-2 certified reference material (CRM – EnviroMAT™) using the same digestion method as for the samples. The CRM metal concentrations and standard deviations are shown in Table 1.

Sediment samples taken for the analysis of hydrocarbons were freeze dried (72 h; -40°C ; 10^{-2} Torr). The dried samples were stored at -20°C until required for extraction. All glassware were washed and heated in a muffle furnace (400°C ; 12 h) while chemicals were purified prior to analysis. The solvents were analytical grade (HPLC, Sigma–Aldrich), and were distilled before use.

A subsample of dry sediment ($\approx 0.6 \text{ g}$) was extracted in a centrifuge tube using a mixture of dichloromethane (DCM):methanol (ratio 9:1, v:v), and $10 \mu\text{L}$ of $5\alpha(\text{H})$ -cholestane ($101 \text{ ng } \mu\text{L}^{-1}$) as internal standard. Activated copper was added to each sample to remove elemental sulfur.

The sample was extracted in a sonication bath (SONICOR SC – 220TH; 50–60 Hz; 30 min.), then centrifuged (Jouan MR23; 15 min, 3000 rpm) and the supernatant transferred to a volumetric flask with the aid of a Pasteur pipette. The whole procedure was

performed three times for the efficient extraction of hydrocarbons from the sediment, and the extracts of each batch combined into one flask for each sample. The solvent was concentrated (to $\approx 1 \text{ mL}$) using a rotary evaporator (Büchi RE111). Residual solvent was removed under a gentle flow of nitrogen. The extracts were separated into two fractions (polar and apolar) using a column of silica gel (0.5 g; 70–230 mesh; 3% deactivated with water), topped up with alumina (Al_2O_3). The hydrocarbon fraction (apolar) was eluted with 4 mL of hexane while the polar fraction was eluted using dichloromethane:methanol (2 mL, 1:1, v:v).

The apolar fraction was dissolved in hexane and analyzed using a Trace 2000 Series gas chromatograph (on-column injector; fused silica capillary column (Agilent J & W DB-5MS, 60 m, 0.25 mm, $0.1 \mu\text{m}$) coupled with a ThermoQuest Finnigan TSQ-7000 mass spectrometer. The oven temperature was initially held at 60°C for 1 min, then heated to 170°C at 6°C min^{-1} and from 170°C to 315°C at $2.5^\circ\text{C min}^{-1}$ and then held for 12 min at 315°C . Helium was used as the carrier gas at a flow rate of 1.2 mL min^{-1} . The MS was operated in “full-scan” mode scanning a mass range from between 50 and 600 Thompsons every second with an ionization energy of 70 eV. The ion source temperature used was 215°C and the interface between the GC and MS was heated to 320°C .

The compounds were identified by comparison of their mass spectra and relative retention times to those available in the literature. In the case of the *n*-alkanes, these were monitoring using the ions m/z 57, 71 and 85 while m/z 191 was used for monitoring the terpanes. Quantitative data were obtained by comparing the peak areas of the internal standard with the compounds of interest (in

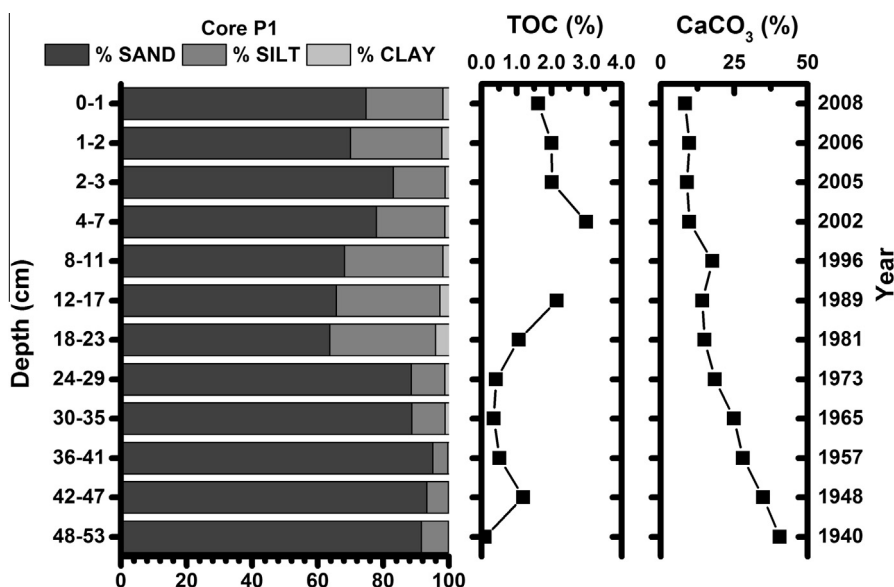


Fig. 1. Vertical distribution of sand, silt, clay, TOC, CaCO_3 and sediment ^{210}Pb date (Grilo et al., 2013) in core P1.

Download English Version:

<https://daneshyari.com/en/article/6357496>

Download Persian Version:

<https://daneshyari.com/article/6357496>

[Daneshyari.com](https://daneshyari.com)