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DOI: 10.1590/S0001-37652012005000021

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Geochemistry of intertidal sediment pore waters from the industrialized Santos-Cubatão Estuarine System, SE Brazil

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Manuscript received on September 9, 2011; accepted for publication on November 30, 2011

ABSTRACT

The geochemical composition of sediment pore water was investigated in comparison with the composition of sediment particles and surface water in an estuary within one of the most industrialized areas in Latin America (Santos-Cubatão estuarine system, SE Brazil). Pore and surface waters presented anomalously high levels of F^- , NH_4^+ , Fe, Mn and P due to two industrial point sources. In the summer, when SO_4^{2-}/Cl^- ratios suggested an enhanced sulfate reduction, the higher dissolved levels observed in pore waters for some metals (e.g., Cu and Ni) were attributed to reductive dissolution of oxidized phases. Results evidenced that the risks of surface water concentration increase due to diffusion or advection from pore water are probably dependent on coupled influences of tidal pumping and groundwater inputs.

Key words: geochemical anomaly, industrial contamination, pore water geochemistry.

INTRODUCTION

The occupation of coastal areas by industrial and urban activities has been recognized as the main cause of sediment contamination by potentially toxic trace elements in many regions (e.g., Rebello et al. 1986, Faria and Sanchez 2001, Molisani et al. 2004, Pereira et al. 2007, Fonseca et al. 2011). This relationship has been systematically observed in the Santos-Cubatão estuarine system (São Paulo State, SE Brazil). Industries settled in the surrounding area

of this system in the mid 1950's caused continuous environmental concerns related to atmospheric, terrestrial and aquatic contamination. In 1984, the São Paulo State Environmental Protection Agency (CETESB) started a pollution-control program to minimize the problems that affected the atmosphere and the hydrologic system of Cubatão City (CETESB 2001). However, recent studies have shown that high metal and metalloid concentrations are currently found within sediments from this coastal region (Abessa et al. 2005, Luiz-Silva et al. 2006, 2008, Torres et al, 2009, Silva et al. 2011).

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The availability of trace elements present in sediments to the aquatic biota can be strongly controlled by physico-chemical conditions, which may present temporal variability (e.g., Luiz-Silva et al. 2006, Ramanathan 2007). Thus, methods that take into account this variability and consider the mechanisms affecting the chemical behavior in the sediment-water interface are important to predict trace element bioavailability to important groups of benthic organisms, such as filter-feeding mollusks. One of the possible methods has been recently applied in the Santos-Cubatão estuarine system, by analyzing acid-volatile sulfide (AVS) and simultaneously-extracted metals (SEM) in the estuarine sediments. Nizoli and Luiz-Silva (2009) assessed the Morrão River sediments (in the northern region of the Santos-Cubatão estuarine system) and showed that lowest AVS and highest SEM (Zn, Pb, Cu, Ni, Cd and Hg) molar concentrations were obtained for sediments collected during the summer, suggesting a lower potential of reactive sulfides to retain metals during this season. In Cananéia estuary (SE Brazil), Ferreira et al. (2007) have also observed lower concentrations of AVS and pyrite-Fe in the summer, which was related to increased crab bioturbation.

Pore water frequently exchanges chemical elements with sediment solid-phases (e.g., Sherman et al. 1998, Tovar-Sanchez et al. 2006). As a result, dissolved elements can be transferred from the solid phase to overlying surface waters, and these exchanges can exhibit a significant seasonality, e.g. because microbial activity is dependent on temperature (Ram and Zingde 2000). Once in the surface water column, the released dissolved elements can interact with suspended matter (composed of mineral phases, non-living organic phases and living plankton) and be resettled within the same site or can be available to be transported to adjacent areas (Turner and Millward 2002). This may threaten these areas in the case of potentially toxic elements transport, often carried in geochemical

forms more reactive than that previously found in bottom sediments particles (e.g., recently-adsorbed forms and/or precipitated into amorphous mineral phases; Machado et al. 2011).

In this study, the geochemistry of sediment pore water was investigated in comparison with the composition of sediment particles and surface water from one of the most contaminated parts of the Santos-Cubatão estuarine system. This is a first evaluation of the variability in the relationship between physico-chemical conditions and major, minor and trace elemental distribution in sediment pore water for the study area.

STUDY AREA

The study area is located in the Morrão River estuary, in the NE part of the Santos-Cubatão estuarine system, São Paulo State, SE Brazil (Fig.1a). It is dominated by a tropical to subtropical climate, favorable to the maintenance of an exuberant mangrove ecosystem, which is a valuable source of food (fish and crustaceans) for human intake and is a habitat for tens of thousands of resident and migratory birds of the northern hemisphere (R H.R. Matos, unpublished data). The steep relief of the area restricts the estuarine region to a narrow land segment that comprises the Baixada Santista (Santos Lowland). The estuary is loaded with sediments derived from the Serra do Mar (Mar Ridge), which consists of metasedimentary rocks such as phyllites, schists, calc-silicate rocks and quartzites. In the estuarine area gneissic-migmatitic rocks also occur (Almeida and Carneiro 1998).

The Cubatão City industrialization started with petrochemical activities in the 1950's (J.M. Couto, unpublished data). Later, other industrial activities were settled down, such as iron and steel (1963), caustic soda (1964) and phosphatic fertilizer industries (1970). The released contaminants include nutrients, trace metals, polycyclic aromatic hydrocarbons and

radionuclides (Braga et al. 2000, Silva et al. 2006, Machado et al. 2008, Luiz-Silva et al. 2008).

The Santos-Cubatão estuarine system has several rivers, which are pathways for industrially-derived elements discharge (Luiz-Silva et al. 2006, Oliveira et al. 2007). For this reason, the Morrão River estuarine

sediments are enriched in many elements, such as Fe, Mn, Cr, Ni, Zn, Ga, Ag, Cd, Sn, Sb, Ba, Pb and Bi associated with a steel plant source, and P, Ca, Be, Sc, Co, Cu, Sr, Y, Zr, Nb, Hf, Ta, Th and U associated with a phosphatic fertilizer industry source (Luiz-Silva et al. 2006, 2008, Machado et al. 2008).

