

# IONIC BEHAVIOR AND ITS ASSOCIATION WITH WASTE STEEL INDUSTRY IN MANGROVE ESTUARINE SYSTEM OF SANTOS - CUBATAO / SP

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**RESUMO** - O sistema estuarino de Santos, situado em Cubatão, representa um dos mais importantes exemplos brasileiros de degradação ambiental por poluição de origem industrial do país. Entre as atividades industriais geradoras de resíduos do estuário, destaca-se a indústria siderúrgica, de especial interesse nesse trabalho. Para produzir aços com propriedades especiais, então é necessário adicionar elementos como manganês, cobre e chumbo que auxiliam na eliminação de impurezas. Os insumos utilizados nos processos siderúrgicos resultam em subprodutos diariamente descartados em área de manguezal que, como se sabe, são sistemas funcionalmente complexos, que se desenvolvem na zona de contato das águas marinha e fluvial. A área escolhida para desenvolver este trabalho serviu para descarte de resíduos durante um período de aproximadamente 30 anos e somente a partir da década de 90. Desta forma não há, portanto, possibilidade de se ter comportamento uniforme relacionado à disponibilidade iônica com o meio ambiente. Neste trabalho tratou-se do comportamento hidrogeoquímico de íons de metais pesados num Aterro Industrial localizado em Cubatão, SP e foram estudados também os mecanismos de fixação e mobilidade de íons poluentes desde a disposição dos rejeitos nos sedimentos de manguezal até sua influência nas águas superficiais, subterrâneas e em sistemas solos/sedimentos.

**Palavras-Chave:** solo, sedimento, manguezal, metais pesados, Cubatão

**ABSTRACT** - The estuarine system of Santos, in Cubatão, is one of the most important examples of environmental degradation by industrial pollution in Brazil. Among the industrial activities that generate waste in the estuary is the steel industry, or particular interest in this study. The molten iron obtained by cooling this mixture is very brittle and cannot be used. The inputs used in the steel making processes result in byproducts discarded daily in mangrove areas that, as it is known, are complex ecosystems that grow in the zone where inland and marine waters meet. The area selected for this study has been used as a waste disposal site for approximately 30 years. Only in the nineties, after the establishment of a state's policy on environmental protection, required the installation of an industrial landfill. This paper addresses the hydrogeochemical behavior of heavy metal ions in an industrial landfill site located at Ilha dos Amores, Cubatão, São Paulo. Also, ion activity in this ecosystem, including disposal of waste in the sediments of the mangrove and its influence on surface water, groundwater (saturated and non saturated zones) and in soil/sediments (mangroves) were studied.

**Keywords:** soil, sediment, mangrove, heavy metals, Cubatao

## INTRODUCTION

In the estuarine system of Santos and São Vicente there are approximately 43% of the 231 km<sup>2</sup> of the mangrove areas of the Coast of São Paulo State (Herz, 1991) and in the City of Cubatão. Only 17% of the coverage area of mangroves is in good condition, that is, 29 km<sup>2</sup>.

Mangrove can be defined as a transitional ecosystem between marine and terrestrial environments in the intertidal zone of estuaries. In the Brazilian coast they can be found from

the far north, in the Oiapoque River (04° 20'N) to Laguna (28° 30's) in Santa Catarina's south-central-coast region (Amaral, 2003). The substrate of this ecosystem consists of muddy sediments rich in organic matter where the typical development of flora occurs, represented by the association of trees and shrubs (Ex: *Rhizophora mangle*, *Avicennia sp*) adapted to variations in salinity and low levels of oxygen (Suguio, 1998).

The estuarine systems of Santos and São Vicente, inserted in the Metropolitan Region of the *Baixada Santista*, in the State of São Paulo, are one of the most important examples of environmental degradation in Brazil caused by air and water pollution of industrial origin in coastal environments. The industrial Complex of Cubatão is considered a major contributor to the degradation process in the *Baixada Santista* region. Degradation occurs as a result of backfilling of mangrove areas for urban and industrial occupation, release of toxic effluents, improper disposal of industrial and domestic solid waste, as well as frequent accident hazards involving oil spills, toxic substances, etc.

Among the industrial activities that generate waste in the Industrial Complex of Cubatão it is worth mentioning the steel industry, of particular interest in this study, which releases to the environment a wide variety of pollutants, including heavy metal ions. The disposal of solid waste originating from different steel production processes, has been occurring for more than three decades in the mangrove areas of Cubatão, São Paulo and due to legal requirements, such waste was the basis for the establishment of an industrial landfill site only in the 90s.

The steel plant in the study area uses iron ore from hematite processed in blast furnaces, to which limestone and coke are added.

Concomitantly to iron ore reduction reactions, due to impurities such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  other reactions occur which produce  $\text{CaO}$ ,  $\text{CO}_2$  and  $\text{CO}$ , as well as  $\text{CaSiO}_3$  and  $\text{Ca}(\text{AlO}_2)_2$  (Sienko, 1977). For every ton of iron produced, half-ton slag is formed (Sienko, 1977; Burgess, 1995).

The crude product leaving the blast furnaces, containing approximately 4 % carbon, 2% of silicon, traces of sulfur and even 1%

phosphorus and manganese is called pig iron or cast iron. Because of its difficult removal in purification operations and because it causes breakdown of steel when worked, sulfur is one of the most undesirable impurities. This is the most common method of obtaining metallic iron and corresponds to 96% of the world production of iron. The energy cost is high, and without an adequate waste management policy, there will be a high negative environmental impact (Kroschwitz, 1995), especially because of the presence of pollutant metal ions, the aim of the present study.

