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Emerging contaminants (Rh, Pd, and Pt) in surface sediments from a Brazilian subtropical estuary influenced by anthropogenic activities

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ABSTRACT

The concentrations of Platinum (Pt), Rhodium (Rh) and Palladium (Pd) were evaluated from a highly impacted estuary in Brazil influenced by industrial pole, highway traffic and sewage outfall. The Santos-São Vicente region presents important economic activities derived from a largest harbor of Latin America and an industrial pole surrounded by intensive highway traffic. Values of Rh varied from 0.08 to 1.7 ng g^{-1} with highest values at stations impacted by domestic waste. Pt ranged from 0.15 to 40.3 ng g^{-1} with highest concentrations located close to the ferryboat traffic. Pd levels varied from 1.05 to 22.0 ng g^{-1} with values >5 ng g^{-1} in 50% of the stations. The spatial distribution of PGEs was not always directly associated with muddy sediments, because high PGE levels found even in sandy sediments. Pollution indexes, including anthropogenic factor (AF), geo-accumulation index (I_{geo}), Enrichment factor (EF), and Pollution Load Index (PLI) were used for evaluating contaminant potential. Based on EF, Igeo, and PLI, 50% of samples of the sediments from Santos-São Vicente Estuarine System (SSV) were classified with significant to strong PGE contamination. All stations on the Santos Channel (SC), São Vicente Channel (SVC) and Bertioga Channel (BC) had AF higher than 80% in at least one of PGE elements, as showed in station 2A, which presented AF <50% for Rh and Pd and 86% for Pt. Despite high anthropogenic enrichment, no correlations among PGE elements were observed in surface sediments. Only two stations presented Pd/Pt, Pt/Rh, and Pd/Rh typical ratios of auto catalyst (st. 14 and Piaçaguera) both located in the vicinity of highways. This could be due to the PGE deposition process in road dust, soil, and water as well as the biogeochemical cycling of PGEs involving organic metallic and inorganic complexes formed in the estuarine and seawaters.

1. Introduction

Until the 1970s, motor vehicles were the main source of pollution emitting toxic gases such as CO and NO_x during incomplete combustion. In the 1960s and 1970s, the introduction of catalysts based on Pt, Rh, and Pd, which combust products as CO_2 and N_2, occurred in European countries and the USA. Through physical and chemical stress of the wash coat layer from the catalyst, Platinum Group Elements (PGEs) are emitted as particulate matter (mainly in the size range between 10 and 30 μm) at rates of up to several hundred nanogram per kilogram per vehicle (Ravindra et al., 2004). As a consequence, an increase in Pt concentration was observed in many environmental compartments, including atmosphere, soils, sediments, interstitial water, coastal and river waters, even in very remote and supposedly untouched areas, such as Antarctic snow (Ely et al., 2001; Soyol-Erdene et al., 2011; Cobelo-García et al., 2008, 2013, 2014; Mashio et al., 2016; Almécija et al., 2015). Increased concentrations of Pt were also recorded in aquatic organisms, including plants, bivalves, and marine mammals,

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contributing to bioaccumulation of this element (Neira et al., 2015; Almécija et al., 2016; Abdou et al., 2018, 2020).

Coastal areas are considered vulnerable locations because 70% of urban populations and economic activities worldwide are located in these regions (Small and Nicholls, 2003). Anthropogenic pressure can have serious environmental consequences, such as contamination by potential toxic metals that are transferred to the marine food chain (McGranahan et al., 2007). The evidence of anthropogenic Pt inputs in urbanized aquatic environments is based on especially on the analysis of sediment cores (Rauch and Morrison, 2008; Tuit et al., 2000).

According to Lustig et al. (1998), organic and inorganic binders can solubilize PGEs, in soils, increasing input to water system in the coastal area demonstrated that up to 30% of Pd in road dust was mobilized by synthetic rainwater at pH 3 (Jarvis et al., 2001). The presence of the organic acid associated with the tropical forest contributes to the acid rainwater and in the vicinity to industrial poles (Moreira-Nordeman et al., 1983, 1986).

Despite of the complexity of marine matrices in ultra-trace levels that require high analytical precision and accuracy for determination, several studies reported Pt and Rh levels in the environment observing distribution in various marine/estuarine matrices as listed in Table 1.

Temporal aspects were also reported, indicating a significant increase in the Pt levels in the sediments since the introduction of the autocatalysts. Pt concentrations presented an increase of 2–19-fold in relation to background values (Cobelo-Garcia et al., 2011; Abdou et al., 2018).

In Brazil, automobile catalytic converters have been in use and mandatory since 1996 with 1.5 g of PGE in their composition. Brazilian vehicles use gasohol, a mixture of gas and alcohol in an 8:2 proportion, and the catalytic converters contain mainly Pd and Rh (Morcelli et al., 2005). Recent studies demonstrated that the cheaper price of Pd resulted in the development of catalytic converters with lower percentages of Pt, constituted mainly by Pd and Rh (Farrauto and Heck, 1999).

Once in the aquatic environment, Rh, Pd, and Pt elements present different chemical speciations due to a favorable thermodynamic for formation of organic and inorganic complexes, depending on pH, salinity, dissolved organic carbon, and Ca^{2+}.

This study aims to determine concentrations of Rh, Pt, and Pd in surface sediments from the Santos-São Vicente Estuarine System (SSV) that includes: Santos Channel (SC), São Vicente Channel (SVC), Santos Bay (SB) and Bertioga Channel (BC). This area contains the largest harbor in Latin America with the most important industrial pole that includes petrochemical, chemical, and fertilizer plants surrounded by mangroves, and the most important and modern highways in Brazil: the Anchieta-Imigrantes System.

Table 1
Concentrations of platinum, palladium and rhodium in marine/estuarine matrices. Concentrations are in min-max according to the references cited above.

Matrices in estuarine and marine environment	Concentrations	References
Seawater		
Estuarine and coastal water (pmol kg^{-1})	<0.015 to 1.32	Cobelo-García et al. (2008, 2013) Mashio et al. (2016, 2020) Abdou et al. (2020)
Atlantic Ocean (pmol L^{-1})	0.16–0.30	López-Sánchez et al. (2019)
Suspended particulate matter (pmol g^{-1})	1.69–8.97	Cobelo-García et al. (2008, 2014)
Sediments (ng g^{-1})		
Platinum	0.18–40	Cobelo-Garcia et al. (2011) Abdou et al., 2018 Almécija et al. (2015, 2016) Monteiro et al. (2019)
Rhodium	0.02–1.5	Monteiro et al. (2019)
Palladium	0.45–39.9	Tuit et al. (2000) Abdou et al., 2018, 2020
Biota (pmol g^{-1})		
Phytoplankton	3–24	
Oysters	1.01	
Mussels	2.44	

2. Study area

2.1. Santos-São Vicente Estuarine System (SSV) – São Vicente (SVC), Santos Channel (SC), Santos Bay (SB) and Bertioga Channel (BC)

Santos-São Vicente Estuarine System (SSV) is located in the coastal area of São Paulo state between latitudes 23° 53′ and 24° 01′ and longitudes 46° 22′ and 46° 19′ (Fig. 1). This region is an important economic region due to the harbor as well as intense industrial and tourism activities. The SSV is composed of three major channels: Santos (SC), São Vicente (SVC) and Bertioga (BC) as well as Santos Bay (SB). The population of this region is ~1 M inhabitants (IBGE, 2019), which almost doubles during the summer. Highway and ship traffic are intense throughout the year with significant number of cars, buses, and trucks (~3000 vehicles/h) on the Anchieta-Imigrantes highway system. During the summer holidays, the number of vehicles reaches ~120,000 a day. The Anchieta Highway has been operating since the 1940s and Imigrantes since the 1970s.

The region also has petrochemical plants, including catalytic reforming, and nitrogen fertilizer plants, including nitric acid production. Both activities also demand PGE catalysts. For each ton of ammonia converted, a high-pressure plant will typically lose more than 1 g of platinum (Hatfield et al., 1982). Even though the rate of catalyst loss is low, it is the second largest operational expense, exceeded only by the cost of ammonia feedstock (Hatfield et al., 1982). The most common catalyst consists of a 90% platinum and 10% rhodium gauze constructed from squares of fine wire. Up to 5% of palladium is also used (EPA, 2010). For reforming catalysts, the percentage of Pt and Pd are 0.24 and 0.25%, respectively (Kim et al., 2010).