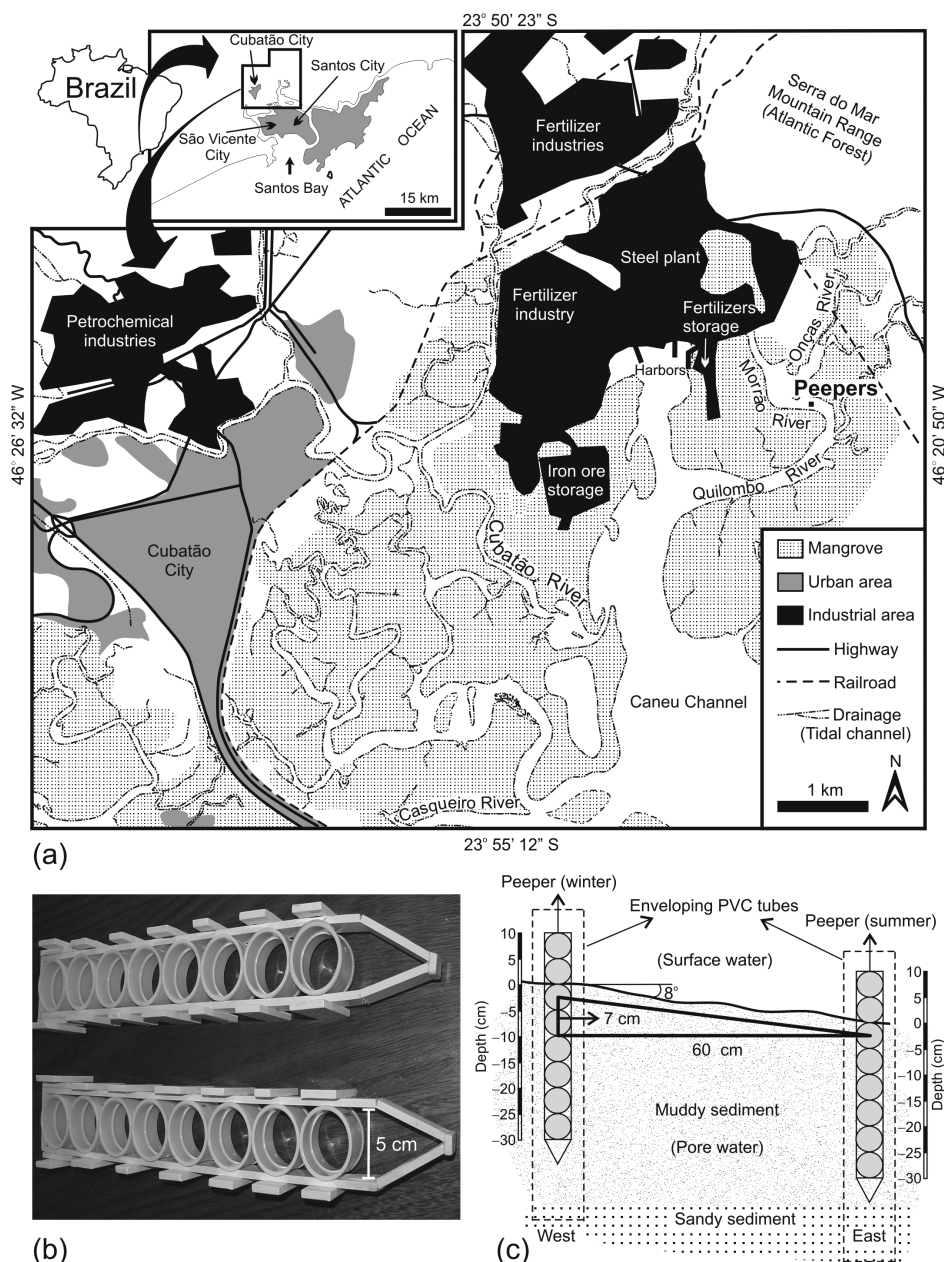


Fig. 1 – Location of the study site (a), peeper-type samplers used in this study (b) and their situation in the Morrão River (c). The enveloping PVC tubes were placed only at the moment of the recovery of the peepers, when the juxtaposed sediment columns were also recovered.

MATERIALS AND METHODS

SAMPLING

Sampling of surface and pore waters was carried out by using peeper-type diffusive devices (e.g., Bertolin et al. 1995, Jacobs 2002, Serbst et al. 2003). Sampling was carried out in 2007 during the summer (February-March) and winter (August-September), at the same site on the Morrão River right bank (23°52'37"S; 46°21'28"W). The sediment geochemistry of this site was previously well documented (Luiz-Silva et al. 2006, 2008, Machado et al. 2008).

All employed plastic ware was decontaminated with HCl 1% (for 24 h). The sampling device consisted of 40-cm length peepers, composed of eight stacked 50 mL cylindrical PVC capsules (Fig. 1b). After drying, 0.22- μm Millipore[®] membranes were glued with silicone to the extremities of each capsule, which were then filled with de-ionized water through a hole (sealed with silicon later). In order to reduce the amount of dissolved oxygen in the water as much as possible, the peepers were immersed in de-ionized water purged with N₂. After five days, the dissolved oxygen level dropped close to zero mg L⁻¹, as indicated by a HORIBA U22 dissolved oxygen sensor. Each peeper was wrapped with a nylon screen, in order to protect the membranes from animals and direct friction with sediments. Each peeper remained in the sediment for 20 days, a time interval considered as satisfactory for chemical equilibrium by ionic diffusion (Carignan 1984, Hesslein 1976). Cumulative rainfall in each sampling period was 200 mm (February-March, 2007) and 17 mm (August-September, 2007).

The peepers were embedded in the sediments so that the two first capsules remained free to make the ionic exchange with the surface water, as shown in Fig. 1b. The sampling site was permanently flooded, even at low tide. The distance between samplers was 60 cm, at a slope of ca. 8°, and there

was a sediment height difference between them of ca. 7 cm (Fig. 1c). After 20 days, the sampling device was removed during low tide, together with the enveloping sediment column where the ionic exchange took place. In order to collect this sediment column, a PVC tube of 10-cm diameter and 1.5 m length was used (Fig. 1c). The PVC tube was cut and sediments from the depth intervals containing each pore water capsule were collected. Water samples in each capsule were recovered with a plastic syringe and rapidly processed for analyses to minimize oxidation. Sediments were collected with a plastic spatula and stored in plastic bags. The water from the two first capsules of each peeper was taken as a single sample of the surface water.

