

EVALUATION OF CONTAMINATION BY POTENTIALLY TOXIC ELEMENTS (PTE) OF SEDIMENTS AROUND THE PETROLEUM TERMINAL PIPELINE “DUTOS E TERMINAIS DO CENTRO SUL (DTCS)”, SP, BRAZIL

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Abstract

The Petroleum Terminal Pipeline “Dutos e Terminais do Centro Sul (DTCS)” is one of the largest petroleum terminals in Brazil. To assess wastewater treatment efficiency of the DTCS and to evaluate the contamination by potentially toxic elements (PTE) of sediments, ten sampling points were studied near the riser output of the submarine outfall in the summer of 2005, 2006 and 2007, and ten sampling points were studied along the São Sebastião Channel (CSS). All data were above the standards required by the Brazilian salt water/brackish Water Directives (CONAMA Resolution 454/2012). However, the sediments near the submarine outfall were enriched by As and Cu, with concentrations exceeding the threshold effect

level (TEL). In 2005 and 2006, the concentrations of Ba, Sr, Ni and Pb exceeded the values established by TEL in some places. Concentrations of As were 69 times higher than that measured in the background station. In 2007, all the analyzed metals almost doubled the concentrations of that found in 2005. High concentrations of PTE in the sediments, namely Ba and As, are a source of contamination that should be considered for the water quality management planning of the DTCS system.

Keywords: Potentially Toxic Elements. Sediments. Submarine Outfall. Petrochemical Effluents.

1. Introduction

Industries, refineries and oil terminals generate several types of solid wastes and effluents, which release large amount of polycyclic aromatic hydrocarbons (PAHs), phenols, surfactants, sulfides, naphthalenic acids and metals (U.S. EPA, 1996). Among metals, Pb, Cd, Cu, Hg, Zn, Cr and Ni are industrial contaminants that require greater environmental control because they are toxic and can be bioaccumulative (Cook, 1977; Haque et al., 1982; Tchounwou et al., 2012).

In Brazil, for a long time, there was no concern in the characterization of industrial effluents and assess their impacts on the marine environment. However, current

Brazilian regulation requires that industries treat their effluents before being discharged, as well as control their discharge (CONAMA Resolution 454/2012). In general, petrochemical effluents undergo a series of physical, chemical and biological processes for the treatment and disposal of petroleum waste and its derivatives (naphtha and diesel) (Beccari and Romano, 2006). These processes occur at Sewage Treatment Stations (ETE), usually installed in the industries.

Despite all wastewater treatment and emission control procedures, it is essential that environmental control agencies carry out rigorous environmental monitoring in

areas where industrial effluents are disposed (CONAMA Resolution 454/2012). However, this does not always occur and when some type of monitoring is performed, it is limited to the analysis of water and industrial effluents. In turn, these analytical results represent only a snapshot of water quality at the time of collection. Therefore, clandestine and discontinued discharges may not be detected by water monitoring and do not allow assessing the emissions impact (Rodrigues Filho, 2002). In addition, surface water monitoring is limited only to the detection of water-soluble elements, which does not define the overall quality of the aquatic environment. For the assessment of an aquatic environment health as a whole, it is also necessary to evaluate the sediment quality (Batley and Simpson, 2013).

Due to the growing number of submarine outfalls deployed in the 1990s, the Companhia de Tecnologia de Saneamento Ambiental (CETESB; Environmental Sanitation Technology Company), a Government Environmental Agency of São Paulo State, began monitoring the waters surrounding the outfalls in this state coast, in 2002 (Duleba et al., 2007). In 2004, sediment sampling campaigns were initiated by an agreement between CETESB and the Geosciences Institute of São Paulo University (Duleba et al., 2007). The present work is part of these surveys carried out by CETESB during the summers of 2005, 2006 and 2007. It aims to evaluate the contamination of sediments by Potentially Toxic Elements (PTE), in the vicinity of an oil refinery, the “Dutos e Terminais do Centro Sul – DTCS” (South Central Oil Pipeline and Outfall - DTCS), and along São Sebastião Channel, São Paulo State, SE Brazil.

2. Study Area

São Sebastião Channel (CSS), with 25 km long, is located between the latitudes 23°40' S and 23°53.5' S and longitudes 45°19' and 45°30' W and separates the mainland from the São Sebastião island. It has variable width, 2 km in its central portion and 7 km in its southern and northern entrances. Its axis, with the deepest depths (30 to 50 m), is displaced to the insular side due to erosion and / or structural geological conditioning. The lowest depths (6 m) occur at the continental side of the channel. The southern and northern entrances have 25 and 20 m depths, respectively, as shown in Fig. 1.

Almeida et al. (1981) inserts the São Sebastião region into the tectonic domain called Joinville Massif, located southeast of the Cubatão fault. This region of the São Paulo coast is cut by the current fault of Bertioga-Caraguatatuba, with direction SW-NE. This fault delimits the São Sebastião Block of the Ubatuba Block, and their tectonic formation is responsible for the establishment of Serra do Mar (a mountain chain) and the relief of the north coast of São Paulo.

According to Garda and Schorscher (1996), São Sebastião Block is formed by migmatites of the Coastal Complex, which contain a metabasic nuclei, surrounded by agmatitic migmatites, amphibolite intercalations and a small body of granitoid rocks. Next to the Bertioga-Caraguatatuba fault, these rocks are cataclased in varying intensity, with bands of protomylonites, mylonites and ultramylonites. São Sebastião Block is also cut by many dikes of basic and ultrabasic rocks (Garda and Schorscher, 1996).

São Sebastião island has genesis linked to alkaline volcanic activity and reactivation of pre-existing faults that occurred in southeastern Brazil at the end of the Cretaceous, represented by the Serra do Mar uplift and Santos Basin subsidence (Almeida, 1976). São Sebastião island, originated from these magmatic events, would be a remnant structure formed from the erosive retreat suffered by Serra do Mar (mountain) (Almeida, 1976).

The CSS was installed in a geological weakness area, depleted and prone to erosion, between São Sebastião Island and Serra do Juqueriquerê (mountain) (Garda and Schorscher, 1996). This channel is oriented according to general structures of the area (SW-NE). It was shaped by the abatement of blocks resulting from the Serra do Mar fault systems.

According to Almeida (1976), the CSS would have been excavated during the last Pleistocene glacial phases. However, Mahiques et al. (1989) attributed the elongated and deep depressions present inside the CSS to tidal excavation processes that occurred during the Holocene transgressive event, the maximum of which occurred at ≈ 5 kyrs BP. Along the CSS, gneiss and alkaline rocks outcrop (CPRM, 2005). Fig. 2 illustrates the main lithological units found in the study area.

Sediment distribution along the CSS is conditioned by geometry, bottom topography and local circulation (Furtado et al., 2008). The geometry of this channel, more specifically its curvature, resembles a fluvial channel, presenting depositional (continental side) and erosive (insular side) margins. The bottom topography of this channel is extremely irregular, with large variations in small space, producing a patching distribution of sediment grain size (Furtado, 1995; Barcellos and Furtado, 1999, 2001; Furtado et al., 2008).

In CSS, there are some areas where the anthropic influence is noticeable (Teodoro et al., 2011; Duleba et al., 2018), which include the central region of the channel, where one of the largest Brazilian petroleum terminal pipeline, known as “Dutos e Terminais do Centro Sul - DTCS” or Almirante Barroso Terminal (TEBAR), of the Brazilian Oil Company Petrobras (Companhia de Petróleo Brasileiro SA) is installed. DTCS serves as an importer and storage for oil and oil products.