An exuberant Atlantic forest and mangroves characterize the vegetation in the study area (Braga et al., 2000; Berbel et al., 2015). The annual rainfall is high and can reach 2500 mm y^{-1} with pluviosity of 760 mm from January to March (DAEE, 2006). Geographical and climate settings contribute to large inputs of industrial and domestic waste in SC (Santos Channel) and SVC (São Vicente Channel) hydrological systems. Studies in this region have investigated water eutrophication and sediment quality (Braga et al., 2000; Hortellani et al., 2005; Berbel et al., 2015).

Despite economic development and a high population rate, Santos has one of the worst rates of sewage treatment (19%) in the State of São Paulo. The disordered urban expansion has degraded mangroves and increased the diffuse sources of sewage (CETESB, 2016).

Bertioga Channel (BC) is a part of the SSV with around 24 km long with mangrove vegetation. This region presents a strong anthropogenic influence because of connection with the Santos Channel that carries an intense movement of loading contaminants, such as excess of nutrients and trace metals in water and sediments (Rodrigues et al., 1999; Braga et al., 2000; Gianesella et al., 2000; Berbel et al., 2015; Kim et al., 2018). The channel narrows significantly along it course influencing the flux with BC waters (Harari and Camargo, 1998; Miranda et al., 1998). As observed in the Santos Channel, this region undergoes dredging, releasing trace metals and other pollutants into the water column (Campos et al., 2006). Moreover, this region has been characterized by intense nautical activity, thus providing some actions by coastal management in order to conserve the ecosystems of the channel (Santos et al., 2006).

The study area was divided into 4 regions (Fig. 1):

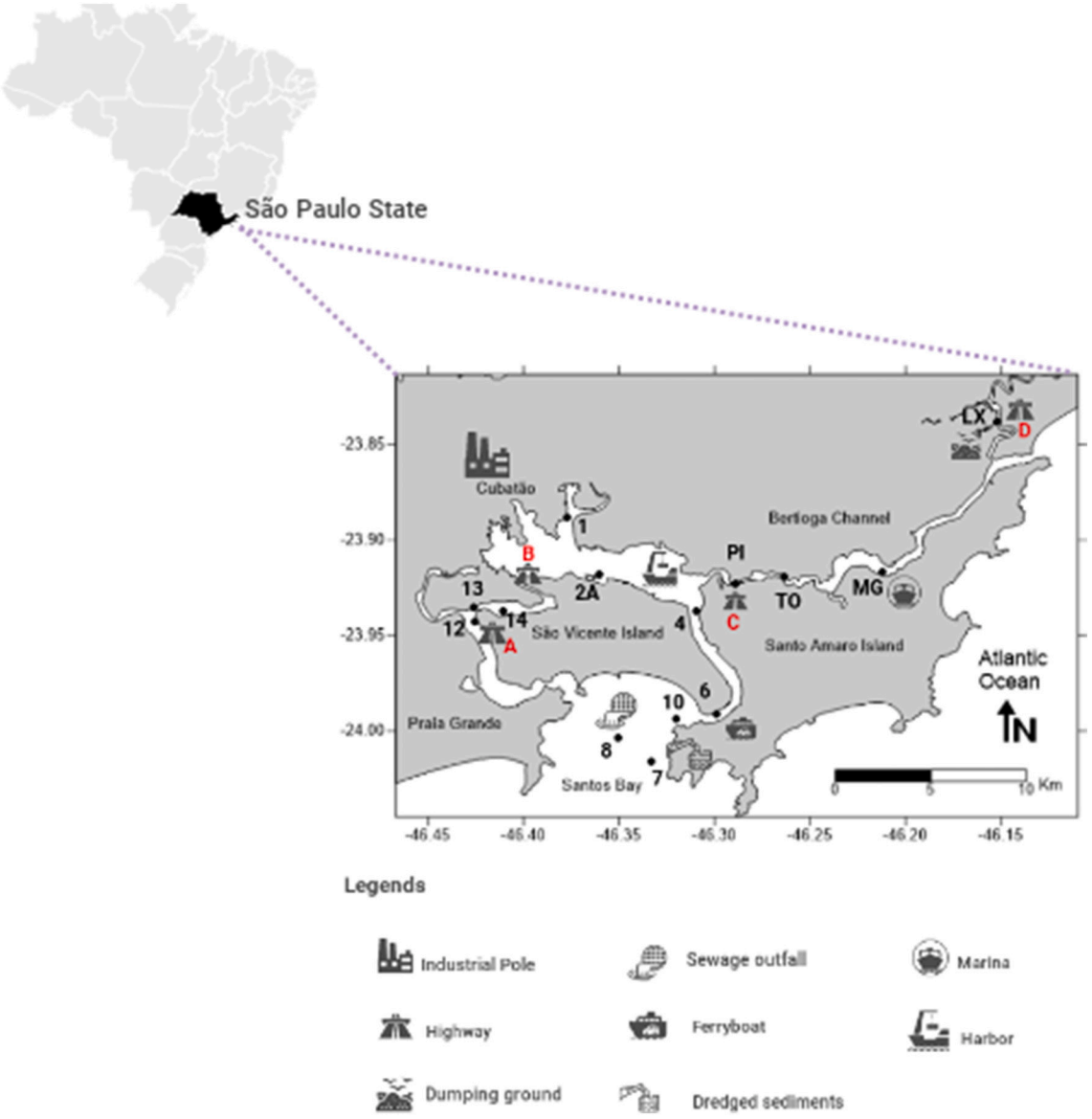

Fig. 1. Study area (a) Santos–São Vicente Estuarine System with the stations in black. Highways (in red): (A) Imigrantes (B) Anchieta (C) Piaçaguera (D) Rio-Santos. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a) São Vicente Channel (SVC): surrounded by mangrove vegetation. This channel is characterized by low hydrodynamic and small rivers that are influenced by industrial and untreated domestic waste *in natura* (st. 14) from the stilts and precarious housing (st. 12). The Channel is also close to Imigrantes highway ~45 m (st. 13).
b) Santos Channel (SC): located in the vicinity of an industrial pole, in the middle (st. 4) and the end of the Channel (st. 6) close to the main avenue of Santos city. Sediment transport is characterized by fluvial discharge with suspended solids from the Serra do Mar to the Santos Channel with unidirectional flow towards the Bay (Fúlfaro and Ponçano, 1976). In addition, several chemical industries in the Cubatão petrochemical complex produce caustic soda, petrochemicals, polymers, and phosphate and nitrogen fertilizers, as well as refine steel and oil (Berbel et al., 2015).
c) Santos Bay (SB): stations 7, 8, and 10 – This region is submitted to marine hydrodynamic, receives waters from both channels and submarine sewage outfall is present in the middle of the bay. Also, SB presents stations with traces of dredged sediments (7), submarine sewage outfall (SSO) at (8) and (10), which is influenced by the SC.
d) Bertioga Channel (BC): Lixão (LX) next to Rio-Santos highway ~150 m, Guarujá Marina (MG), Trecho Oeste (TO), and Piaçaguera (PI) - next to Piaçaguera highway ~150 m.

3. Material and methods

3.1. Bottom water sampling

The sampling occurred in August 2006 on board of the Albacora vessel in Santos – São Vicente Channels (SC and SVC) and Santos Bay (SB). Bertioga Channel was sampled in September 2018 using Lilica boat. The bottom water samples were collected using Hydrobios® and van Dorn bottles for analyses of dissolved oxygen (DO), pH, salinity, and suspended particulate matter (SPM) to measure the percentage of organic matter (%SPOM). Temperature was measured using a protected reversing mercury thermometer (precision ±0.01 °C). Salinity was determined using a Beckman RS-10 induction salinometer with precision ±0.001. DO was analyzed by Winkler method (1888) with an automatic Methrohm (Grasshoff et al., 1983). DO saturation (%DO) was calculated by equations in Aminot and Chaussepied (1983) based on

thermohaline condition and the DO values in situ. The pH was measured using a portable pH meter from Orion®, with a combined glass electrode with an accuracy of ±0.001. For % SPOM, the samples were filtered through pre-weighed glass filters (Whatman GF/F® 47 mm) to determine total suspended particulate matter. The particulate samples were dried (60 °C, 24 h) and weighted in analytic balance (±0.0001 g) for suspended particulate matter (SPM). After weighting, the filters were placed in a furnace at 450 °C for 4 h and weighted again. The SPOM as calculated according to Eq. (1).

$$\%SPOM = \left(\frac{SPM - SPM\ furnace}{SPM}\right) \times 100 \quad (1)$$

3.2. Sediment sampling

The surface sediment samples (0–5 cm) were collected using an inox van Veen crab along the Santos-São Vicente Estuarine System in August 2006 (Albacora vessel) and in the Bertioga Channel in September 2018 (Lilica boat). The sediments were frozen at −20 °C and later dried for 48 h. After drying, the sediment was ground to a powder with a mortar and pestle and then sieved to <2 mm prior to chemical analyses of organic carbon, total nitrogen, platinum group elements (PGEs), and total scandium. Grain size analysis was performed by the method described by Suguio (1973). The background reference was a sediment from a 610-year-old core obtained at Saco do Mamanguá with 92% mud (Rodelli et al., 2019).