SAMPLE TREATMENT AND CHEMICAL ANALYSES

Sediment samples were dried at 40 °C and pulverized in a mill with agate balls for total chemical analysis. The X-ray fluorescence spectrometry was employed for solid-phase chemical analyses using a Philips PW 2404 spectrometer. Pressed pastilles were prepared for the determination of some trace elements (As, Cu, Mo, Ni, Pb and Zn) using 9 g of sample and 1 g of wax (Potts 1992). For the determination of major and minor elements (Si, Al, Fe, Mn, Mg, Ca, Na, K and P) glass disks were prepared by ashing at 1000 °C. In this case, 0.4 g of sample, 6.0 g of lithium tetraborate and 0.2 g of lithium nitrate were used (Potts 1992). Duplicate analyses were carried out for all samples (relative percentage differences were within 8%) and certified reference materials were analyzed (SRM 1646 and GSD 12). Accuracies ranged from 90% to 105%. The loss-on-ignition method (550 oC ashing for 5 h) was used to estimate organic matter content (Heiri et al. 2001).

Pore water samples were separated into two aliquots. One was acidified (1.0% v/v) with high-purity nitric acid and analyzed by ICP-OES (Fe, Ni and P) or ICP-MS (Si, Al, Mn, Zn and As). For analytical quality control, SLRS-5 certified

reference material was used. The reproducibility of certified values was better than 90%, while accuracies ranged from 95% to 102%. Blanks were prepared with deionized water and introduced in the peeper PVC capsules. The blanks yielded results below the instrumental detection limits.

Physico-chemical measurements (pH, Eh, temperature and electrical conductivity) and ion analyses by liquid chromatography (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , Cl^- , SO_4^{2-} , NO_2^- , NO_3^- and PO_4^{3-}) were carried out using the non-acidified water sample aliquot. The ion analyses presented an ionic balance within 8%. The electric conductivity data were used to calculate the salinity of each sample according to APHA (1998). Measurements of Eh and pH were carried out by using platinum- and glass-combined electrodes, respectively. The Eh values were recalculated for the standard hydrogen electrode (Nordstrom and Wilde 2005).

DATA TREATMENT

The slope on the river bank surface that separates the peepers (Fig. 1c) was considered in the comparison of data collected in both seasons. In order to improve data comparability (summer vs. winter), depth profiles were drawn adopting a displacement of approximately 7 cm of the summer profile in relation to the winter profile (Fig. 1c). This adjustment was supported by the similarity of the Al and Si distribution patterns, which are conspicuous textural and mineral markers for sediments (Mason et al. 2004). The adjustment (superposition) of summer and winter profiles according to the Al and Si distribution allowed an appropriate comparison of data from equivalent sedimentary layers.

The possible differences in the results from different sampling periods were evaluated by using a one-way ANOVA. Possible associations between the elements were assessed using Pearson's correlation analyses. The threshold significance level was 0.05.

RESULTS AND DISCUSSION

COMPOSITION OF THE SEDIMENTS

The textural characteristics of the summer and winter profiles were similar, as indicated by visual examination, with the predominance of fine sediments, whereas sandy sediments occurred at deeper (>30 cm) layers (Fig. 1c). Nizoli and Luiz-Silva (2009), who studied the sediment texture by laser diffraction in profiles collected a few meters from the site of this study, observed fine-grained (silt + clay) contents varying between 90 and 100% in the first 30 cm depth of two cores. According to these authors, below this depth the sediments are in fact sandy (57 to 78% of sand fraction), as represented in Fig. 1c.

Fig. 2 shows the concentrations of organic matter (OM), major, minor and trace elements along the sedimentary solid-phase profiles. The estimated OM content showed a significant variability (ANOVA, $p < 0.05$) between the profiles investigated (Fig. 2b-j), although similar average values were found (Fig. 2a). In general, the major and minor element concentrations varied along the investigated profiles, but the average values were statistically similar (ANOVA, $p < 0.05$), except those for Ca, which showed higher levels in the winter profile. Some elements seem to represent the geogenic (natural) composition of the sediments, such as Al (2.81 to 4.29%), Si (8.51 to 18.8%), K (0.58 to 1.16%), Na (0.96 to 1.26%) and Mg (0.78 to 1.63%). Previous studies have shown that Al, K and Mg are elements of geogenic origin in the Santos-Cubatão estuarine system sediments specially related to the clay minerals and feldspars (Luiz-Silva et al. 2008, Machado et al. 2008). Sodium and Si are associated with these minerals and to other siliciclastic and halogenic (e.g., halite) components, which must be geogenic in this environment. Preliminary mineralogical data of the Morrão River sediments have quartz,

muscovite, illite, kaolinite and feldspars as the main minerals derived from weathering of host rocks (R.R. Assis et al. unpublished data). Additionally, halite (of marine source) is another mineral present in the sediment samples. This may

be the main reason why the Na–K relation (main markers for alkaline feldspars) is not prominent in the profiles of Fig. 2h–i.

It is important to note that the input from the iron and steel metallurgy (iron ore) and the fertilizers