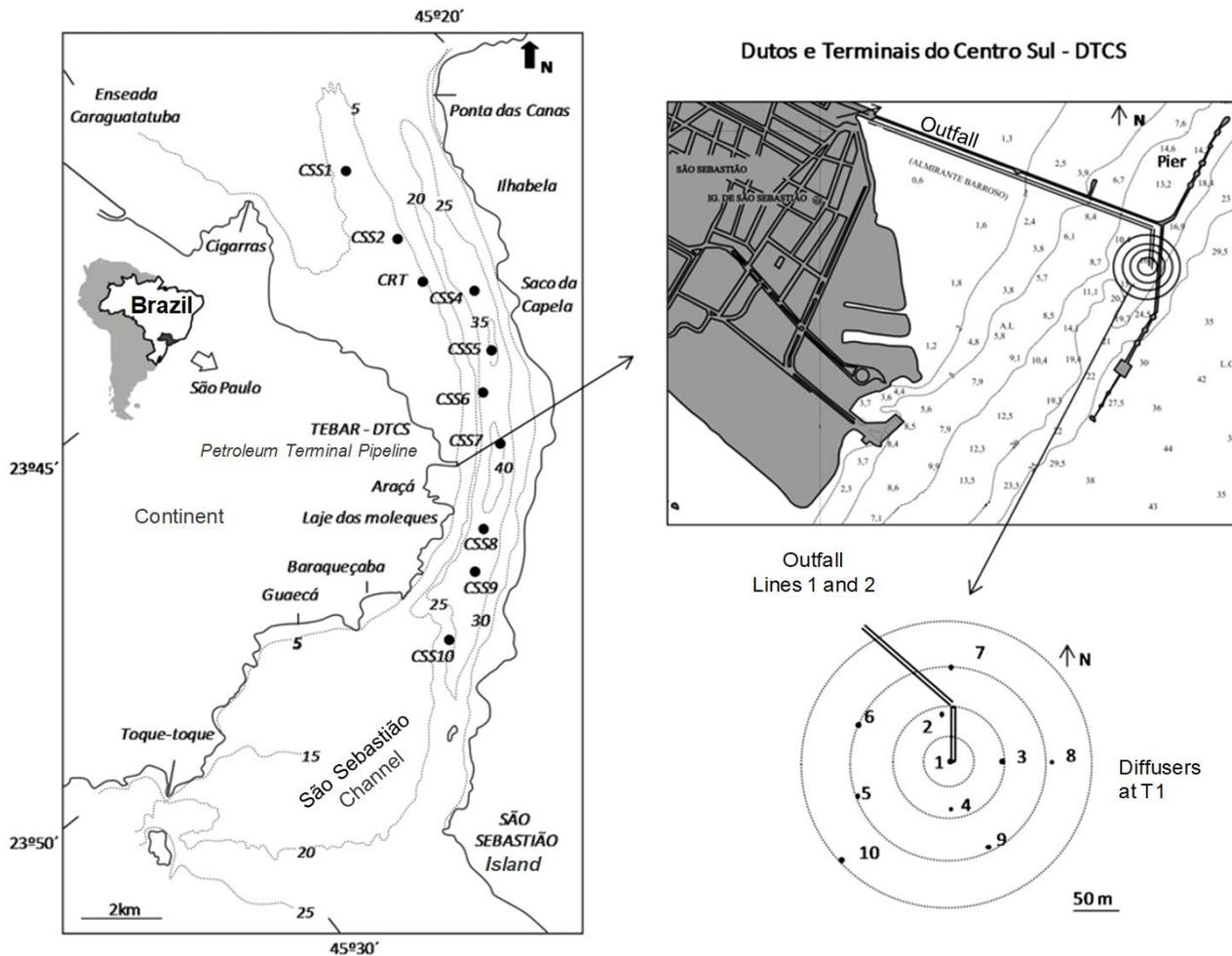


Fig. 1. Sampling sites collected along the São Sebastião Channel (CSS) and around the “Dutos e Terminais do Centro Sul” - DTCS (South Central Oil Pipeline and outfall - DTCS).

The DTCS terminal receives, stores and transfers oil for further treatment in refineries located in São Paulo State interior. In addition, the DTCS transfer crude for exportation and supply other national refineries. The terminal consists of an oil pipeline that connects a set of 40 storage tanks (on land) to two platforms located in the middle of the CSS (1 km from the coast) (Fig. 1).

The DTCS outfall, made of high-density polyethylene (HDPE), has 3 km long. It is divided into two parallel lines (1.6 km and 1.4 km long; Fig. 1). At the end of each outfall, there is a diffuser section with three vertical pipes facing the surface, each one with 1.5 m long and 0.15 m diameter. The maximum outflow of this outfall is $0.208 \text{ m}^3 \text{ s}^{-1}$ (Duleba et al., 2018).

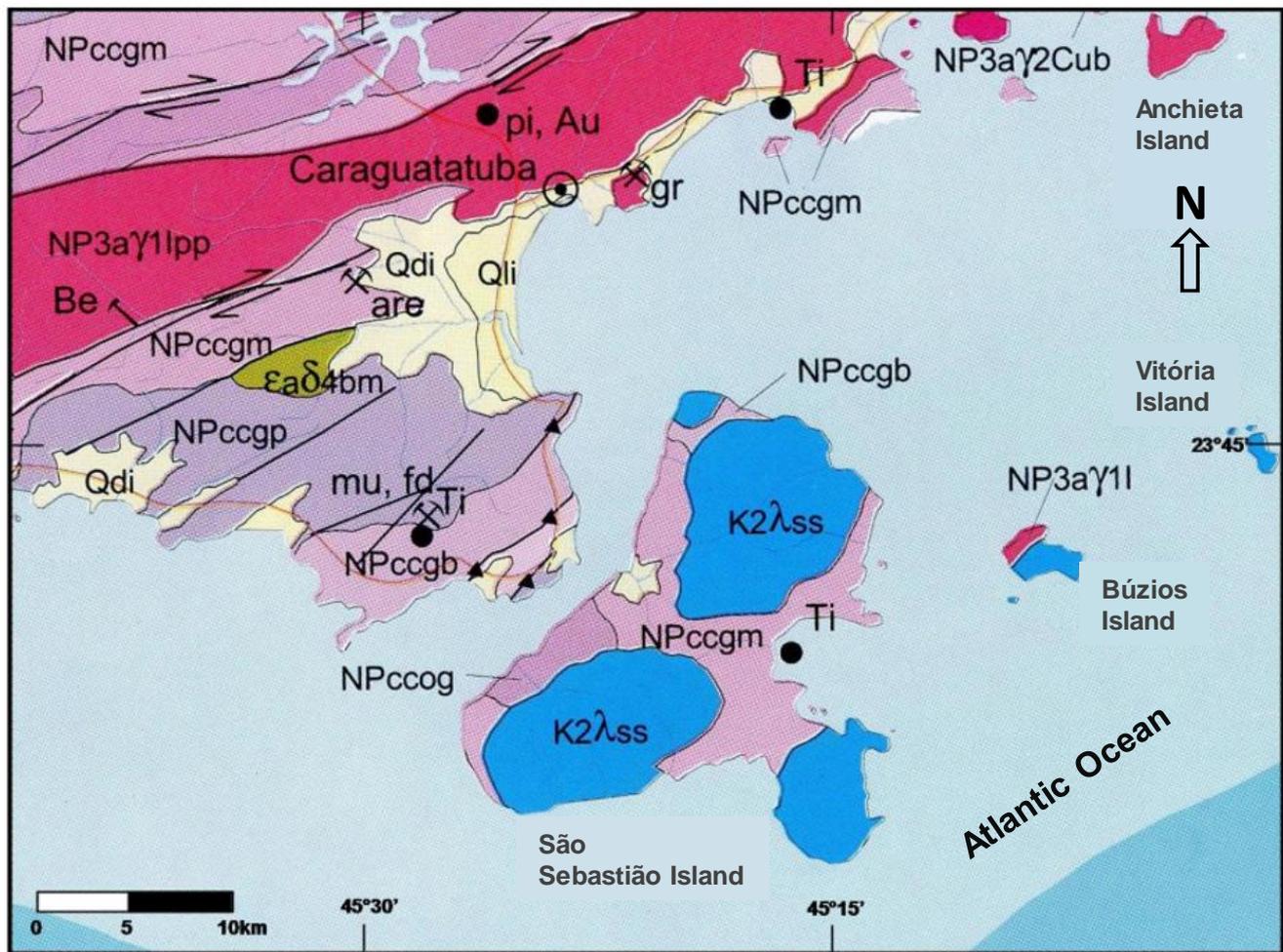
3. Materials and Methods

A sample grid of concentric circles spaced every 50 m (Fig. 1) was used, which allowed to cover the area under the direct influence of the effluent disposal. In this sampling pattern, sediment samples were collected from 10 locations:

one near the diffusers and nine at a progressively longer distance from the diffusers. Sampling events were carried out during the summers of 2005, 2006 and 2007. Also, ten other sampling stations (called CSS), located far from the emissary launch site and distributed along the São Sebastião Channel (CSS), were selected. The station CSS3-CRT was chosen as a background reference (Fig. 1).

The location of the sampling stations was obtained by GPS (Global Positioning System). Hydrographic and hydrochemical data from the water column (surface, half height and near the bottom) were acquired at each sampling station, such as depth, temperature, salinity and dissolved oxygen, obtained by using a CTD Seacat probe. A Petersen open top grab sampler was used to collect sediments for particle size and geochemical analysis.

The particle size analyzes were performed using the screening and pipetting techniques described according to Suguio (1973). Sediment classification was based on Shepard (1954) ternary diagrams, based on the results obtained by the percentages of sand, silt and clay in the samples.