3.3. Organic carbon and total nitrogen

Organic carbon (C_{org}) and total nitrogen (N_{total}) in the sediment samples were determined with a LECO CNS 2000 analyzer after the addition of 10% HCl to remove carbonates. The quantification limit for C_{org} and N_{total} was 0.003%. The certificate reference materials, SCO-1 and SDO–1, from the United States Geological Survey (USGS) were used to calibrate the instrument.

3.4. Platinum, rhodium, and palladium analyses in estuarine sediments

The PGE measurements were performed by chemical separation based on Spada et al. (2012). In brief, 0.400 g of estuarine sediment samples (grain size <2 mm) were placed into a Teflon bomb (using Xpress 55 mL Teflon vessels rated at 180 °C) with aqua regia (6 mL HCl 37% and 2 mL HNO_3 65%) in a microwave oven MARS 5 –CEM oven (1200 W, 180 °C, 18 min). After digestion, the samples were centrifuged. An aliquot of 10 mL of digest samples were diluted with Milli-Q 18Ω water to 20 mL. The extracted sub-samples (10 mL) were evaporated almost to dryness on a hot plate at ~80 °C. This treatment was repeated twice more to complete extraction and remove HNO_3. The resulting residues were dissolved in 2 mL of concentrated HCl and heated again to almost dryness. The residue was dissolved in 14 mL of 0.5 mol L^{-1} HCl. Interferences were subsequently removed by chromatography using 3.5 mL of cation-exchange column (Dowex 8 – 200 - 400 Mesh Sigma–Aldrich). The resin was contained in 12 mL Poly-Prep chromatography columns (2 mL bed volume with 10 mL reservoir, Bio-Rad Laboratories). Each Poly-Prep cation-exchange column was prepared with 3.5 g of cleaned resin. The resin was first equilibrated with 10 mL of 0.5 mol L^{-1}. HCl and the eluent was collected in a polyethylene tube. After, sample passed through the column, another aliquot of 2 mL of HCl 0.5 mol L^{-1} was added for washing resin. Then, a solution of 0.5 mL (5 μg kg^{-1}) of ^{115}In was used as internal standard and the volume was completed to 5 mL. Then, the solution was shaken for 30 s in a vortex for complete homogenization before quadrupole ICP –MS analyzer.

A Nexion 300D ICP-Mass Instrument was used for ^{195}Pt, ^{105}Pd and ^{103}Rh determinations at Nuclear and Energy Research Institute (IPEN). For the polyisotopic elements Pt and Pd, at least three isotopes were monitored to compare with values reported in reference materials. Then, the isotope with the least isobaric or polyatomic interferences was used. Daily optimization was performed using a 1 μg L^{-1} NexIon Setup solution (PerkinElmer), consisting of Be, Ce, Fe, In, Li, Mg, Pb, and U in 1% HNO_3. Formation of oxides ($^{156}CeO^+/^{140}Ce^+ \leq 0{,}035$) and doubly charged ions ($^{70}Ce^{++}/^{140}Ce \leq 0.035$) was minimized by adjusting nebulizer gas flow. Auto lens voltage was adjusted to maximize ion transmission based on $^{9}Be > 3000$, $^{24}Mg > 20{,}000$, $^{114}In > 50{,}000$, and $^{238}U > 40{,}000$ cps. Calibration was performed with multi-element standards containing Pt, Pd and Rh standard solution from SPEX Industries, Inc. Nickel cones were cleaned using abrasive "Silver", detergent and 2% HNO_3 by ultra-sonication for 5 min approximately once every 80 samples or when ^{115}In sensitivity used as standard Internal was decreased by ~25%.

Quantification limit (QL) was determined according to the equation (INMETRO, 2018):

$$LQ = X_m + 10{*}s$$

where:

Xm = average of blank concentration ($n = 6$)
S = average of standard deviations (n = 6)

The quantification limits were 0.064 ng g^{-1} for Pt, 0.023 ng^{-1} for Pd and 0.010 ng g^{-1} for Rh for mass of 400 mg. The recovery of ICP-MS analyses was evaluated by using a reference material consisting of used auto catalyst (BCR 723 – road dust) and uncertainty of the samples analyses, expressed as Relative Standard Deviation (RSD%), was below 10%.

3.5. Scandium analyses

Total scandium was determined by instrumental neutron activation analysis (INAA); approximately 200 mg of sediment (duplicate samples) and approximately 150 mg of reference material were weighed and sealed in pre-cleaned double polyethylene bags for irradiation. The samples and reference materials were irradiated for 16 h under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1} in the IEA-R1 nuclear reactor at the Nuclear and Energetic Research Institute (IPEN-SP). Two counting series were made after one week of decay and after 15–20 days. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector with resolutions of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co, respectively. The methodology validation according precision and accuracy was performed by analyses of Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA) and BEN (Basalt – IWG-GIT) certified reference materials.

3.6. Data treatment

The spatial distributions of the parameters were presented in graphics using Surfer 10®. The statistical treatment for the obtained data used Spearman correlation to verify the relationship among variables. Spearman correlation was chosen due to the non-normality of data. The normality test was done with Shapiro – Wink test (Graph Pad 5).

3.7. Sediment quality indexes

The pollution indexes currently used will be evaluated in addition to the traditional enrichment factor. Some complementary indexes are listed in the Table 2.

Scandium was chosen as normalizing element because of low mobility, presents predominantly natural sources and reflects the grain size variation (Wen, 1998).

Table 2
Equations used to calculate the SQI indexes, where *Ci* is the concentration of the studied element in ng g^{-1}; X is the level of the normalizer element (Sc); n is the number of elements ($n = 3$).

Index	Equation	Observation	References
Enrichment factor	$EF = \frac{\left(\frac{Ci}{X}\right)sample}{\left(\frac{Ci}{X}\right)background}$	Quantify the element concentration related to background values	Zoller et al. (1974)
Geoaccumulation index	$Igeo = log\ 2\left(\frac{\frac{Ci}{\%mud\ sample}}{\frac{1.5 \times BG}{\%mud\ background}}\right)$	This equation is an adaptation that considers the percentage of mud to standardize the samples	Muller (1986) modified by Kim et al. (2018)
Pollution load Index (PLI)	$PLI = \sqrt[n]{FC1 + FC2 + FC3 + FCn}$ $FC = C_{sample}/C_{background}$	This calculation represents how many times the concentration exceeds the background value and provides a general approach to assess the toxicity of a particular sample	Tomlinson et al. (1980)
Anthropogenic factor (%AF)	$AF\ (\%) = \left(1 - \frac{1}{EF}\right) \times 100$	This equation indicates Anthropogenic contribution	Boust, 1981; Almécija et al. (2015)

4. Results and discussion

4.1. Quality control data

The results of the quality control data are presented in Table 3. Recovery rates for Pt were 88% for the standard reference material BCR 723 (Road dust):

Table 3: The content median ± U (Expanded Uncertainty whit K = 2 and 95% confidence interval) ($n = 3$) and recovery (%) of Pt, Pd and Rh in Road Dust (BCR 723).