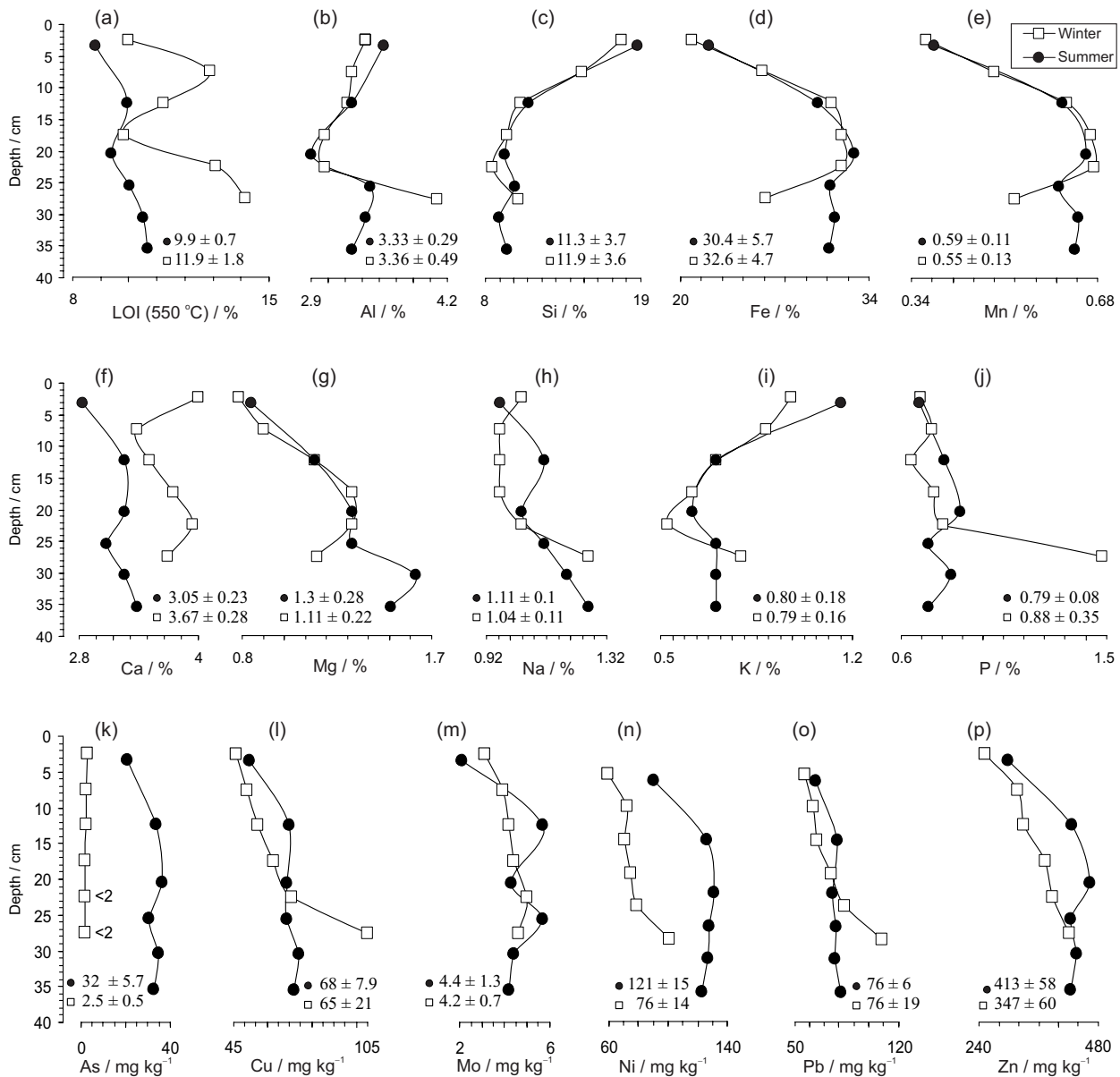


Fig. 2 – Total concentrations of (a) organic matter (LOI at 550 oC), (b) Al, (c) Si, (d) Fe, (e) Mn, (f) Ca, (g) Mg, (h) Na, (i) K, (j) P, (k) As, (l) Cu, (m) Mo, (n) Ni, (o) Pb and (p) Zn in the summer and winter profiles (averages \pm SD are shown).

industry (phosphatic ore and phosphogypsum) are the main anthropogenic sources in the area (Luiz-Silva et al. 2006, 2008, Machado et al. 2008). These sources explain the high Fe (range of 21.1 to 36.6%), Mn (0.35 to 0.67%), Ca (2.64 to 4.0%) and P (0.65 to 1.58%) concentrations in the investigated profiles (Fig. 2d–f, j) when compared to geogenic background values documented by Luiz-Silva et al. (2008) for the Morrão River sediments ($4.69 \pm 0.12\%$ Fe, $0.65 \pm 0.08\%$ Mn, $0.41 \pm 0.05\%$ Ca and $0.073 \pm 0.006\%$ P).

Among the trace elements investigated, average As, Ni and Zn concentrations in the summer profiles were significantly higher than those for the winter profiles (ANOVA, $p < 0.05$), whereas the average Cu, Mo and Pb concentrations were statistically similar (Fig. 2k–p). The trend for a higher concentration of trace elements in the Morrão River sediments during the warm and wet season has already been documented by Luiz-Silva et al. (2006) who attributed to physico-chemical factors (see discussion below) the main causes of concentration variations. In another tropical estuarine area (Hong Kong), Lau (2000) also observed a similar seasonality strongly dependent on the physico-chemical conditions.

SALINITY AND CONSERVATIVE ELEMENTS

Salinity and the concentrations of conservative elements (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- and Br^-) in pore and overlying surface waters are shown in Fig. 3a–i, which also shows average values (\pm standard deviation) for each profile. Conservative elements are directly related to the salinity of seawater and they occur in constant proportions throughout the oceans, although their concentrations may vary because of dilution or evaporative concentration (Faure 1998). In the study area, salinity was lower in the summer (17.5 ± 0.8 ‰) than in the winter (20.4 ± 1.5 ‰), in opposition to Na^+ , K^+ , Mg^{2+} and F^- concentrations.

Li^+ and Ca^{2+} concentrations varied less, whereas Cl^- and Br^- concentrations were higher in the winter. These results indicate that seasonal effects (mainly due to rainfall-influenced freshwater discharge) controlled the observed variability in pore water salinity. In addition to freshwater input, the saline water recharge during rising tides can be important in determining the salinity of the upper layers of ground water within coastal sediments, being the subterranean salinity plume extended with the tidal pressure rising (e.g., Santos et al. 2008). Therefore, it might be expected that tidal flooding affect the trace element geochemistry in pore waters (e.g., Santos-Echeandía et al. 2010).