Legend

- CENOZOIC**
-  Qdi – Undifferentiated detrital cover: unconsolidated sand, silt, clay and gravel. Qli - Undifferentiated coastal deposits: sand, silt and clay.
- MESOZOIC**
-  K2λss – Alkaline plutonic complexes (São Sebastião) - nordmarkite, at the edges of stocks, syenite, locally nepheline.
- PALEOZOIC**
-  εαδ4bm – Mafic suite: metagabbros, diorites, quartzodiorites, enderbites, amphibolites and, subordinately migmatites with diverse structures (Complex Bairro do Marisco)
- NEOTROTEROZOIC**
-  NP3aγ1lpp – High K calcium-alkaline granites Type I: (Hornblende) - porphyric granite, sometimes equigranular, rosy gray, with garnet and biotite facies (Papagaio Peak)
 -  Npccog – Orthogneiss unit: calcium-alkaline orthogneiss migmatitic, (Hornblende) - porphyroid granite, Biotite granite and augen gneiss
 -  NP3ccog – Paragneiss unit: kinzigit gneiss with ancient nuclei as biotite restite, chalcosilicate and amphibolite rocks.
 -  NPccgm – Migmatitic gneissic granite unit: hornblende-biotite gneiss, porphyroid granite and augen gneiss
 -  Banded Gneiss Unit: monzogranite migmatite gneiss, with quartz-feldspathic and mafic bands

Fig. 2. Geological map of the study region (modified from CPRM, 2005).

Sediment samples for geochemical analysis were dried in an oven at temperatures $<60^{\circ}\text{C}$ and pulverized in a Retsch vibrating disc mill with agate pan, to obtain a particle size $\leq 60\ \mu\text{m}$. Subsequently, calcium carbonate, total organic carbon, total nitrogen, total sulfur contents were determined.

The analytical procedure for obtaining calcium carbonate contents was performed by mass difference after adding 10% hydrochloric acid (Gross, 1971). Sediment classification according to calcium carbonate content was performed according to the proposition of Larssoneur et al. (1982). According to these authors, sediments with CaCO_3 contents: $<30\%$ are lithoclastic; between 30 and 50% lithobioclastic; between 50 and 70%, biolitic and; $>70\%$ bioclastics. After determining the carbonate contents, the acid treated sediment was submitted to organic carbon analysis.

Another portion of sediment (not treated with acid), was submitted to total nitrogen and total sulfur analyses. The analyze of organic carbon and nitrogen was performed with the LECO® CHN-1000 apparatus. Sulfur analyzes were performed using LECO® SC-432. Based on the organic carbon, total nitrogen and total sulfur data, the C/N and C/S ratios were calculated, that allowed to estimate the origin of the organic matter and the redox state of the depositional environment (related to the sulfide reduction in the decomposition of the organic matter), respectively.

According to Stein (1991), C/N values <6 indicate organic matter of marine origin and, >15 organic matter of continental origin. Intermediate values are related to mixed marine and continental sources.

According to Hedges and Keil (1995), C/S values between: 1.5 and 5 indicate periodic events of anoxia in water column and sediment; >5 correspond to oxide sediment and water column and; <1.5 anoxic sediment and water column.

Metal concentrations were analyzed according to the U.S. EPA. (1996) and CCME (2001) methods: 0.5 g of dry sediment was solubilized with 6 mL g^{-1} of aqua *regia*, i.e. $\text{HNO}_3 + \text{HCl}$ (1: 3), and heated in a water bath at $\sim 90^{\circ}\text{C}$ for 60 minutes. After cooling, the solutions were filtered through a mixed cellulose ester membrane (diameter 45 μm); deionized water was added to obtain a solution volume of 10.0 mL.

This method does not quantitatively extract all elements of the sediment, but only those that are potentially available by natural leaching or biological processes. The leachable fraction of sediments includes metals and other elements of natural or anthropogenic origin, which are associated with organic matter or surface aggregates to clay minerals. Therefore, there is no attack on crystalline fragments, consisting of silicate matrix and associated elements.

Concentrations of chemical elements such as Arsenic (As), Barium (Ba), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Scandium (Sc),

Strontium (Sr), and Zinc (Zn) were determined with an ICP-MS (Perkin Elmer, model Elan 9000). Data acquired was certified with British Columbia Certified Assayer and standard quality control sediments from the American National Standards Institute, Inc.

Results obtained in this work were compared to the guide values of CONAMA 454/2012 resolution. These resolutions establish general guidelines and procedures for the evaluation of dredged material, aiming at the management of its deposition in Brazilian jurisdictional waters or emerged areas. These resolutions define quality criteria from two levels: level 1 - threshold below which a low probability of adverse effects for biota is expected and; level 2 - threshold above which a probable adverse effect for biota is expected.

Results obtained in this work were compared to reference values adopted by the Canadian Council of Ministers of the Environment (CCME, 2001). The limits for compounds considered harmful in sediments to the marine biota defined by CCME (2001) also were used. In this CCME (2001) classification, the lowest value or threshold effect level (TEL) or ISQG (Interim Sediment Quality Guideline) level, represents the concentration below which it is expected to occur rarely adverse biological effects. The highest value, the probable effect level (PEL), indicates the concentration above which adverse toxicological effects will often occur. Concentrations that fall between the ISQG and PEL levels indicate that toxicological effects may eventually occur on the biota.

The enrichment factor (EF) was also calculated for all evaluated elements, in order to establish the anthropogenic or biogenic contribution *versus* crustal origin. The EF compares the ratio of the concentration of the element in the sample to a normalizing reference element and the corresponding ratio of a theoretically unenriched reference site called background, given by the formula ($\text{CC} = \text{concentration}$; $\text{elem} = \text{element}$):

$$EF = \frac{\text{CC of sample elem} / \text{CC of the reference elem in sample}}{\text{CC of the elem in the background} / \text{CC of the reference elem in the background}}$$

For this study, scandium (Sc) was chosen as the normalizing element, since it is an element without industrial applications and has almost entirely crustal origin (Lee et al., 1994; Grousset et al., 1995; Liu et al., 2003). In this case, most authors use the total elemental concentrations i.e. unbleached, for comparison with the World Middle Shale background (e.g. Turekian and Wedepohl, 1961). In contrast, as the methodology chosen was leaching, it was preferred not to use the Middle World Shale as a reference. Thus, for this study the CSS3-CTR site, from the São Sebastião Channel (CSS), in a distant area of the region under the influence of the outfalls, was used as a reference place.

4. Results

4.1 Sediment grain size

Table 1 presents the results of the particle size analyzes performed on sediment samples collected in the summer campaigns of 2005, 2006 and 2007, around the DTCS outfall and along the CSS.

4.1.1 DTCS submarine outfall in summer of 2005

In all the sampled sites in summer of 2005, the sediment had high percentages of fine fraction, ranging from 67.75 to

87.63% ($= 81.46 \pm 6.78\%$) (Table 1). Sand percentages ranged from 0.74 to 27.5% ($= 16.72 \pm 7.9\%$). Figure 3 shows the particle size distribution in each analyzed station and a graph with the sediment classification (according to Shepard, 1954).

Gravel fraction reached 5% and 13% at sample sites T4 and T5, respectively. According to the classification proposed by Shepard (1954) sediments collected near the DTCS outfall in summer 2005 are classified as: silt at sites T3 and T5; sandy silt at sites T4, T7 and T9; clay silt at sites 1, 2, 7 and 10 and; clayey silt at site 8 (Table 1).

Tab. 1. Particle size of the sediment collected around the DTCS underwater outfall (T1-T10) in and along the São Sebastião Channel (CSS1- CSS10) the summer of 2005, 2006 and 2007.

Sites	2005		2006		2007	
	Sediment Classification	Fine fraction %	Sediment Classification	Fine fraction %	Sediment Classification	Fine fraction %
T1	clayey silt	82.6	silty sand	48.0	clayey silt	83.3
T2	clayey silt	87.5	silt	84.0	clayey silt	90.1
T3	silt	83.4	sandy silt	80.0	sandy silt	64.7
T4	sandy silt	67.8	silty sand	53.7	clayey silt	78.7
T5	silt	86.2	silt	99.7	silt	88.3
T6	sandy silt	78.5	sandy silt	71.4	clayey silt	92.3
T7	clayey silt	87.6	sandy silt	68.5	sandy silt	85.1
T8	clay silty sand	72.5	sandy silt	79.3	clayey silt	84.2
T9	sandy silt	81.5	sandy silt	80.9	clayey silt	89.7
T10	clayey silt	87.1	silt	93.1	clayey silt	78.9
CSS1	silty sand	43.8	—	—	—	—
CSS2	silty sand	26.6	—	—	—	—
CSS3-CRT	sand	14.9	—	—	—	—
CSS4	sand	4.7	—	—	—	—
CSS5	sand	14.7	—	—	—	—
CSS6	sandy silt	64.3	—	—	—	—
CSS7	clayey silt sand	51.7	—	—	—	—
CSS8	clayey silt	81.5	—	—	—	—
CSS9	clayey silt	64.0	—	—	—	—
CSS10	clayey silt sand	42.1	—	—	—	—

3.1.2 DTCS submarine outfall in summer of 2006

The sediment samples collected around the DTCS outfall in the summer of 2006 showed grain size with predominance of silt classes and no clay content. In these samples, fine fraction percentages ranged from 48% to 99.7% ($= 75.9 \pm 16.1\%$) and sand percentages ranged from 0.30% to 52% (Fig. 4).