4.1.1. Physical and chemical water properties

Physical and chemical water properties were different in the Santos and São Vicente Channel than in Santos Bay. Temperature varied from 21.81 to 23.50 °C (Fig. 2a) and salinity varied from 24.94 to 34.32, demonstrating the predominance of brackish water associated with values lower than 30, located in the inner part of estuary (st. 1, 2A, 4, 12, and 13) in Fig. 2b. Salty waters (>30) were present in all samples at Santos Bay (sts 7, 8 e 10). Salinity increased moving from the middle part of the estuary to the bay (Berbel et al., 2015). DO values varied from 2.83 to 6.12 mL L^{-1} (Fig. 2c) with low values (<4.00 mL L^{-1}) observed in SVC (st. 12, 13 and 14), because of shallow waters that difficulty an effective water renovation contributing to low values that can influence in DO saturations (%DO). SVC presented values of 55% (st. 13) indicating the predominance of oxidation process, as a consequence of this region is surrounded by stilts and houses with precarious sanitary installations associated with low hydrodynamic (Fig. 2c). Values higher than 100% were found in st. 6, indicating a super-saturation associated with the bottom water where hydrodynamic is more intense. pH values were from 7.69 to 8.62. Values lower than 8 are associated with brackish water that decreases the buffer capacity with spatial distribution (Fig. 2d). The SPM in the water column is an important factor to know the interaction of the PGEs elements in direction to the sediments. In general, SPM values varied from 35.83 to 85.00 mg L^{-1}. The highest concentrations were located at SC, mainly in stations 2A and 6, in function of the hydrodynamic and the harbor fluid mud (Siqueira et al., 2005; Carneiro et al., 2017). On the other hand, SVC presented low values ranged between 35.83 and 42.50 mg L^{-1} (Fig. 2e). The proportion of organic matter in the SPM corresponds to a parameter that influences the chemical process of the PGEs (Turner et al., 2006). Highest percentages of SPOM were found in São Vicente Channel stations (st 12–14) that are surrounded by mangrove vegetation and domestic installations that may contribute with percentages above 22%. O the other hand, lowest values of % SPOM were located at station 2A (19.5%) (Fig. 2f). The Santos Bay and Santos Channel also showed values of % SPOM associated with the hydrodynamic and the outfall sewage.

In Bertioga Channel (BC), water temperature varied from 20.90 to 22.00 °C (Table 1 – Supplementary Material) with the minimum associated with inner stations. Salinity varied 21.01 to 27.94, in LX and the maximum value was located at station PI, maybe associated with flood tide. In general, BC showed salinity values lower than 30. DO values varied from 3.90 (TO) to 4.44 mL L^{-1} in LX. The %DO showed the low value of 74% in TO station. Gianesella et al. (2000) also verified low saturation of DO, with a minimum of 50% in the inner stations of BC, mainly during the summer. The pH values presented a minimum value of 7.60 at MG, and a maximum of 7.84 in PI. SPM showed the lowest value of 31.47 mg L^{-1} and highest percentages of SPOM in LX (25.4 %).

Table 3
The content median ± U (expanded uncertainty whit K = 2 and 95% confidence interval) (n = 3) and recovery (%) of Pt, Pd and Rh in used catalytic (BCR 723).

	Pt (ng g^{-1})	Pd (ng g^{-1})	Rh (ng g^{-1})
Certified	81.3 ± 2.5	6.1 ± 1.9	12.8 ± 1.3
Obtained	60.8 ± 1.0	4.8 ± 0.6	9.4 ± 0.2
Recovery rate (%)	75	79	74

4.2. Sediment properties

4.2.1. Distribution of C_{org} and N_{total}

C_{org} and N_{total} in sediments varied from 0.67 to 6.26% and 0.01% to 0.44%, respectively (Table 4). According to Romankevich (1984), values from 0 to 2% (low), from 2 to 4% (intermediated) and up to 4% is considered high levels. Values of C_{org} higher than 4% were found at stations 1, 2, 2A, 12, 13, and 14 associated with high mud content in sediments (>80%). Values of C_{org} and N_{total} from SC and SVC are extremely high in relation to the sediments with no anthropogenic source such as Mamanguá (C_{org} 1.71% and N_{total} 0.19%). As % SPOM, C_{org} and N_{total} percentages are associated with organic matter inputs from precarious house surrounded by mangroves that favour pollutants accumulation.

Significant correlations were found among C_{org}, and N_{total} ($r > 0.70$, $p < 0.01$) (Table 2 - Supplementary material). The highest values of C_{org}/N_{total} indicate mixture of terrigenous and marine organic matter as observed in the inner part of SC and SVC. The C_{org}/N_{total} values (>10) are related to compounds rich in refractory organic carbon, as humic acids, lignin, and cellulose. These substances are more resistant to decomposition than most other labile components, such as carbohydrates, proteins, and lipids. In this study, the values varied from 7 to 15, indicating the predominance of terrestrial organic matter.

4.2.2. Spatial distributions of platinum, rhodium, and palladium in sediments in the Santos-São Vicente Estuarine System (SSV)

In SSV, rhodium (Rh) varied from 0.080 to 1.67 ng g^{-1}; palladium (Pd) varied from 1.05 to 22.0 ng g^{-1}; and platinum (Pt), from 0.18 to 40.3 ng g^{-1} (Table 4). High levels of Rh were located at stations 4 (1.67 ng g^{-1}), 8 (1.61 ng g^{-1}), and 10 (0.73 ng g^{-1}) in SB, SC and at LX (1.53 ng g^{-1}), where the dumping ground is located. The highest

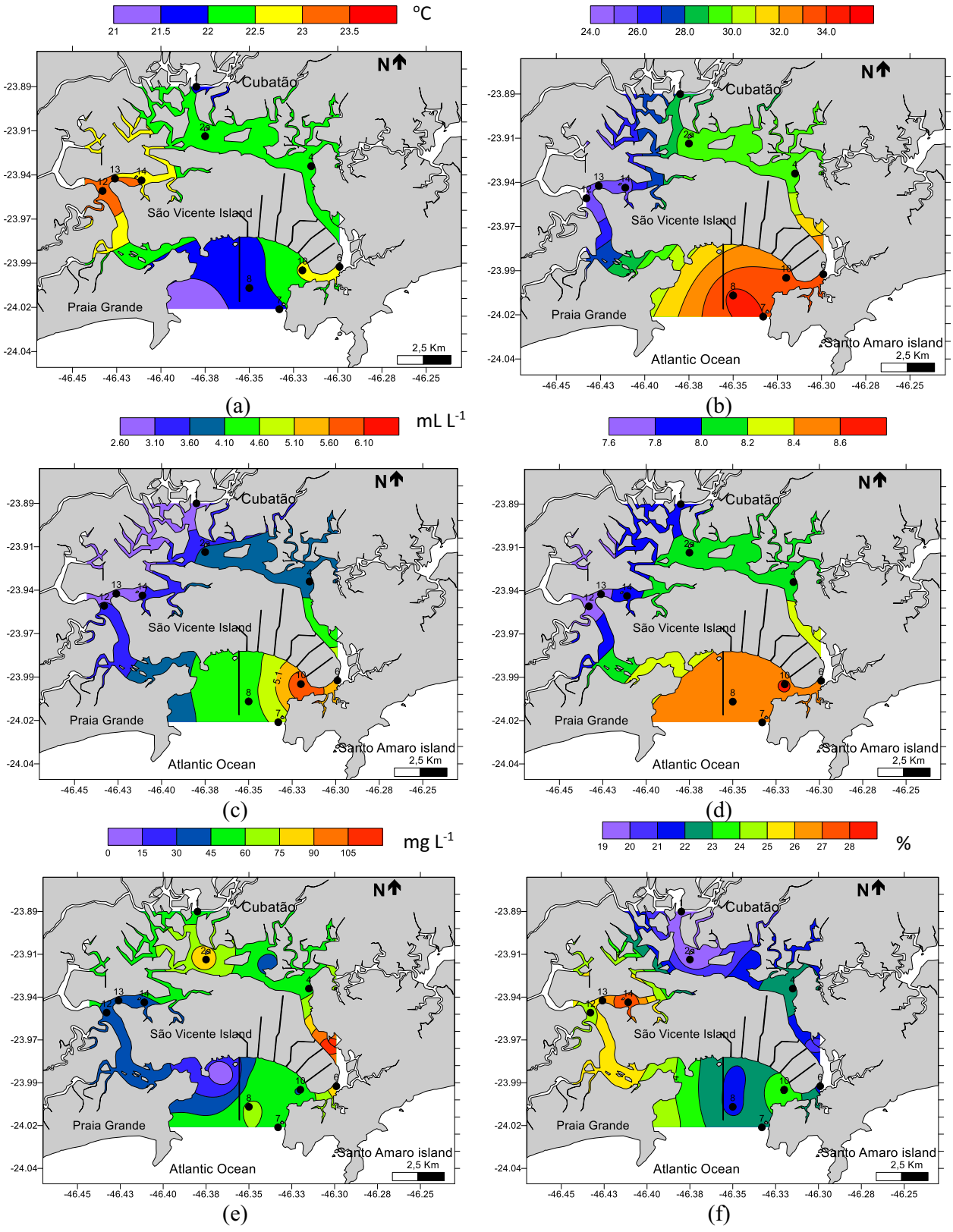

Fig. 2. Spatial distribution of temperature (°C) (a) salinity (b); DO in mL L^{-1} (c); pH (d); SPM (e) and % SPOM (f) in Santos (SC) and São Vicente Channels (SVC) and Santos Bay, São Paulo, Brazil, in the winter of 2006.