Chloride is a conservative element (biologically and chemically non-reactive) that is generally used as a normalizer of other solutes to improve the identification of processes that consume or liberate these solutes and to identify origins of water (McGowan and Martin 2007). Fig. 4 shows the molar ratios between conservative elements and Cl^- and the average molar ratios between these elements and Cl^- for seawater (Taylor and McLennan 1985). Li^+/Cl^- ratios were uniform along the summer and winter profiles and similar to the average seawater Li^+/Cl^- ratio (0.04) (Fig. 4a). Lithium is an element free of anthropogenic influence in the study area (Luiz-Silva et al. 2006, 2008), and the Li^+/Cl^- ratio indicates that there are no in situ diagenetic reactions that can alter the composition of surface and pore waters. The other conservative elements normalized by Cl^- showed large variations. Na^+ and K^+ showed an identical behavior, with higher normalized values in the summer, in which the average seawater ratios were exceeded (Fig. 4b, c). Mg^{2+} and Ca^{2+} showed a similar behavior, but only in part of the summer profiles the ratios exceeded average seawater ratios (Fig. 4d, e).

Lower Na^+/Cl^- , K^+/Cl^- , $\text{Mg}^{2+}/\text{Cl}^-$ and $\text{Ca}^{2+}/\text{Cl}^-$ ratios than those for seawater in the winter suggest a stronger mixing with freshwater. Once

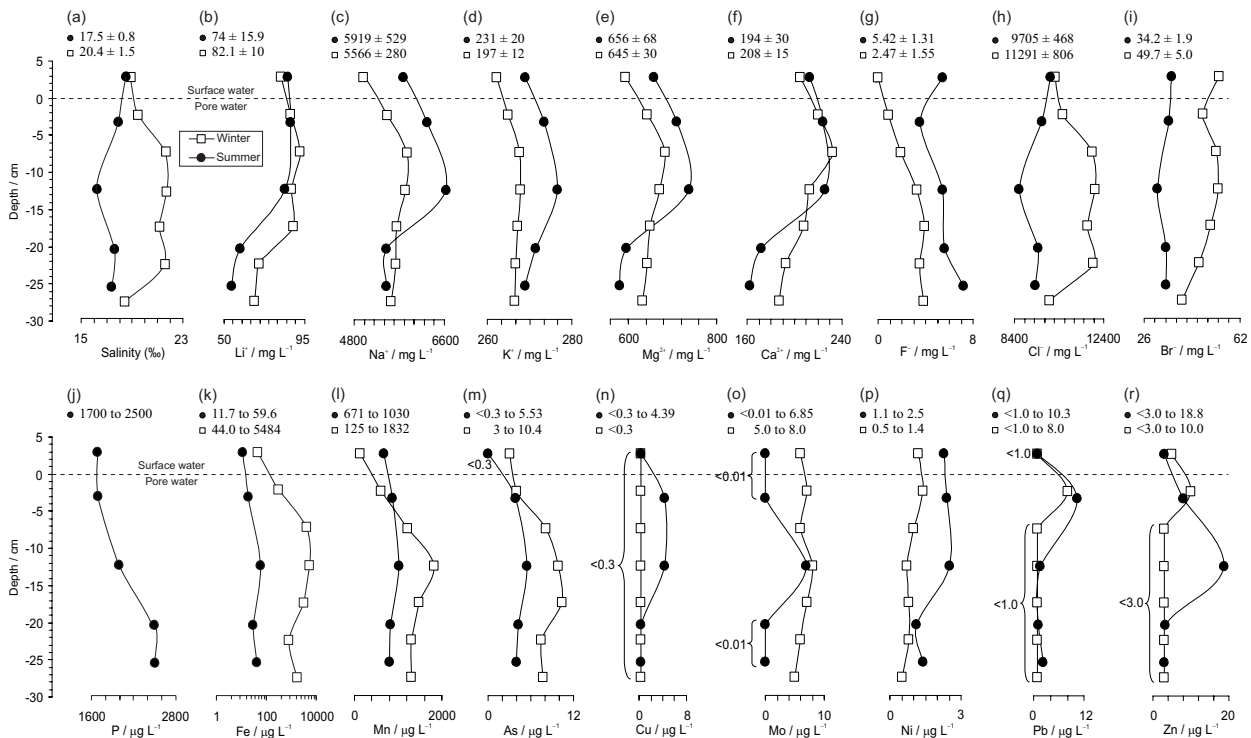


Fig. 3 – Pore water and surface water composition in the summer and winter profiles. Upper row: salinity (a) and concentrations of the conservative elements (b) Li^+ , (c) Na^+ , (d) K^+ , (e) Mg^{2+} , (f) Ca^{2+} , (g) F^- , (h) Cl^- and (i) Br^- . Lower row: concentrations of the non-conservative elements (j) P (only in the summer), (k) Fe (logarithmic scale), (l) Mn, (m) As, (n) Cu, (o) Mo, (p) Ni, (q) Pb and (r) Zn. Averages \pm SD are shown (pore and surface waters).