Compared to 2005, there is an increase in sand percentages in 2006: sandy silt was observed at sites T3, T6, T7, T8 and T9; silty sand at sites T1 and T4 and; silt at T2, T5 and T10 (Table 1, Fig. 4).

4.1.3 DTCS submarine outfall in summer of 2007

As in 2005 and 2006, the sediments analyzed are predominantly muddy, with fine fraction percentages ranging from 64.71% to 90.14% ($= 83.53 \pm 8.05\%$) and sand from 7.21% to 32.08% ($= 16.09 \pm 7.2\%$). Except for T3, there was a predominance of muddy sediments, reaching percentages $>78\%$ (Fig. 5). At the T3 site, a significant percentage of sand was observed, i.e. 32.08%, as well as the presence of gravel (3.21%). Sandy silt was observed at T1, T3 and T7, silt at T5 and clayey silt at T2, T4, T6, T8, T9 and T10. Overall, in this sampling event a decrease in sand percentages was observed in 2007 (Fig. 5).

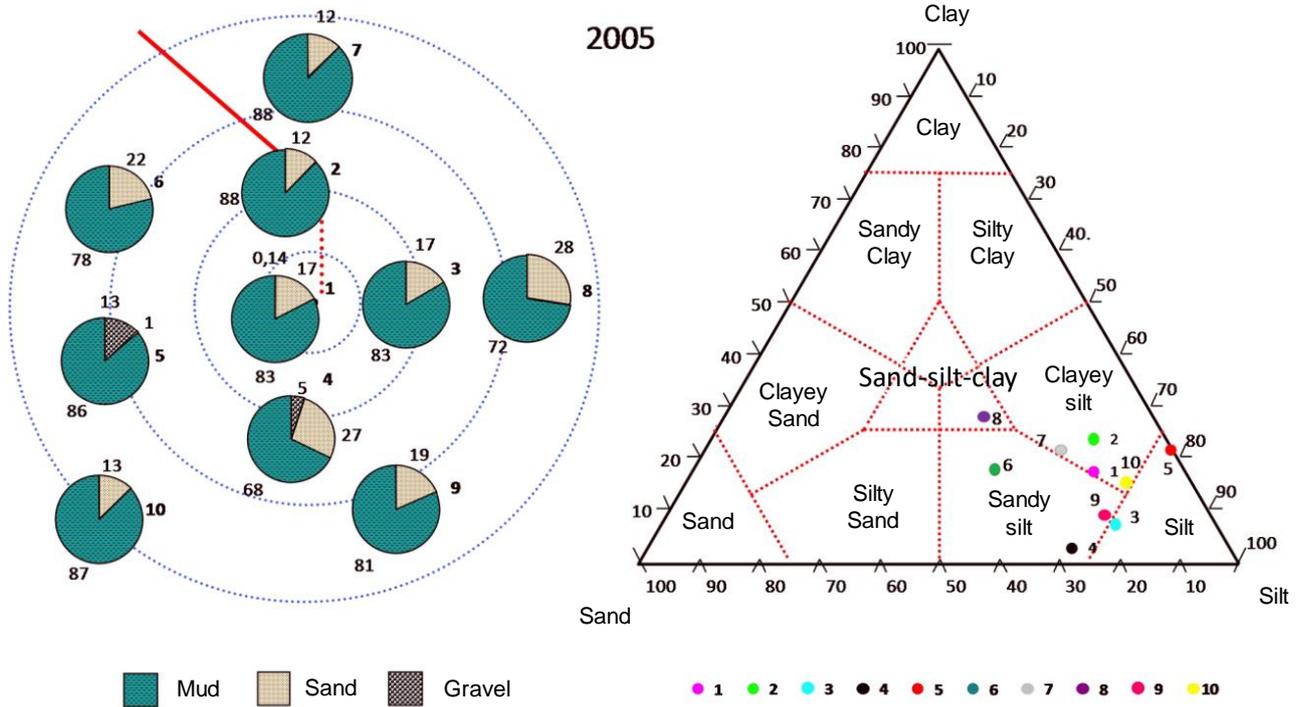


Fig. 3. Particle size distribution and classification of sediments collected around the DTCS outfall in summer 2005 (according to Shepard, 1954).

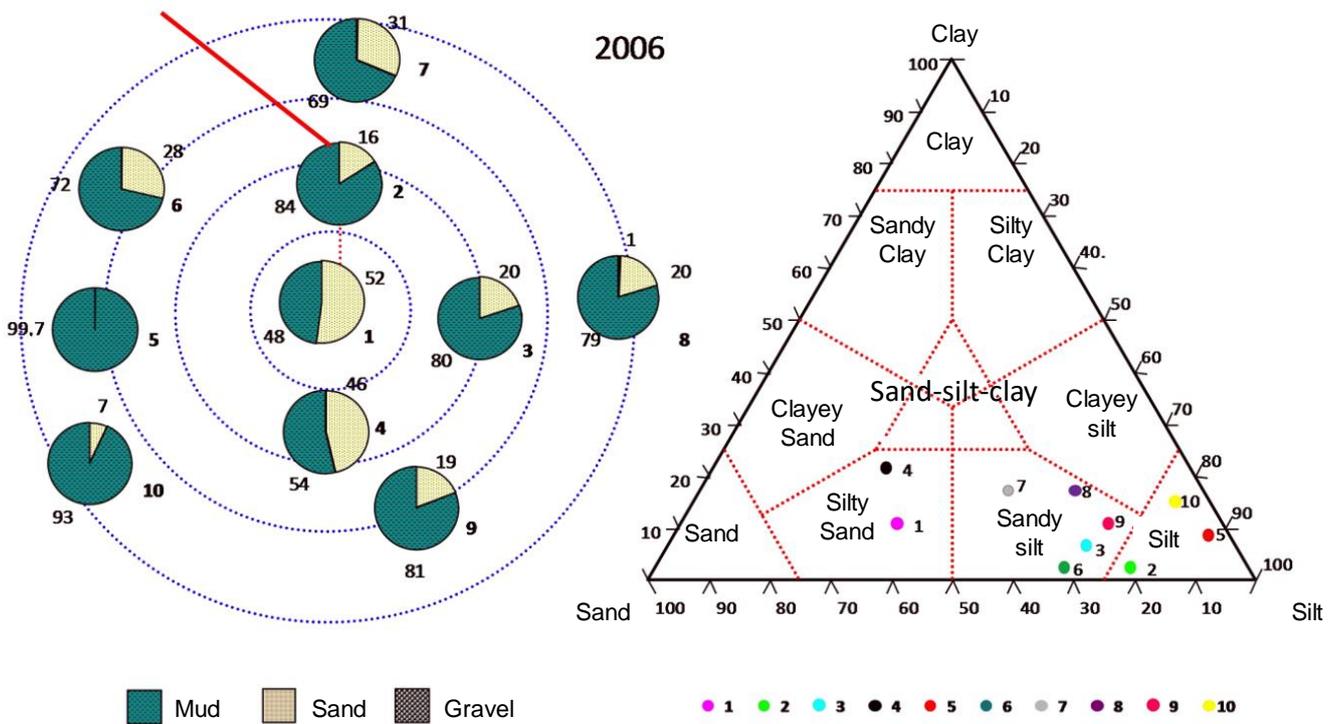


Fig. 4. Particle size distribution and classification of sediments collected around the DTCS outfall in summer 2006 (according to Shepard, 1954).