Table 4
Values of C_{org}, N_{total}, and mud in %; Rh, Pd, and Pt in ng g^{-1}; and Sc in μg g^{-1} in regions of Santos-São Vicente Estuarine System and Bertioga Channel. C_{org}/N_{total} is molar ratio and Pt/Rh, Pt/Pd, and Pd/Rh ratios are in w/w.

Stations	Depth	C_{org}	N_{total}	C_{org}/N_{total}	Rh	Pd	Pt	Pt/Pd	Pt/Rh	Pd/Rh	Sc	Mud
	(m)	(%)	(%)	Molar ratio	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})		w/w		(μg g^{-1})	(%)
Santos channel												
1	6.1	6.26	0.41	15	0.15	2.22	2.84	1.3	18.9	14.8	13.22	93
2A	12.2	4.40	0.44	11	0.08	1.37	1.09	0.8	13.4	17.0	12.21	95
4	7.6	4.15	0.33	11	1.67	22.0	0.54	0.0	0.3	13.2	11.55	90
6	7.8	2.13	0.22	10	0.39	9.23	40.2	4.4	103	23.7	6.52	33
Santos Bay												
7	7.9	0.67	0.08	8	0.31	11.7	0.24	0.0	0.8	37.9	5.14	24
8	9.1	2.19	0.04	7	1.61	1.05	0.18	0.2	0.1	0.7	3.22	3
10	9.1	1.44	0.11	14	0.73	5.25	0.15	0.0	0.2	7.2	5.46	35
São Vicente Channel												
12	4.8	4.07	0.29	13	0.12	2.38	0.86	0.4	7.1	19.5	6.73	34
13	4.9	6.50	0.44	14	0.19	6.59	1.23	0.2	6.5	34.7	10.23	96
14	6.0	6.60	0.38	15	0.19	1.27	1.96	1.5	10	6.7	12.96	98
Bertioga Channel												
TO	10	nd	nd	nd	0.44	7.02	0.39	0.1	0.9	16.0	14.66	100
LX	5.8	nd	nd	nd	1.53	10.3	0.23	0.0	0.1	6.7	5.34	8
PI	7.0	nd	nd	nd	0.38	2.37	3.32	1.4	8.7	6.2	13.77	90
MG	3.3	nd	nd	nd	0.20	2.04	0.74	0.4	3.7	10.2	11.68	96
MAN[a]	–	1.73	0.19	–	0.08	0.35	0.19	0.6	2.5	***4.5***	***15.18***	***93***
UCC[b]	–	–	–	–	0.06	0.40	0.40	–	–	–	***7***	–

**nd: not determined.
[a] ***MAN*** is the reference site.
[b] Upper continental crust (UCC) - Wedepohl (1995).

concentrations of Pt were located at stations 6 and PI, with values of 40.2 and 3.32 ng g^{-1} respectively. Scandium contents varied from 3.22 to 14.66 μg g^{-1}, with high levels in the inner estuary and decreasing towards the bay as well as mud content. Palladium presented extremely high concentrations (>5 ng g^{-1}) at several stations in SSV (4, 6, 7, 10, 13, TO and LX) (Fig. 3c).

Generally, total phosphorus, toxic metals, C_{org}, N_{total}, S_{total} and scandium concentrations in sediments were well correlated to mud contents and decreased towards the Bay as shown in Table 2 in Supplementary Material (Braga et al., 2000; Siqueira et al., 2005; Berbel et al., 2015; Kim et al., 2019). In contrast, the distribution pattern of PGEs was irregular, and the highest concentrations of PGEs were associated with sandy sediments, as in station 8 (Fig. 3a), with high levels of rhodium in the Submarine Sewage Outfall (SSO). Palladium was evident at stations 7 and 10 (Fig. 3b) and high platinum concentrations were found at station 6 in the western part of the Bay, close to the end of the Santos Channel (Fig. 3c). This trend was pointed out by Sutherland et al. (2008) and Ruchter and Sures (2015). The maximum Pt values were observed in the inner part of the system, near the ferryboat station and the port. The former found Pt bearing particles predominately between 63 and 250 mm fractions in Alb River with Pt levels reaching 30 ng g^{-1} in sandy sediments. High concentrations in estuarine sediments were also reported in high traffic station in Tagus estuary by Almécija et al. (2015) and in Toulon Bay (Abdou et al., 2018).

Rh, Pd, and Pt concentrations were in a similar the range as some studies with surface sediments presented in Table 5, mainly in relation to Pt and Rh, where the maximum observed is similar range to that observed in Tagus Estuary (Portugal). The Pd maximum value was lower than the maximum observed in Boston Harbor (39.9 ng g^{-1}, Tuit et al., 2000). Lowest values of Rh were found in SVC with a median of 0.19 ng g^{-1}. For all stations of SSV, the median was 0.34 ng g^{-1} and lower than Tagus Estuary (0.55 ng g^{-1}) reported by Monteiro et al. (2019). The most interesting aspect was the high Rh in sandy sediments of SSO, in the middle of the Bay system and is in agreement with Monteiro et al. (2019) that reported that a clear affinity of Pt to the fine-sized fraction (mud) of the sediments was observed, but not for Rh.

4.3. Environmental aspects: sediment quality guidelines and possible PGE sources

This study applied the sediment quality guidelines, which are a useful tool for an initial qualitative assessment of the potential adverse effects of chemical contaminants on benthic populations (Birch, 2018). However, it is based on the bulk concentration, which does not reflect bioavailability (Kim et al., 2019). The classification for the Enrichment Factor (EF), Geoaccumulation Index (Igeo), and Pollution Load index (PLI) adopted in this study are presented in Table 6.

EF, Igeo, PLI, and Anthropogenic Factor are also presented in the Table 7. The EF data following Sutherland (2000), indicated that the Rh was exceptionally high (99) at station 8, located on the SSO in the Santos Bay (st.8), followed by the LX station (57) near dumping ground drainage, both influenced by domestic waste. The chemical industries such as steel, fertilizers and oil refinery may also release large quantities of dissolved Pt and Pd, which could behave very differently from the small metallic particles released from autocatalysis due to the vicinity of industrial pole (1 and 2 A). Low circulation in these channels contributes to pollutants supply such as dissolved nutrients (Braga et al., 2000; Berbel et al., 2015), toxic metals (Hortellani et al., 2005) and hydrocarbons (Bicego et al., 2006).

On the other hand, strong contamination was observed at stations 4 and 10, under the influence of the harbor traffic in the Santos Channel. The Pd exhibited high EF in the Santos Bay (st.7) and the Santos Channel (st.4) and after the end in the damping ground (LX). In the case of Pt, the EF showed an exceptionally high value (494) close to ferryboat near station 6, where the traffic is intense. High Pt enrichment was also observed close to Piaçaguera (st. PI) and Imigrantes highway in São Vicente (st 12 and 13). In relation to the I_{geo}, station 6 presented the highest values for Pt and Pd, whereas the highest I_{geo} for Rh was located in the SSO (st.8) and in Bertioga Channel close to the dumping ground site (LX).

Based on EF, Igeo, and PLI in sediments from the SSV, around 50% of samples could be classified as significant to strong.