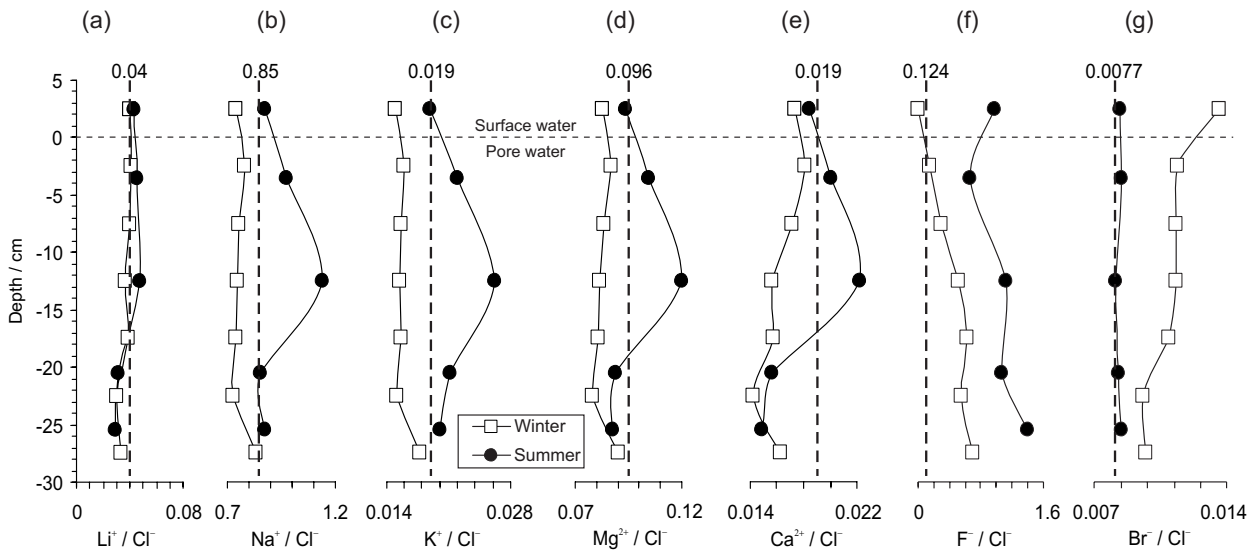


Fig. 4 – Pore water and surface water profiles of molar ratios of conservative elements to Cl^- in the summer and winter. (a) Li^+/Cl^- , (b) Na^+/Cl^- , (c) K^+/Cl^- , (d) $\text{Mg}^{2+}/\text{Cl}^-$, (e) $\text{Ca}^{2+}/\text{Cl}^-$, (f) F^-/Cl^- and (g) Br^-/Cl^- . The seawater average ratios are indicated by dashed lines.

low ratios have been found in both surface and pore waters, it is possibly affected by groundwater flow. Alternatively, diagenetic reactions may alter the cationic concentrations in the water, as well as the cationic exchanges in clay minerals and halides. In general, the equilibrium of Na^+/Cl^- , K^+/Cl^- , $\text{Mg}^{2+}/\text{Cl}^-$ and $\text{Ca}^{2+}/\text{Cl}^-$ ratios in surface waters with seawater was observed during the summer. In this season, this equilibrium was broken in pore waters with increases in element/ Cl^- ratios, specially between sediment top and 15 cm depth, possibly as a result of cationic desorption from minerals and/or dissolution of halides. These higher ratios along this depth interval can be explained by the longer residence time of the pore waters as a consequence of the lower permeability of the muddy sediments. Below the 15-cm depth, Na^+/Cl^- and K^+/Cl^- ratios decreased in the summer and reached values close to those for seawater, whereas $\text{Mg}^{2+}/\text{Cl}^-$ and $\text{Ca}^{2+}/\text{Cl}^-$ ratios remained below the average ratios for seawater and close to the values found in the winter. The decrease in these ratios below 15 cm in the summer profile can be explained by the influence of groundwater, which could flow in the sandy layer immediately below the profiles investigated (Fig. 1c).

The F^-/Cl^- ratios were usually higher than the average ratios for seawater (up to ca. 12 times) in the profiles studied, which suggests strong anthropogenic influence in the F^- concentrations in the summer and winter waters, with higher values registered in the warm season (Fig. 4f). The excess of F^- can be associated with the input from the fertilizer industries in the study area. This type of influence was shown by Grace et al. (2008) who studied the behavior of fluoride in the Babitonga Bay estuarine waters (Santa Catarina State, Southern Brazil) and found F^- concentrations from 1.0 to 136 mg L^{-1} .

Bromide followed Cl^- behavior (highest values in the winter; Fig. 3h, i), differing from F^- , alkaline and alkaline earth elements (Fig. 3b–g). The Br^-/Cl^- ratio in pore and surface waters revealed the equilibrium with seawater only in the

summer, whereas there was an excess of Br^- in the winter (Fig. 4g). This indicates a different temporal variability in Br^- and Cl^- input. Previous studies have not been conclusive, but Br^- is known to be much more involved in organic cycling than Cl^- (e.g., Mahn and Gieskes 2001), and its relationship with Fe and Mn cycling has been frequently found (e.g., Leri et al. 2010). In the present study, the concentrations of Br showed a behavior similar to Fe concentrations, with all values below the seawater value in the winter (seawater average = 67 mg L^{-1} ; 31 to 36 mg L^{-1} in this study), but more elevated levels were found in the summer (40 to 54 mg L^{-1}). The same mechanisms that promoted Fe enrichment may be also contributing to determine the Br^- excess in relation to Cl^- during the dry season. Additionally, increasing Br^- concentrations in pore waters may evidence that this anion was regenerated due to the diagenetic decomposition of organic matter (Mahn and Gieskes 2001, Martin et al. 1993). Unpublished data in the study area show that Br^- concentrations in surface water are higher in the winter (29 to 40 mg L^{-1}) than in the summer (18 to 27 mg L^{-1}), and further research is necessary to understand the mechanisms involved in Br^- cycling in this particular environment.

IONIC COMPOUNDS, pH AND Eh

The pH, Eh, SO_4^{2-} , $\text{SO}_4^{2-}/\text{Cl}^-$ molar ratios and NH_4^+ results are shown in Fig. 5, as well as the average values (surface and pore waters) in each season (\pm standard deviation) and the $\text{SO}_4^{2-}/\text{Cl}^-$ molar ratio in seawater (0.05; based on Taylor and McLennan 1985). Some anionic compounds that are not shown (NO_2^- and NO_3^-) presented concentrations below the detection limits of the method (< 0.002 and $< 0.01 \text{ mg L}^{-1}$, respectively), reflecting the reducing nature of the environment, as corroborated by elevated NH_4^+ levels (see below).

The pH of surface and pore waters (Fig. 5a) was slightly acid to neutral in the winter ($6.66 \pm$