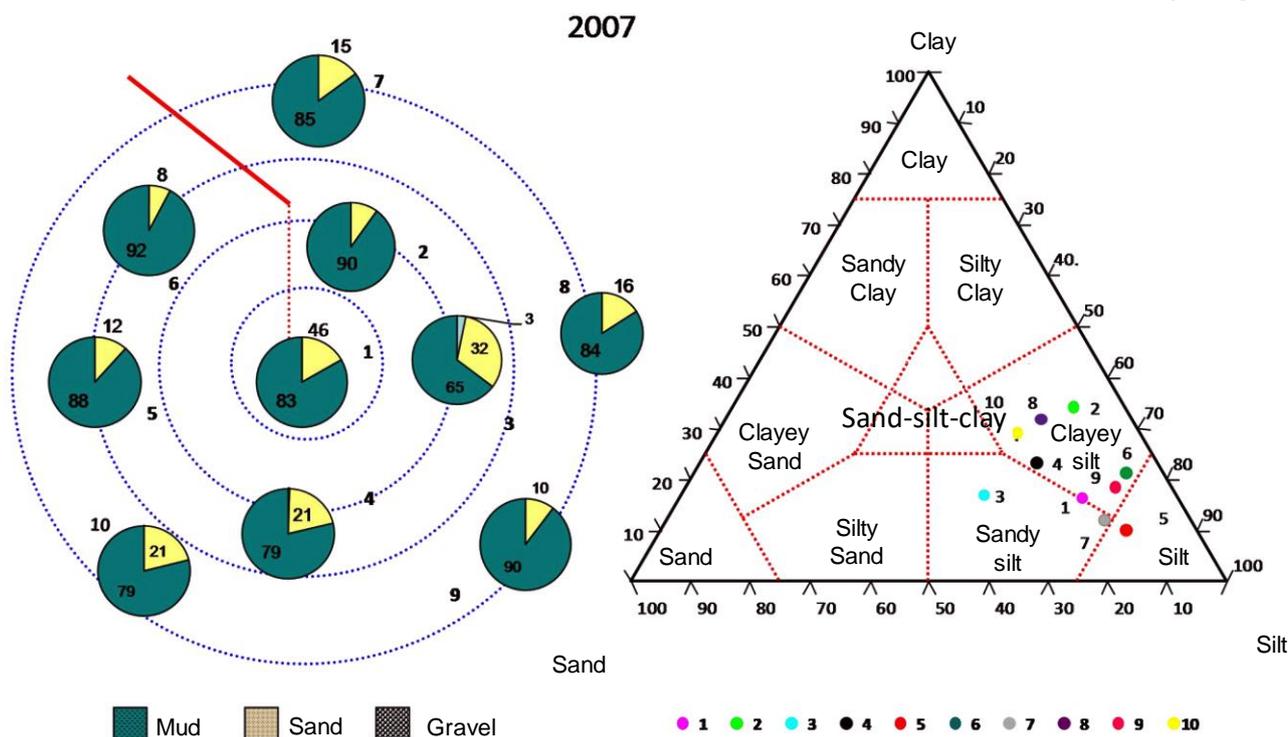


Fig. 5. Particle size distribution and classification of sediments collected around the DTCS outfall in summer 2007 (according to Shepard, 1954).

4.1.4 São Sebastião Channel

The sediments collected along the São Sebastião Channel (CSS) tended to be sandy, with silty sand at CSS1 and CSS2 and silty-clay sand at CSS10 (Table 1). However, at sites CSS8 and CSS9, clay silt was observed. These granulometric results are in agreement with data of Furtado et al. (2008) who described the sedimentary dynamics of CSS.

The particle size distribution of sediments along the CSS is heterogeneous, with a slight predominance of sandy fraction. The northern portion of this channel, where the CSS1 and CSS4 stations are located, is marked by the predominance of sand (51.63% to 77.13%, = 65.45%), with high contents of fine and very fine sand in the stations CSS1 to CSS3-CRT, and medium to very coarse sand at CSS4 station. In the central portion (stations CSS5 to CSS8) and south (stations CSS9 and CSS10), there is alternation of predominance between sandy and fine fraction. The highest mud concentration was observed in CSS8 station (74.3%).

4.2 Potentially Toxic Chemical Elements (PTE)

4.2.1 PTE in DTCS Submarine Outfall Region

The geochemical results related to PTE are presented in Table 2. Arsenic concentrations ranged from 6.2 to 8.6 mg kg⁻¹ (mean 7.2 ± 0.8 mg kg⁻¹; Table 2). The lowest concentration of As was observed at T3 (2005) and the highest at T5 (2007). This distribution pattern was repeated in the three years of study, i.e., the lowest values were always

found at stations T3 and T8, located in deeper regions, off the pier, and the highest in the T5. From Table 2 it can be observed that: all obtained PTE values are two or three times higher than that observed at the control site, where most concentrations are above the TEL value, and; there is a progressive increase in the values from 2005 to 2007 (Fig. 6).

Barium concentrations ranged from 23.4 mg kg⁻¹ (2005, T5 site) to 338 mg kg⁻¹ (2006, T1 site), with a mean of 51.7 ± 64.3 mg kg⁻¹. In each analyzed year, the observed values presented different distribution patterns, but, in general, high values tended to occur in the T4 site. Two extremely high values were detected at the T1 site in 2006 (338 mg kg⁻¹) and at the T3 site (216 mg kg⁻¹) in 2007, which are about 18 times higher than the control site value (18.7 mg kg⁻¹). Except for these two values, the others are almost twice as large as the control station. The highest concentrations were observed in 2006 (Fig. 7).

Cadmium values ranged from 0.01 to 0.19 mg kg⁻¹ (mean 0.04 ± 0.03 mg kg⁻¹). The lowest value was found at T6 (2005) and T1 (2007) and the highest at T4 (2006) (Table 2). Except for the values found at sites T4 (2006), T9 (2005 and 2006) and T10 (2006), the spatial distribution of values is relatively homogeneous over the three years of study. In general, the highest concentrations occurred in 2006. All values are below the TEL limit but are higher than the value obtained at the control site (<0.01 mg kg⁻¹). At location T4 the value observed in 2006 is about 19 times higher than the background (Fig. 8).

Tab. 2. Concentrations of toxic metals and other elements present in sediments from the DTCS outfall region and along the CSS in summer 2005, 2006 and 2007 and the limits of ISQG (*Interim Sediment Quality Guideline*) and PEL (*Probable Effect Level*). Higher concentrations in bold.