All stations in of SSV had Anthropogenic Factor (AF) greater than 80% for at least one of studied elements, as in the case of station 2A, which presented AF <50% for Rh and Pd, but 86% for Pt. Based on Kim

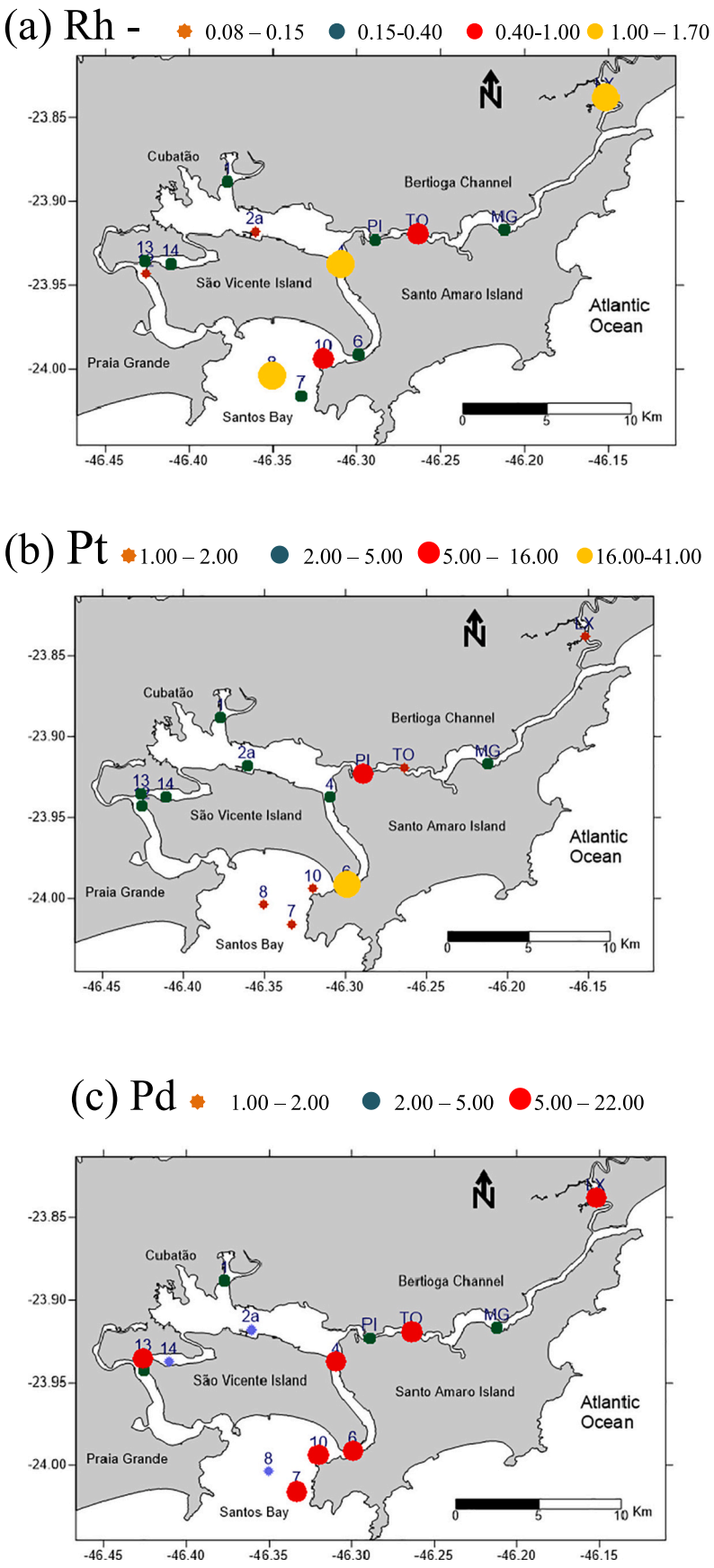

Fig. 3. Spatial distributions of element concentrations in Santos-São Vicente Estuarine System: rhodium (a), platinum (b) palladium (c). All concentrations are in ng g^{-1}.

Table 5
Comparative values of Pt, Rh, and Pd in surface sediments in relation to this study.

Region	Pd	Pt	Rh	References
Boston Harbor	0.58–39.9	0.89–12.5	nd	Tuit et al. (2000)
Tagus Estuary –Prodelta	nd	9.5	nd	Cobelo-Garcia et al. (2011)
Alb River - Germany	nd	45.0	nd	Ruchter and Sures (2015)
Tagus Estuary – Portugal	nd	2.8–40.0	nd	Almécija et al. (2016)
Toulon Bay- France	nd	12–16	nd	Abdou et al., 2018
Tagus Estuary – Portugal	nd	0.55–1.5	0.02–1.3	Monteiro et al. (2019)
Santos – São Vicente –Bertioga – Brazil	1.05–22.0	0.55–40.2	0.08–1.67	This study

nd: no determined.

Table 6
Classification of each index according to reference level.

	EF	Igeo	PLI
No contamination	<2	<0	0–1
Moderate	2–5	0–2	1–2
Significant	5–20	2–4	2–3
Strong	20–40	4–5	>3
References	Sutherland (2000)	Muller (1986)	Singh et al., 2002

et al. (2019) (Table 6), Bertioga is classified as a pristine area for traditional toxic metals. However, two important highways with heavy traffic – the Piaçaguera (PI) and Rio-Santos (LX) – are located in Bertioga Channel. Based on our results, Bertioga and Santos System experience intense atmospheric sources of PGEs from heavy traffic with AF greater than 70% for all PGEs in most stations, and station 6 showed an intensive signal due to the intense road traffic close to ferryboat demonstrated mainly by the Pt values.

In the innermost stations of the SC and SVC, we found an enrichment of Pt in the stations close to the industrial pole (1 and 2A stations) and MG, as well as an enrichment of Pd and Pt in SV (12, 13 and 14) and PI (Bertioga). Pt enrichment at MG can be explained based on Gonçalves et al. (2013). These authors reported about potentially toxic metals in sediment cores from Bertioga Channel. Despite of low values of these metals, high sedimentation rate was observed in inner points of the channel at Largo do Candinho, in the vicinity of MG, that can be influenced in enrichment of Pt.

The average estimated deposition rates of PGEs are 15,300 ng m^{-2} y^{-1} in SC-SVC, 12,590 in Bertioga and 225.2 in Santos Bay and are comparable to a deposition rate of other sites as shown in Table 8.

According to Ely et al. (2001), similarities of Pt/Pd, Pt/Rh, and Pd/Rh ratios could be used as evidence to infer anthropogenic contamination from catalytic converters. In this study Pt/Pd = 1–2.5, Pt/Rh = 5–16 and Pd/Rh = 4–9. For this study, no consistent PGE bivariate ratios were found in the majority of stations, as shown in Fig. 4a, b, and c. Only two stations (PI and st.14) presented all the PGE ratios for catalytic converters. At SSV stations, approximately 21% were within the field of Pt/Pd ratio; 36% for Pt/Rh; and 29% Pd/Rh region.

In Tagus Estuary, The Pt/Rh varied from 0.48 to 39 Monteiro et al., 2019) while in study area Pt/Rh presented values between 0.1 and 103 (Table 4). Monteiro et al. (2019) reported that the ratio between 0.48 and 4 correspond to the reference signature. The largest difference on Pt/Rh mass ratio (1.5–39) was observed in industrialized areas in Tagus estuary similar to SC (0.3–103). In chemical sites from Tagus Estuary, highest values of Pt/Rh were found with a range of 25–39. In stations 1 and 2A, values of Pt/Rh ratios were 13.4 and 18.9 respectively. On the other hand, the Pt/Rh mass ratio should be observed with caution. In this study, values less than 4 do not mean that they are reference values as shown in stations 4, 8 and LX with low values of Pt (0.18–0.40 ng g^{-1}) but high values of Rh (1.53–1.67 ng g^{-1}).

The averages of PGE ratios for Santos-São Vicente Estuarine system were plotted along a background sediment for Mamanguá (MAN). Certified reference materials were used for road dust (BCR 723), catalyst (CRM 2557), industrial catalysts AR 405 (reforming catalytic – petrochemical industries 50–50% for Pd and Pt), and for nitric acid catalyst, which we called NTC (nitric acid converter with 90% Pt and 10% Rh) for comparisons. A comparison with Bandeirantes highway roadside (traffic with 30,000 vehicles/day), and the most important thoroughfares in the city of São Paulo: Tietê Avenue (TA), Pinheiros Avenue (PA) and 23 de maio avenue (23 M) are included in Fig. 5.