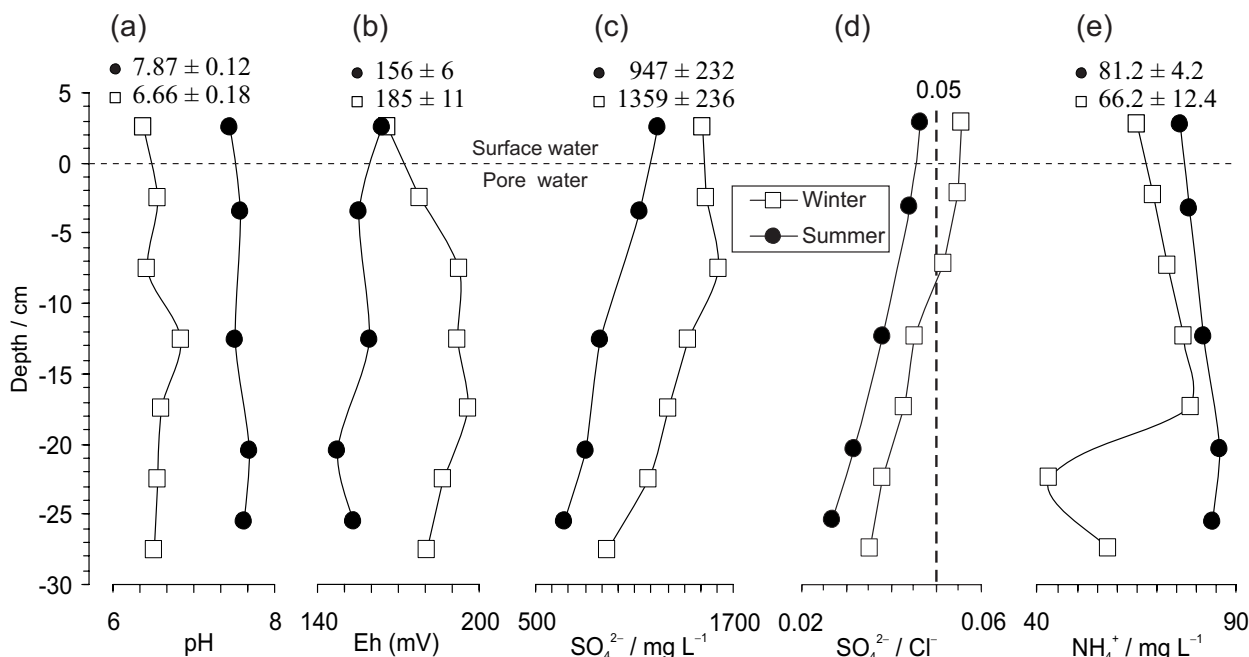


Fig. 5 – Values of (a) pH, (b) Eh, (c) SO_4^{2-} , (d) $\text{SO}_4^{2-}/\text{Cl}^-$ (the seawater average value is indicated by a dashed line) and (e) NH_4^+ in pore and surface waters in the summer and winter. The average pH, Eh, SO_4^{2-} and NH_4^+ concentrations (\pm standard deviation) in each profile (pore and surface waters) are indicated.

0.18) and alkaline in the summer (7.87 ± 0.12). A more oxidizing condition in the winter sampling may possibly explain this difference, since it can promote sulfide oxidation, causing lower pH (Gueiros et al. 2003, Otero et al. 2006). In general, a slight tendency for higher pH values with depth was observed in both profiles, and this trend was also observed in sedimentary profiles in the Cananéia estuary (São Paulo State) by Ferreira et al. (2007). An increase in pore water alkalinity with increasing depth could be expected due to organic matter decomposition processes (Aragon et al. 1999, Gueiros et al. 2003).

The Eh values of surface and pore waters were suboxic in both seasons (Fig. 5b). No seasonal variation of redox potential was observed in the surface water, but Eh varied significantly in the pore waters, with higher values in the winter (185 ± 11 mV) in comparison with the summer (156 ± 6 mV). In the summer, a trend of Eh decreasing with depth

was observed. Differently, a trend of increasing redox potential occurred up to 20 cm of depth in the winter. Below this depth, the Eh values decreased with depth. The most probable explanation for the Eh differences between seasons is the expected enhancement of respiratory microbial activity in the warmer period, resulting in a larger consumption of electron acceptors such as dissolved oxygen and sulfate (see discussion below). The redox potential pattern seen in the summer profile is in agreement with that reported by Ferreira et al. (2007) in Cananéia estuary sediments (São Paulo State), which found more varied values (-140 and 366 mV). A similar behavior was observed in other tropical (Bava and Seralathan 1999) and temperate climate (Canário et al. 2003) estuaries. Nizoli and Luiz-Silva (2009) found Eh values more reducing in the summer (12 ± 35 mV) than in the winter (57 ± 39 mV) in sediment cores from the Morrão River, which is in agreement with the present study.

Sulfate concentrations were lower in the summer and decreased with depth in both seasons (Fig. 5c). The decrease can be interpreted as a consequence of a higher anaerobic activity in the deepest regions of the sediment (Otero et al. 2006). Regarding the SO_4^{2-} seasonal variation, it is likely that sulfate-reduction is a process particularly important during the summer, when the microbiological activity is more intense. This is consistent with the negative correlation between pH and Eh ($r = -0.996$; $p < 0.001$; $n = 5$) and the SO_4^{2-} deficit in the summer samples in relation to seawater (Fig. 5d). The inverse relationship between pH and Eh is consistent with the redox process and has been systematically shown in other studies (Madureira et al. 1997, Otero et al. 2006). However, the correlation between pH and Eh in the winter samples was not significant. Otero et al. (2006), studying the pore waters in the Cananéia estuary (São Paulo State) during the winter, indicated that oxidation of sulfidic phases (sediment and water) can be an important factor regulating pH levels.

The NH_4^+ levels were very high and seasonally contrasting ($81.2 \pm 4.2 \text{ mg L}^{-1}$ in the summer and $66.2 \pm 12.4 \text{ mg L}^{-1}$ in the winter; Fig. 5e). In general, the values increased with depth (except in the deeper samples of the winter profile), a fact also observed by Mozeto et al. (2001) in the sedimentary environment of the Guarapiranga reservoir (SE Brazil). The NH_4^+ seasonality shown in Fig. 5e was also observed by Moser et al. (2005) in the Santos Channel (close to the study area), though the values were very low ($0.45 \pm 0.02 \text{ mg L}^{-1}$ in the summer and $0.04 \pm 0.02 \text{ mg L}^{-1}$ in the winter for overlying surface water). A thesis on the Santos Bay environmental quality (Abessa unpublished data) also found low NH_4^+ values (up to 1.21 mg L^{-1}) in overlying surface water. High NH_4^+ concentrations found in the present study must be linked to anthropogenic contributions (fertilizers industry) and a release from pore to surface water,

which must be diluted towards the Santos Bay. Very high values (up to $4399 \text{ } \mu\text{M}$ or 79.4 mg L^{-1} NH_4^+) were also found in an estuary of SE India and attributed to a contamination by fertilizers (Rajkumar et al. 2008).