Sampled Stations	Arsenic (As)			Barium (Ba)			Cadmium (Cd)			Cobalt (Co)			Chromium (Cr)			Copper (Cu)			Nickel (Ni)			Lead (Pb)			Scandium (Sc)			Strontium (Sr)			Zinc (Zn)		
	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007
Unity	mg kg ⁻¹			mg kg ⁻¹			mg kg ⁻¹			mg kg ⁻¹			mg kg ⁻¹			mg kg ⁻¹			mg kg ⁻¹			mg kg ⁻¹			%			mg kg ⁻¹					
Detection limit	0.1			0.5			0.01			0.1			0.5			0.01			0.1			0.01			0.1			mg kg ⁻¹			0.1		
Level1(CONAMA454/2012)	8.2						1.2						81			34			20.9			46.7									150		
Level2(CONAMA454/2012)	70						9.6						370			270			51.6			218									410		
TEL (CCME, 2001)	7.24						0.7						52.3			18.7			15.9			30.2									124		
PEL (CCME, 2001)	41.6						4.2						160			108			42.8			112									271		
Year	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007
T1	6.6	8.4	8.9	34	338	60.8	0.02	0.04	0.01	6.6	7.8	7.8	34.2	36.4	37.7	9.16	10.7	10.9	13.4	14.8	14.8	18	18.4	21.8	5	5.4	5.5	5	5.4	5.5	51	61	59.8
T2	7.3	7.9	8.4	32.4	33.6	68.8	0.02	0.03	0.03	7.4	7.9	7.3	35.4	36.2	36.5	10.1	9.95	10.1	14.1	15	14.9	19.7	19.2	21.5	5.1	5.3	5.4	5.1	5.3	5.4	56.8	57.5	59.2
T3	6.2	6.3	6.7	36.9	36.8	217	0.02	0.04	0.03	6.2	6.8	6	29.9	32.1	31	9.43	13.8	12	13.4	12.8	13.1	16.5	20.6	17.3	4.2	4.5	4.1	4.2	4.5	4.1	45.7	57.5	69.4
T4	7.5	8.8	8.5	23.8	60	50.4	0.04	0.19	0.02	6.8	5.9	7.2	37.1	30.8	34	36	108	9.21	13.3	14.9	13.9	13.4	36	18.3	4.4	3.6	5.2	4.4	3.6	5.2	67.3	136	52.9
T5	7.8	8.7	9.6	32.6	34.8	30.8	0.02	0.04	0.03	8.5	7.2	7.6	41.4	35.9	37.7	11.1	11.2	10.6	17.1	14.4	15.8	22.1	20.7	21.9	5.8	5.5	5.7	5.8	5.5	5.7	66.6	59	58.5
T6	6.6	7.2	8.6	36.5	26.2	31.3	0.01	0.02	0.03	6.7	6	7.4	32.3	28.9	36.2	8.94	8.65	10.1	12.5	10.9	14.3	17.3	16.1	21.8	4.7	4.3	5.6	4.7	4.3	5.6	51.5	46.2	57
T7	7.7	7	9.2	23.4	28.7	30.2	0.02	0.02	0.03	6	6.2	7.8	28.3	28.8	39.6	7.83	8.84	10.8	11	11.7	15.5	15.5	16.4	22.1	4.5	4.1	5.9	4.5	4.1	5.9	44.5	49.5	59.4
T8	6.2	8	8.2	24.5	38.5	27.6	0.04	0.03	0.03	5.9	7.7	7.6	27.3	38.9	36	13.3	20.6	31.5	11.1	14.9	15.4	14.6	18.2	20.2	4.1	5.5	5.3	4.1	5.5	5.3	48.9	55.5	56.2
T9	7.7	7.8	7.8	29.3	36	35	0.05	0.05	0.03	6.2	7.8	8	31.9	35.3	38.4	34.8	14.2	11.4	13.2	15	16.1	15.6	31	23.4	4.6	5.4	5.4	4.6	5.4	5.4	54.2	63.4	63.2
T10	8.6	8.5	8.9	30.2	33.5	29.7	0.02	0.03	0.06	7	7.8	6.9	32.5	37.1	35.4	8.93	32	38.1	12.5	15.5	17.2	16.8	19.3	19.8	4.7	5.5	5	4.7	5.5	5	50.2	65.3	70.5
Maximum	8.6	8.8	9.6	37	338	217	0.1	0.2	0.1	8.5	7.9	8	41	39	40	36	108	38.1	17	16	17	22.1	36	23.4	5.8	5.5	5.9	5.8	5.5	5.9	67	136	71
Minimum	6.2	6.3	6.7	23	26	28	0	0	0	5.9	5.9	6	27	29	31	7.83	8.65	9.21	11	11	13	13.4	16.1	17.3	4.1	3.6	4.1	4.1	3.6	4.1	45	46	53
Meam	7.2	7.9	8.5	30	67	58	0	0	0	6.7	7.1	7.4	33	34	36	15	23.8	15.5	13	14	15	16.9	21.6	20.8	4.7	4.9	5.3	4.7	4.9	5.3	54	65	61
Standard deviation	0.8	0.8	0.8	5.1	96	58	0	0.1	0	0.8	0.8	0.6	4.2	3.6	2.4	10.9	30.5	10.3	1.7	1.6	1.2	2.52	6.56	1.86	0.5	0.7	0.5	0.5	0.7	0.5	7.9	26	5.6

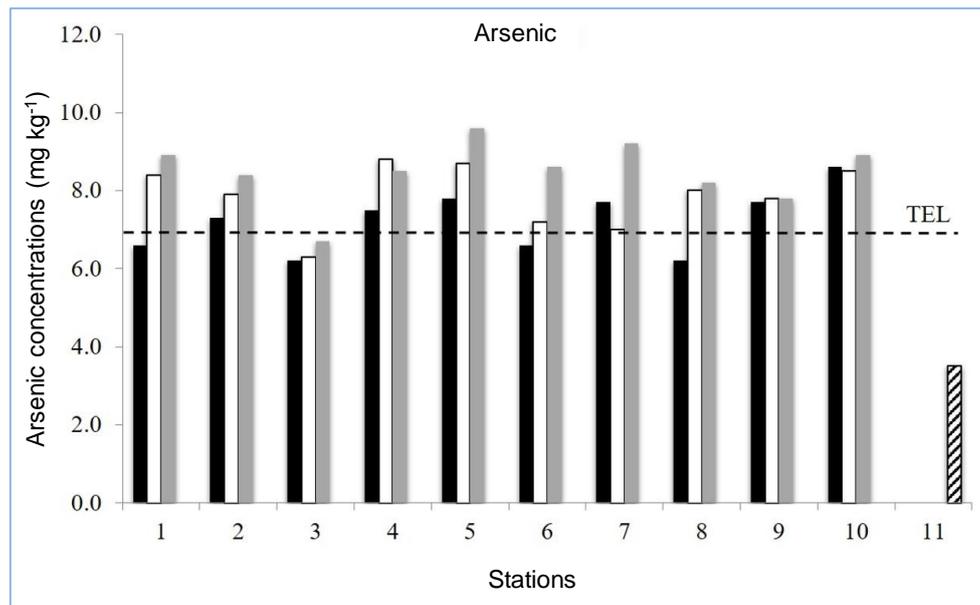


Fig. 6. Arsenic concentrations (mg kg^{-1}) in relation to the TEL value for the years 2005 (black), 2006 (white) and 2007 (gray) at stations 1-10 (T1-T10), in the region of DTCS submarine outfall. Reference station indicated as 11.

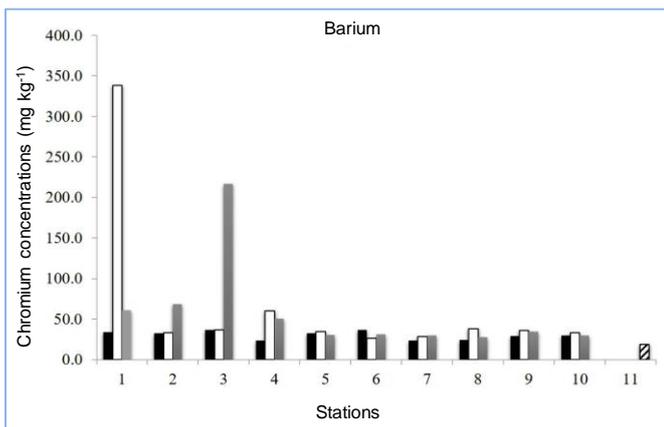


Fig. 7. Barium concentrations (mg kg^{-1}) for the years 2005 (black), 2006 (white) and 2007 (gray) at stations 1-10 (T1-T10) in the DTCS undersea outfall region. Reference station indicated as 11.

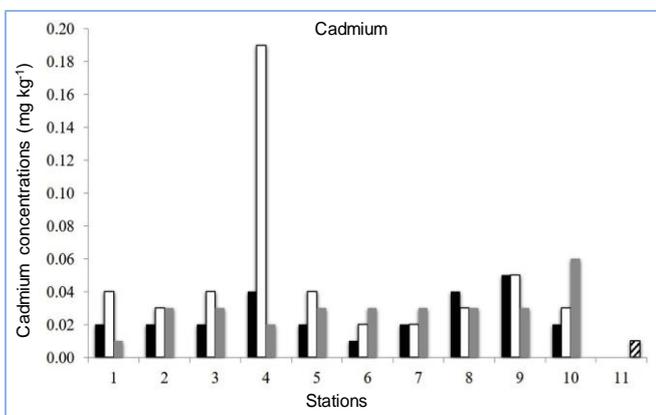


Fig. 8. Cadmium concentrations (mg kg^{-1}) for the years 2005 (black), 2006 (white) and 2007 (gray) at stations 1-10 (T1-T10) in the DTCS undersea outfall region. Reference station indicated as 11.

Cobalt data ranged from 5.9 mg kg^{-1} to 8.5 mg kg^{-1} (mean $7.1 \pm 0.8 \text{ mg kg}^{-1}$). The lowest concentration was observed at T8 (2005) and the highest at T6 (2005). The highest concentrations occurred in 2006 and 2007. All values obtained in the studied stations were higher than that found in the control site (2.7 mg kg^{-1}) (Fig. 9).

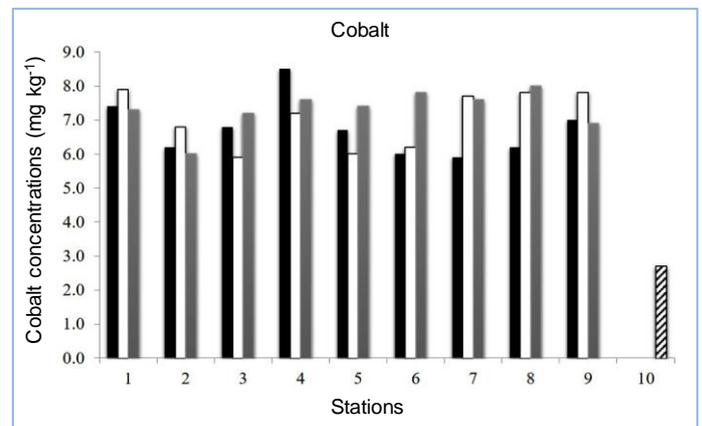


Fig. 9. Cobalt concentrations (mg kg^{-1}) for the years 2005 (black), 2006 (white) and 2007 (gray) at stations 1-10 (T1-T10) in the DTCS undersea outfall region. Reference station indicated as 11.