The regions of Rh, Pt and Pd values for stations 1, 2A, 14 and PI (in grey) in the ternary diagram correspond to the region of industrial catalysts (AR-405), indicating an influence of the industrial pole, with concentrations that vary between 1.09 and 2.87 ng g^{-1} of Pt. In the blue region, stations 4, 7, 10, LX and TO are distinguished from the others with very high levels of palladium. Meanwhile LX and station 7 have different sources. The sediment from station 7 is from dredging

Table 7
Results for Enrichment Factor (EF), Geoaccumulation index (Igeo), Pollution Index (PLI), and Anthropogenic Factor (AF) of Pd, Rh, and Pt in this study. Result in bold indicates significant/strong contamination in relation to PGE only, based on the limits presented in Table 6.

Region	EF Rh	EF Pd	EF Pt	Igeo Rh	Igeo Pd	Igeo Pt	PLI	AF Rh %	AF Pd %	AF Pt %
Santos Channel (SC)										
1	2	3	**17**	1	2	**4**	**3**	55	61	**94**
2A	1	2	**7**	0	0	**2**	2	24	41	**86**
4	**28**	**29**	4	**4**	−1	2	**3**	**96**	**97**	**73**
6	**12**	**21**	**494**	**4**	**7**	**9**	**6**	**92**	**95**	**100**
Santos Bay (SB)										
7	**12**	**35**	4	**4**	0	**2**	2	**92**	**97**	**74**
8	**99**	5	4	**9**	**2**	**5**	**3**	**99**	**80**	**77**
10	**26**	**15**	2	**5**	−1	1	**2**	**96**	**93**	55
São Vicente Channel (SVC)										
12	4	**5**	**10**	**2**	1	**4**	2	**72**	**81**	**90**
13	4	**10**	**10**	1	0	**3**	**2**	**73**	**90**	**90**
14	3	1	**12**	1	1	**3**	**2**	**64**	33	**92**
Bertioga Channel (BC)										
Trecho oeste	**6**	**7**	2	**2**	−1	1	**2**	**83**	**86**	52
Lixão	**57**	**29**	3	**8**	1	**4**	**3**	**98**	**97**	**70**
Piaçaguera	**5**	3	**19**	**2**	**2**	**4**	**3**	**82**	62	**95**
Marina Guarujá	3	3	**5**	1	0	**2**	**2**	**71**	**62**	**80**

Table 8
Comparative table of Pt accumulation rate with other studies. PGEs accumulation rate = sedimentation rate (cm y^{-1}) × sediment density (g cm^{-3}) × PGE concentration (ng g^{-1}). (2) To calculate the average of Pt, Rh, and Pd accumulation rate for Santos-São Vicente Estuarine System (SSV), Santos Bay, and Bertioga surface sediments, we adopted for SC-SVC: 0.83 cm y^{-1}; Bertioga: 0.86 cm y^{-1} (Ferreira et al., 2014); Santos Bay: 0.09 cm y^{-1} (Tessler et al., 2006) and sediment density of 1.20 g cm^{-3} (Minardi, 1988).

	Pt	Pd	Rh	References
	Accumulation rate (ng m^{-2} y^{-1})			
Urban environment – Germany	2190–6250	219–986	292–1460	Schäfer et al. (1999)
Thoreau's bog	8000	680	22	Rauch et al. (2004)
Tagus estuary – low traffic	6600	–	–	Almécija et al. (2015)
Tagus estuary – high traffic (0–2 cm)	310,000	–	–	Almécija et al. (2015)
Tagus estuary – high traffic (2–4 cm)	17,000	–	–	Almécija et al. (2015)
St. 6	431,600	99,530	4220	This study
SC-SVC	15,300	69,400	4290	This study
Bertioga	12,590	58,620	6910	This study
Santos Bay	225.2	71,160	1040	This study

sediments from the port with several sources and LX is an old dumping ground. Station 10 is the entrance to the channel, receiving sediments from Cubatão estuary and automobiles, close to the main avenue of Santos that goes towards the ferryboat. In the orange region (st 12, 13 and MG) is the region with roadside soils from Bandeirantes highway and the main São Paulo avenues (Morcelli et al., 2005; Ribeiro et al., 2012). Stations 13 and 14 are close to the Immigrants Highway. Sources of PGEs in MG station may be also associated with autocatalysts.

4.4. PGE in surface estuarine sediments: biogeochemical aspects in a subtropical estuary

According to the studies of Lustig et al. (1998), PGEs can undergo solubilization by organic and inorganic ligands in soils such as humic acids, L-methionine, triphosphates, and especially Pd, which forms soluble organic metal complexes. However, this process is as long as 60 days.

In SSV, the sediment transport is influenced by tide and unidirectional flux from high estuary (sts. 1 and 2A) to station 6 (Harari and Camargo, 1998, 2003). The movement of saline water during the rising tide influences the physical and chemical properties, such as pH of water and the suspended materials, particularly the colloidal and humic substances. As the saline water enters into the estuary, the interactions between organic matter and metals increase due to the presence of electrolytes. The flocculation process is not limited to clays and organic complexes, but also occurs in the soluble organometallic complex formed with humic materials and most of the metal ions (Rashid, 1985). Moreover, high pluviosity (2500 mm y^{-1}) contributes to continental drainage that leaches PGEs, which undergo geochemical processes in rivers in the soluble form. The experiments of Turner (2007) and Cobelo-García et al. (2008) found that PGEs removed from the aqueous phase to the particulate phase appeared to proceed via both coagulation of organic/colloidal associations and adsorption to estuarine sediment particles.

However, the mechanisms for Rh, Pd, and Pt removal from the aqueous to particulate phase are different and depend on pH, salinity, Ca^{2+}, and organic matter (Turner, 2007). In fresh water, the main chemical species of platinum is $Pt(OH)_2$. As the river particles enter the estuary, the release of the Pt adsorbed in these particles takes place through the intrusion of saline waters, causing the equilibrium process adsorption-desorption transform into the chemical species $PtCl_5(OH)^{2-}$ (Cobelo-Garcia et al., 2013; Mashio et al., 2016). Rhodium removal is sensitive to pH increase and may occur predominately from adsorption of cationic species of the form $[RhCl_{6-x}(H_2O)_x]^{x-3}$, where x = 0 to 6, and in river water complexation by organic ligands may have also occurred. In freshwater, Rh complex is stable in solution and estuarine waters with increased pH caused by tides and ions, as salting out and coagulation take place. The high values of rhodium and low values of platinum in SSO are in agreement with Monteiro et al. (2019). Possibly, anticancer drugs are sources of Pt and concentrations of this element have already been detected in sewage and wastewaters (Vyas et al., 2014). Thus, Monteiro et al. (2019) reports that an increase in dissolved Pt in waste water effluents was detected and that during the treatment a reduction in the concentration of dissolved Pt takes place, while Rh remains unchanged. Then, the effluent treatment reflects in Pt and Rh concentrations in sediments as observed in SSO. Despite the possible low concentrations of the dissolved fractions of Pt and Rh that are introduced into the marine environment, the water input (5.3 m^3 s^{-1}, CETESB, 2016) results in detectable values in the order of ng g^{-1} in sediments, mainly from Rh.

High levels of Rh in sediments from saline waters and under tidal influence in 4 and LX stations were observed. In addition, our results show that Rh is correlated with salinity ($r = 0.55$), DO (0.58) and pH ($r = 0.58$). Pd speciation was predicted to be dominated by organic complexes (Turner, 2007) but no correlation between Pd and organic matter was found ($r < 0.50$). On the other hand, Pt showed high correlation with C_{org} ($r = 0.73$) and N_{total} ($r = 0.62$) in contrast with Rh. The affinity of Pt towards C_{org} indicates that its distribution is governed by the sediment characteristics or by a group of several parameters (Monteiro et al., 2019). SVC, SC and BC channels show high levels of organic matter (>4% C_{org}), high levels of both dissolved organic matter (>600 μmol L^{-1} DOC in Bertioga – Sutti et al., 2019) and suspended particulate matter (>20% SPOM).