NON-CONSERVATIVE ELEMENTS IN WATER

The concentrations of some non-conservative elements in surface and pore waters of the summer and winter profiles (P, Fe, Mn, As, Cu, Mo, Ni, Pb and Zn) are presented in the Fig. 3j-r. Non-conservative concentrations ratios to chloride are not constant (Faure 1998). Other non-conservative element concentrations (e.g., Al and Si) were below the ICP-MS detection limits ($26 \text{ } \mu\text{g L}^{-1}$ Al; $2 \text{ } \mu\text{g L}^{-1}$ Si). Despite these elements having been detected in the sediments (Fig. 2), the low concentrations in water samples are explained by their low solubility in the pH conditions found in the study area (6.44 to 8.03), since Al is more soluble in pH levels < 4.6 and > 8 , whereas Si is more soluble in pH levels > 9 (Faure 1998).

Dissolved P data were determined only for the summer sampling, ranging between $1,700$ and $2,500 \text{ } \mu\text{g L}^{-1}$. The lowest value was found in the surface water, and increasing values occurred in pore water with increasing depth (Fig. 3j). Many studies have shown that the behavior of P in coastal sediments is related to the iron redox cycle (e.g., Sherman et al. 1998). Under more oxidizing conditions, phosphate is strongly adsorbed by iron oxy-hydroxides, whereas more reducing conditions favor its mobility from the sediments to the pore waters (Bava and Seralathan 1999). The trend of a negative correlation between P and Eh ($r = -0.77$; $n = 5$; significant only at $p < 0.12$) supports this hypothesis.

The well-known redox sensitive behavior of metals like Fe and Mn has favored the evaluation of their diagenetic processes (e.g., Santos-Echeandía et al. 2009). Beck et al. (2008) recently demonstrated that pore water levels of Fe near $35 \text{ } \mu\text{M}$ ($\sim 2,000 \text{ } \mu\text{g L}^{-1}$) can occur within surface

layers of a tidal flat in the German Wadden Sea, in which pore water flow and exchange are significant and affected by tidal driven pressure gradients, besides diffusion. The behavior of Fe in surface and pore waters (Fig. 3k) seems to be strongly affected by seasonality (or its coupling with tidal influence), reaching a remarkably higher concentration range in the winter (44 to 5,484 $\mu\text{g L}^{-1}$) than in the summer (11.7 to 59.6 $\mu\text{g L}^{-1}$). Manganese (Fig. 3l), As (Fig. 3m) and Mo (Fig. 3o) concentrations also exhibited a trend of increasing in the winter, but in a much lower extent. A consistent trend of higher concentrations in the summer was observed for Ni (Fig. 3p) in surface and pore waters. Copper and Zn (Fig. 3n,r) showed much higher values in the summer for at least one depth interval. Lead profiles could not be compared, since most levels were not detected.

The variations in P, Fe, Mn, As, Cu, Mo, Ni, Pb and Zn levels in surface and pore waters of the study area is influenced by several binding phases in the sediments (e.g., organic matter, oxides, sulfides, carbonates and aluminosilicate minerals) whose relative abundance may be influenced by physical-chemical conditions. These conditions may be affected by seasonal variability in rainfall and freshwater discharge (e.g., Gueiros et al. 2003), which may also influence the distribution of trace elements near the sediment-water interface (e.g., affecting concentrations in surface water and pore water advection and diffusion). Acid-volatile sulfides (AVS) are considered as particularly important phases that can influence the metal distribution in anoxic/suboxic conditions (Di Toro et al. 1990, Burton et al. 2005, Machado et al. 2010). In sediments from the study area, Nizoli and Luiz-Silva (2009) concluded that the AVS levels are lower in the summer ($0.87 \pm 1.1 \mu\text{mol g}^{-1}$) than in the winter ($5.8 \pm 9.2 \mu\text{mol g}^{-1}$). Higher AVS levels in the winter can contribute to explain the lower pore water levels of Cu, Ni and Zn in this period. Although additional studies are necessary, the mechanism involving metal

binding to reactive sulfides seems to be important in determining the retention of these elements within the sediment solid phase.

CONCLUSIONS

The estuarine sediments from the Morrão River presented many anomalous constituents of solid-phases and pore waters attributable to industrial point sources, as recorded mainly for F^- , NH_4^+ , Fe, Mn and P. Iron, Mn and P anomalies were consistent with previous studies in the same site, whereas the cationic (NH_4^+) and anionic (F^-) anomalies were recorded for the first time in this contamination hot spot within the Santos-Cubatão estuarine system. A seasonal variability in the anomalous concentrations in both solid and dissolved phases was evidenced, particularly for the observed higher levels of Fe and lower levels of F^- and NH_4^+ during the winter. Seasonal variability in the river water discharge was evidenced as an important factor affecting pore water composition, while tidal water and groundwater mixing were considered additional influences. Higher pore water levels of potentially toxic trace metals (Cu, Ni and Zn) during the summer were also recorded. Consequently, the risks of surface water concentration increase in the case of diffusion or advection from pore water are likely time-dependent, being pore water chemistry influenced by a coupling between seasonal variability in freshwater input (surface and ground waters) and tidal effects.

ACKNOWLEDGMENTS

The authors are grateful to two anonymous reviewers for their contributions to improve the manuscript quality and to Dr. G. M. Garda for assistance with the text. We thank the Fund for Research and Extension of the State University of Campinas, the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Process No. 08-11511-8) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support.

RESUMO

A composição geoquímica das águas intersticiais de sedimentos foi estudada em comparação com a composição das partículas sedimentares e de águas superficiais em um estuário de uma das áreas mais industrializadas da América Latina (sistema estuarino de Santos-Cubatão, sudeste do Brasil). Águas intersticiais e superficiais apresentaram altos níveis de F^- , NH_4^+ , Fe, Mn e P, devido a duas fontes industriais pontuais. No verão, quando as razões SO_4^{2-}/Cl^- sugeriram aumento na redução do sulfato, os níveis mais elevados de alguns metais dissolvidos nas águas intersticiais (como Cu e Ni) foram atribuídos à dissolução reductiva de fases oxidadas. Os resultados sugerem que os riscos de aumento nas concentrações das águas superficiais por difusão ou advecção das águas intersticiais provavelmente dependem de influências conjuntas do aporte de águas de maré e águas subterrâneas.

Palavras-chave: anomalia geoquímica, contaminação industrial, química de águas intersticiais.

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