Chromium levels ranged from 27.3 mg kg^{-1} to 41.4 mg kg^{-1} (mean $34.4 \pm 3.6 \text{ mg kg}^{-1}$), with the lowest and highest values at sites T8 and T5, respectively, both in 2005. The highest concentrations were found in 2007 and 2006. No values were found to exceed the TEL limit and all were higher than the control site (Fig. 10).

Copper values ranged from 7.83 mg kg^{-1} to 108.3 mg kg^{-1} (mean $18.1 \pm 19.4 \text{ mg kg}^{-1}$), being the lowest observed at T7 (2005) and largest at the T4 site (2006). The highest

concentrations occurred in 2007 and 2006. The values found at stations T4 (2005), T8 (2006 and 2007), T9 (2005) and T10 (2006 and 2007) exceeded the TEL limit (Table 2). The anomalous value found at location T4 (2006) has exceeded the PEL limit. All values are higher than the control site value (Fig. 11).

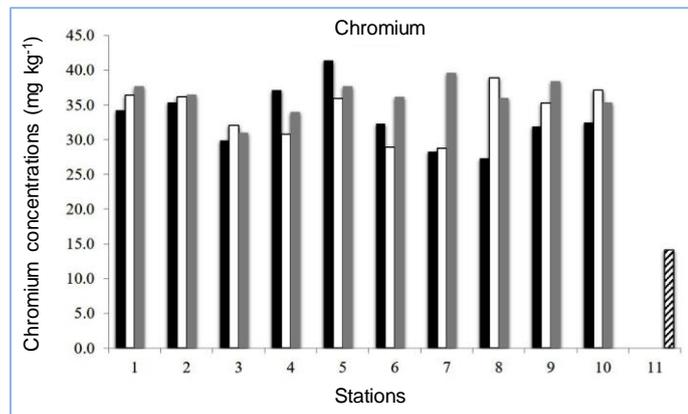


Fig. 10. Chromium Concentrations (mg kg^{-1}) for the years 2005 (black), 2006 (white) and 2007 (gray) at stations 1-10 (T1-T10) in the DTCS undersea outfall region. Reference station indicated as 11.

Mercury data range from 12 to 37 mg kg^{-1} (mean $28.5 \pm 66 \text{ mg kg}^{-1}$). Some values, such as those observed at locations T4 and T10 (2005), are lower than the value of the control site.

Nickel contents ranged from 10.9 to 17.2 mg kg^{-1} (mean $14.1 \pm 1.7 \text{ mg kg}^{-1}$), with the lowest and highest values at T6 sites (2006) and T10 (2007), respectively. All Ni values were higher than that recorded in the control site. Only the concentrations determined for the T5 (2005) and T10 (2007) stations exceeded the TEL value. In general, there was a progressive increase in values from 2005 to 2007 in most of the sample stations.

Lead concentrations (mean $19.8 \pm 4.5 \text{ mg kg}^{-1}$) ranged from 13.44 mg kg^{-1} (station T4, 2005) to 35.98 mg kg^{-1} (station T4, 2006). Lead concentrations were higher than the TEL limit only at station T4 (2006), being three times greater than the control-site value. The highest Pb concentrations were recorded in 2007 and secondarily in 2006.

Scandium values ranged from 3.6 to 5.9 mg kg^{-1} (mean $5.0 \pm 0.6 \text{ mg kg}^{-1}$; Table 2). The lowest and highest values were found at T4 (2006) and T10 (2007), respectively. All values are higher than the background.

Strontium levels ranged from 44.5 mg kg^{-1} to 163.3 mg kg^{-1} (mean $59.8 \pm 16.01 \text{ mg kg}^{-1}$). Except for the highest values found at T4 and T1 in 2006, the other concentrations tended to increase progressively from 2005 to 2007.

Zinc concentrations ranged from 44.5 to 136.3 mg kg^{-1} (mean $59.8 \pm 16.01 \text{ mg kg}^{-1}$). The lowest Zn content was recorded at station T7 (2005) and the highest at station T4

(2006). Only the station T4 in 2006 presented a value above TEL. In general, the highest concentrations occurred in 2007.

4.2.2 PTE in São Sebastião Channel

The concentration of most of the analyzed elements is much lower than that observed around the DTCS emissary. The highest CSS values were almost always found in the central portion of the channel, particularly at station CSS8, located near the Araçá outfall. However, some relatively higher values, such as Ba, were found at station CSS10. The lowest values were always found at station CSS, located on the island bank, opposite to Ilhabela and station CSS9, off Praia Grande and Laje dos Moleques. The concentrations found in the southern portion of the channel are higher than those observed in the north one. Most of the analyzed elements presented, along the CSS, concentrations are below the TEL limit (Table 3).

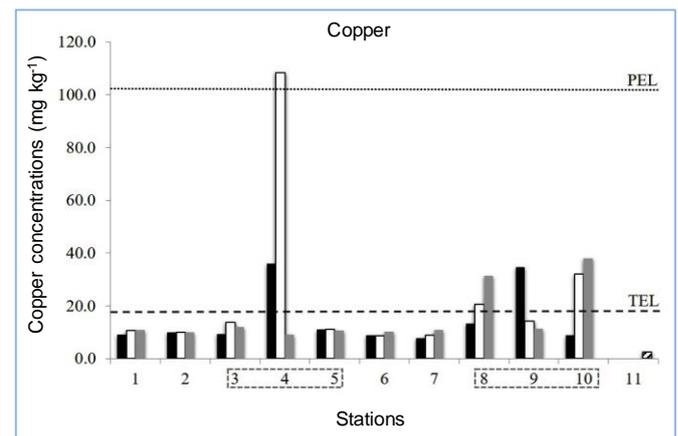


Fig. 11. Copper concentrations (mg kg^{-1}) in relation to the TEL and PEL values for the years 2005 (black), 2006 (white) and 2007 (gray) at stations 1-10 (T1-T10) in the DTCS submarine outfall region. Reference station indicated as 11.

4.2.3 Enrichment Factor

Table 4 shows the enrichment factor (EF) values for each analyzed chemical element. According to the classification of Lu et al. (2009) most of the elements around the emissary and throughout the CSS have concentrations similar to that of crustal origin. However, the anthropogenic impact was detected at several sampling sites during the three years of collection. In 2005, CSS4, CSS8 and CSS9 are moderately to significantly enriched in Cd and Cu, and CSS3-CTR is moderately enriched in Cd.

In 2006, stations: CSS1 was significantly enriched in Ba; CSS4 was moderately enriched in Ba, Pb and Zn, significantly enriched in Cd and very enriched in Cu; CSS9 was moderately enriched in Cd, Cu and Pb and; CSS5, CSS7 to CSS10 were moderately enriched in Cu.

Tab. 3. Concentrations of metals recorded along the CSS. The thresholds of TEL (Threshold Effect Level) and PEL (Probable Effect Level) are also indicated. In dark gray, values above PEL. CSS3 - CRT, reference station for background values.

Sampling Stations	Arsenic (As)	Barium (Ba)	Cadmium (Cd)	Cobalt (Co)	Chromium (Cr)	Copper (Cu)	Nickel (Ni)	Lead (Pb)	Scandium (Sc)	Strontium (Sr)	Zinc (Zn)
Unity	mg kg ⁻¹										
Detection limit	0.1	0.5	0.01	0.1	0.5	0.01	0.1	0.01	0.1	0.5	0.1
Level 1 (CONAMA 454/2012)	8.2		1.2		81	34	20.9	46.7			150
Level 2 (CONAMA 454/2012)	70		9.6		370	270	51.6	218			410
TEL (CCME. 2001)	7.24		0.7		52.3	18.7	15.9	30.2			124
PEL (CCME. 2001)	41.6		4.2		160	108	42.8	112			271
CSS1	6.4	23.0	0.01	5.6	26.5	6.40	10.2	13.44	3.7	89.2	39.8
CSS2	4.5	23.3	<0.01	4.1	19.5	3.83	6.6	8.56	2.4	47.4	29.8
CSS3 - CRT	3.5	18.7	<0.01	2.7	14.1	2.57	5.3	6.47	1.9	127.1	19.9
CSS4	1.7	15.0	0.01	1.2	5.8	2.72	2.5	4.01	1.1	182.4	11.7
CSS5	8.3	23.7	0.02	4.0	21.1	5.30	7.9	11.04	3.0	324.6	31.2
CSS6	7.7	30.4	0.01	7.1	34.6	9.25	13.9	17.99	4.9	108.1	52.4
CSS7	6.1	24.4	0.02	5.8	28.5	8.23	12.2	15.58	4.0	251.5	43.1
CSS8	7.4	32.4	0.03	8.6	43.6	11.86	17.7	23.47	6.0	152.1	63.9
CSS9	5.2	16.3	<0.01	4.5	22.5	5.78	9.5	12.09	3.0	132.0	33.0
CSS10	7.2	58.2	<0.01	5.5	28.8	7.46	11.7	14.39	4.4	134.7	43.3
Maximum	8.3	58.2	0.0	8.6	43.6	11.9	17.7	23.5	6.0	324.6	63.9
Minimum	1.7	15.0	0.0	1.2	5.8	2.6	2.5	4.0	1.1	47.4	11.7
Meam	5.8	26.5	0.0	4.9	24.5	6.3	9.8	12.7	3.4	154.9	36.8
Standard deviation	2.1	12.4	0.0	2.1	10.6	3.0	4.4	5.7	1.5	80.7	15.2