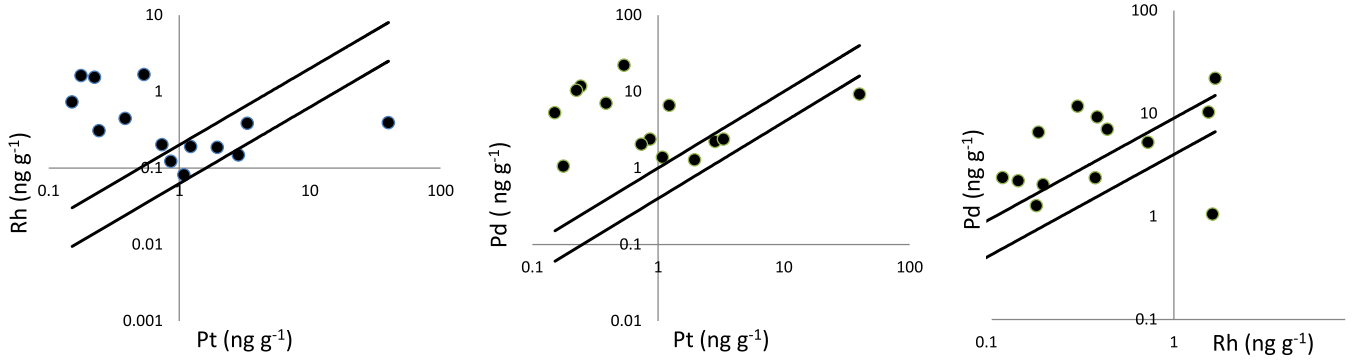

Fig. 4. Bivariate logarithmic-scatterplot of (a) Pt and Rh; (b) Pt and Rh; and (c) Pd and Rh values in ng g^{-1} in Santos-São Vicente and Bertioga estuarine surface sediments. The line indicates (a) Pt/Pd region of 1.0–2.5; (b) Pt/Rh region of 5–16; and (c) Pd/Rh of 4–9.

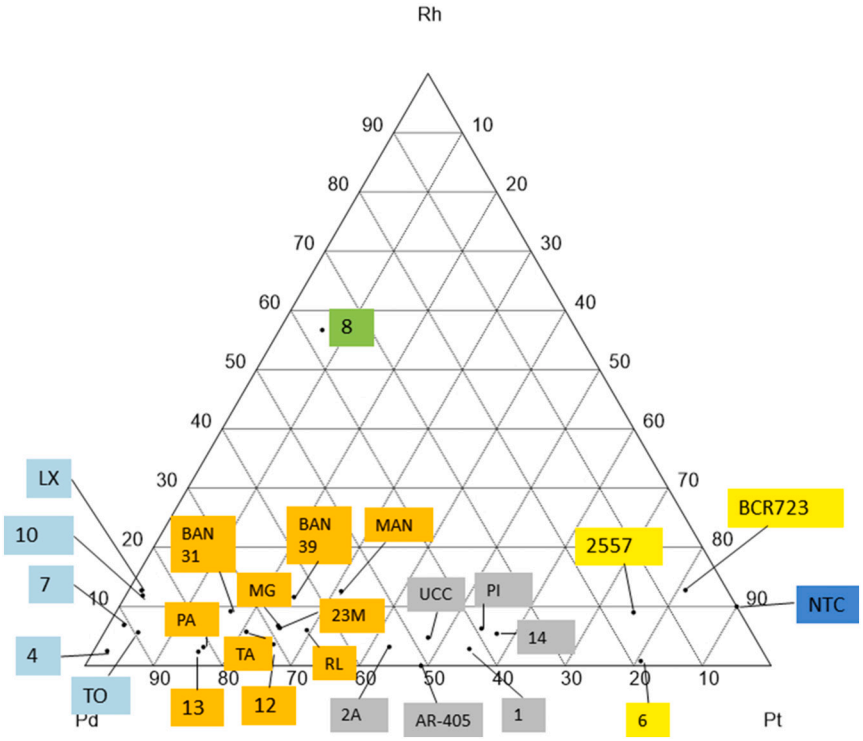

Fig. 5. Means of Pd, Pt, and Rh relative proportions for Santos-São Vicente (numbered stations) and Bertioga (lettered stations) in surface sediments compared to a base line sediment from MAN and UCC (upper continental crust – Wedepohl, 1995); BCR 723 (road dust); CRM 2557 (auto catalyst); Ban31, and Ban39 (Bandeirantes - SP348 highway roadside – Morcelli et al. (2005)); AR 405 (reforming catalyst from Kim et al. (2010)); NTC (catalyst for nitric acid production – EPA, 2010); PA (Pinheiros Avenue); TA (Tietê Avenue); and 23 M (23 de maio avenue) in soils from the city of São Paulo (Ribeiro et al., 2012).

In addition to the lack of correlation among of Rh, Pd, and Pt, bioaccumulation process by benthonic/planktonic organisms can change PGE ratios in the sediment. The facility to bioaccumulation of Pd in relation to Pt and Rh is mentioned by Zimmermann et al. (2005). The average concentration of PGEs in freshwater crustacean *Asellus aquaticus* were 25 ng g^{-1} for Pt, 13.5 ng g^{-1} for Rh, and 110.5 ng g^{-1} for Pd (Moldovan et al., 2001). For *Corbicula sp*, freshwater bivalve, platinum levels varied between <0.05–1.3 ng g^{-1} (Ruchter and Sures, 2015). In relation to coastal environments, Abdou et al. (2020) reported that high levels of Pt in phytoplankton in Genoa Harbor (23.74 pmol g^{-1}–4.63 ng g^{-1}), Arcachon Bay (11.76 pmol g^{-1}–2.29 ng g^{-1}) and in Gironde estuary (3.01 pmol g^{-1}–0.59 ng g^{-1}) showing Pt is biogeochemically reactive to algae as other essential and anthropogenic trace elements. In addition, Abdou et al., 2018 reported that an 8-fold increase of Pt concentrations (from 0.12 to 0.80 ng g^{-1}) in farmed mussels *Mytilus galloprovincialis* from 1985 to 2015. This studies show that phytoplankton and other organisms might play an important role in Pt partitioning. Moreover, its sorption could control Pt and maybe other PGEs budget in coastal environments.

5. Conclusion

High levels of Rh, Pd, and Pt with anthropogenic contribution are found in sediments of the Santos-São Vicente and Bertioga (BC) Channels, which are mainly characterized by mud with high levels of organic matter because they are surrounded by mangroves, low oxygen concentrations and low hydrodynamic favoring the deposition of particulate matter and pollutants. Santos Bay with sandy sediments exhibits high levels of Rh, Pd, and AF > 70%, mainly in sewage outfall (st. 8) and at the entrance to the Bay (st.7), which corroborates with previous studies where coarse sediments presented high levels of PGEs. The organic complexes and SPM availability could collaborate to the deposition of PGEs, mainly Pt as shown in discussion. Potential PGEs sources to sediments may be from ongoing industrial activities, fossil fuel combustions, and regional traffic as well as domestic waste and sewage outfall.

Pt reveals the intense anthropogenic influence close to the ferryboat (st. 6), which is characterized by intense vehicle traffic from Santos to Guarujá and vice-versa. We found evidence of the Rh association with the disposal of domestic and urban effluent by the SSO.

The PGE ratios showed no correlation in estuarine and bay sediments, demonstrating different sources involved in soils, road dust, and rain inputs to the estuary and the bay by urban sewage via SSO. Added to these processes, flocculation of organic metallic complexes formed by saline influence as well bioaccumulation of PGE in benthonic organisms can modify the PGE ratio in an estuarine system.

In the studied hydrological system, the sediments showed different contributions along the estuary from activities that introduce industrial sewage, dust from fuel combustions, and from regional traffic as well as domestic waste and sewage outfall. In the estuary, processes such as flocculation of organic metallic complexes by saline wedge as well as bioaccumulation of PGE in benthonic organisms change the PGE ratio in sediments.

Further studies of PGEs are needed in this complex environment as well as in the pristine regions, considering the time variation and the biogeochemical processes involving the behavior of these elements, for further knowledge about anthropogenic influence and its role as pollution indicators.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.111929.

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