Tab. 4. Enrichment factor at sampling stations located around the DTCS and at control site (CSS3 – CRT).

Sampling Stations	Arsenic (As)			Barium (Ba)			Cadmium (Cd)			Cobalt (Co)			Chromium (Cr)			Copper (Cu)			Mercury (Hg)			Nickel (Ni)			Lead (Pb)			Scandium (Sc)			Strontium (Sr)			Zinc (Zn)		
	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007	2005	2006	2007
T1	1	1	1	1	6	1	1	1	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	1	0	1	1	1
T2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	1	1	1
T3	1	1	1	1	1	5	1	2	1	1	1	1	1	1	1	2	2	2	1	1	1	1	1	1	1	1	1	1	1	1	0	0	1	1	1	2
T4	1	1	1	1	2	1	2	10	1	1	1	1	1	1	1	6	22	1	0	1	1	1	1	1	1	3	1	1	1	1	1	1	1	1	4	1
T5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	1	1	1
T6	1	1	1	1	1	1	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	1	1	1
T7	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	1	1	1
T8	1	1	1	1	1	1	2	1	1	1	1	1	1	1	1	2	3	4	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	1	1	1
T9	1	1	1	1	1	1	2	2	1	1	1	1	1	1	1	6	2	2	0	1	1	1	1	1	1	2	1	1	1	1	1	0	0	1	1	1
T10	1	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	4	6	1	1	1	1	1	1	1	1	1	1	1	1	0	0	0	1	1	1
CSS3	-	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
CRT	-	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

< 2 deficient or poorly enriched

2-5 moderately enriched

5-20 significantly enriched

20-40 very enriched

>40 extremely enriched



Therefore, it can be observed that, in 2006, the area surrounding the outfall was greatly affected by the DTCS effluent, presenting Ba and Cu concentrations above the background. In 2007 stations CSS8, CSS9 and CSS10 presented moderate enrichment in Cu.

5. Discussion

An oil terminal pipeline basically generates two types of dumping: the first comes from the drainage of the terminal and vessel tanks bottom and the second one from oil-contaminated rainwater runoff and industrial effluents (fire water and valve leaks). Each of these two types of waste is routed separately to two sewage lines: line 1 and 2, and routed to *wastewater treatment plant* (WWTP). Type 1 dumps (line 1) receive physical and chemical treatment, with flotation and addition of hydrogen peroxide, sulfuric acid and caustic soda steps. Type 2 dumping (line 2) is treated by density difference in so-called industrial Oil/Water Separator Systems (SAO).

Subsequently, the two treated effluent types are mixed and sent to the submarine outfall. In its final portion, where the diffusers are located, the effluents are discharged into the sea in a moderately hydrodynamic area, with a NE-preferential current of 0.40 to 0.60 m s⁻¹ (Almeida et al., 1981). Theoretically, this circulation would be sufficient to provide the effluent dilution effect, as demonstrated in computer modeling, performed from the CORMIX and FLUENT programs (Fortis et al., 2007).

However, studies performed by Teodoro et al. (2009, 2011) demonstrated that the outfall induced an alteration in the particle size and chemical characteristics of the region surrounding the DTCS. Data of this work, based on seasonal results of 10 stations collected around the emissary, gave similar indication, showing that there was a progressive increase of As content from 2005 to 2007.

The highest As content in CSS, are restricted to the central part of the channel, near São Sebastião Port and DTCS outflow. The lowest values of this element were found at CSS4, located near Ilhabela and also at the control station (CSS3-CTR).

Oil contains several metals in its composition, including Cr, As, Cd and Cu. Chromium is considered autochthonous, associated with the hydrocarbon matrix (Giles, 2003). Whereas As, Cd and Cu are generally allochthonous, resulting from contamination during the well production process (Giles, 2003).

Most oil-bound As and Cu come from corrosion inhibitors used in drilling wells or biocides that are applied in storage tanks (Wellman et al., 1999). Concentrations of As in crude oil range from 2.4 to 1630 µg kg⁻¹ with an average of 15 µg kg⁻¹ (Matschullat, 2000). Although crude oil contains low concentrations of As, microbial degradation of petroleum contaminants may increase the dissolution of Fe and Mn hydroxides and / or oxides associated with As in

sediments. Oil biodegradation can also produce bicarbonate that can absorb or dissolve As from minerals. According to Henke (2009), for instance, in England aquifers, groundwater As concentrations >70 µg L⁻¹ are associated with the biodegradation of petroleum contaminants.

Accidental oil spills can release significant amounts of As to sediment. For example, soils around oil tanks in Los Angeles (USA) typically have <0.5-8 mg kg⁻¹, whereas in heavily contaminated soils, As concentrations range from 30-2300 mg kg⁻¹ (Henke, 2009). Therefore, from the obtained results it is possible to infer that the concentration of As found around the outfall may be linked to the effluent.

Cadmium is widely used in metal coating as anti-corrosion protection in wells or tanks. Crude oils as well as other petroleum products (e.g. solvents) have relatively high Cd concentrations (OTI Wilberforce, 2016). For this reason, Cd is often found in production water from oil terminals and petrochemical industries. Like As, Cd found in sediments is probably related to the effluent released by the DTCS.

According to the classification of Lu et al. (2009), sediments with EF values: <2, are poorly or even minimally enriched; 2 to 5 are moderately enriched; 5 to 20 are significantly enriched; from 20 to 40 are very enriched and; >40 are extremely enriched.

In addition to As, two very high EF-Ba values were found both in 2006 and 2007, as well as relatively high EF-Sr values. These high EF-Ba and EF-Sr values may be related to the effluent from the DTCS outfall. According to the study of McTeir et al. (1993), in underwater oil producing waters, concentrations of ions of SO₄²⁻, Ba²⁺ and Sr²⁺ are high. These elements form BaSO₄ and SrSO₄ precipitates, resulting in deposits on the pipe walls and oil tanks. As the DTCS effluent also comes from the production waters of the terminal and vessel tanks bottom drainage, it may be relatively enriched in these elements.

The production waters are enriched in Ba due to the use of barite mineral, in ground form, near the oil well drilling mud, which eventually permeates the wells' walls. Due to its density, barite is used to fluidize the drilling mud flow (bentonite) used to facilitate sediment drilling. After drilling and oil extraction, the production water is enriched in Ba. Sr is commonly associated with barite due to its ionic affinity with Ba.

Therefore, the high concentrations of metals found in sediments near the DTCS may be related to local contamination sources, which may harm the benthic fauna. According to Duleba et al. (2018), the enrichment in metals in available phases of the sediment are negatively affecting benthic fauna, particularly foraminifera, in this region. According to these authors, in samples collected in non-impacted areas of the CSS (background, station CSS3 - CRT), it is in general necessary, to analyze 10 and 20 cm³ of sediment in order to find 100 living foraminifera. In the region under the direct influence of the DTCS outfall it is necessary to analyze more than 200 cm³ of sediment to find

a few living foraminifera. These data reveals that this area has stressful environmental conditions, which is reflected in the small size of living meiofaunal communities.

6. Conclusion

The results analyzed in this work reveal that sediments from the DTCS region constitute the final deposit of particulate material and associated pollutants. The sediments around the DTCS are very enriched in As and Ba. These two elements should reach toxic concentrations causing damage to living meiofaunal communities and the coastal ecosystem of that region. The obtained results allow us to assume that environmental monitoring in the study area is important in order to analyze the evolution of the situation.

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