The selected study area is the industrial landfill at *Ilha dos Amores*, Cubatão, São Paulo, which has been active for around 20 years, on a rectangular floor area of 6000 m<sup>2</sup> (200m x 300m). The industrial landfill is located in a mangrove area where significant physico-chemical phenomena are observed in the liquid column, in sediments and in the contact surface of these two media.

Although the industrial landfill site was designed to accommodate inert waste, receiving about 11,000 tons/month of industrial waste, it is referred in the Register of Contaminated LAND provided by CETESB as contaminated by heavy metals and other substances (CETESB, 2007).

The harmful effects of heavy metal ions are widely known, and, thus, it is not necessary to justify studies on the environmental impact of these ions. The importance of and the need for an in-depth understanding of the behavior of such waste in relation to environmental impact is therefore evident. Studies like this one allow understanding the hydrogeochemical processes associated to transformations, which are a consequence of disposal of such waste on sediments of mangrove ecosystems, as well as in adjacent surface and groundwater.

## GEOLOGY

The study area is located over areas of the Holocene, of the Quaternary Period. Quartz, kaolinite, gibbsite, illite, phlogopite, montmorillonite and feldspar occur in isolated spots within the sediments, and secondarily heavy metals such as epidote, sillimanite, amphiboles and pyroxenes can be found.

Gneisses of the Coastal Complex, very close to the study area, which eroded and formed higher ground were added to these sediments (Ferrer, 2001). According to Rodriguez (1998) this Coastal Complex is formed by migmatites, porphyroblast granitic gneisses, biotite-gneisses and peraluminous gneisses. These are sandy

and silty-sandy sites with a large amount of organic matter derived from the accumulation and decomposition of plant mangrove species.

Most sedimentary deposits of *Baixada Santista* are directly related to transgressive episodes, generating two sediments: Pleistocene sediments deposited in mixed environments continental and Holocene consisting of clays and sands containing shells deposited at sites of erosion of pleistocene sediments (Fluvial-lagoon and bay sediments). The mangroves, sedimented on these sites, can be found on the

banks and bottoms of channels, tidal arms and drainage networks. They can sometimes exhibit chaotic mixtures of sandy clays and clayey sands (Massad, 1999)

The waste deposits of the Encosta are essentially made of sludge sand, pebbles and blocks coming from the intense and long process of differential erosion that has accumulated over time large volumes of debris on the slopes and the foot of Serra do Mar (FUNDUNESP, 2000).

## HYDROGRAPHY AND HYDROGEOLOGY

The rivers that bathe Cubatão are short and torrential due to the proximity of *Serra do Mar*. Due to the almost nonexistent slope in the sedimentary plane that separates Serra do Mar from the coast, the alluvial process is very intense, and, thus, meanderings resulting from the combined action of erosion/accumulation of fluvial waters and mangroves are formed.

The Cubatão Basin has approximately 180 km<sup>2</sup>, and in the study area the fluvial network encompasses Cubatão River which flows into Canal Piaçaguera through two arms (western and eastern): the Piaçaguera and Mogi rivers, interconnected through a channel.

Runoff from *Serra do Mar* and underlying nearby hills recharge the aquifers, and their waters are discharged at rivers bordering the Atlantic Ocean. The intervention between aquifer waters and the ocean occurs through

advection and effusion, generating a saline wedge.

The study area has typical mangrove vegetation and is influenced by tidal fluctuations with fluvial dynamics of drainage type. The presence of waters of different chemical natures associated to effluvium processes (runoff, stream where waters recede) and outflow (river discharge) that characterize the region cause the free surface waters and upper groundwater brackish.

The changes observed in the potentiometric surface indicate that groundwater flow occurs radially, from the central area to the surrounding water bodies, represented by Piaçaguera Channel and Cubatão River. Influence of tidal fluctuations in the water table behavior was also observed.

## GEOMORPHOLOGY

The area is included in the Morphostructural Units Cenozoic Basins, Morphostructural Subunit *Planície Litorânea Santista* (Ross & Moroz, 1997).

The Coastal Planes (*Planícies Litorâneas*) have altitudes 0 - 20 meters and slopes of less than 2%. They are composed predominantly of

unconsolidated sediments and sandy/loamy (clayey) river sediments also unconsolidated, as well as gravel.

The soils are hidromorphic Podzol and hydromorphic. These are areas with poor drainage density, with meandering and anastomosed style (Ross & Moroz, 1997).

## CLIMATE

The region of Cubatão has an annual rainfall greater than the average recorded in the State of São Paulo (1443 mm). The dry period in the state occurs from April to September, the month of August being the driest (monthly

rainfall less than 100 mm). The wet season is October-March, January being the wettest month with an average of 300 mm. In 2009, the rainfall was 26% higher than the historical average of the previous 14 years (1817 mm).

The short and long term heavy rains are highly favorable to the reduction of air pollution, causing deposition of particulates and relative reduction in the concentration of pollutant gases.

The high relative average humidity of air throughout the year (70% to 90%) in the Cubatão region is unfavorable from the point of view of air pollution. The region has high rainfall, especially during the summer months, ranging from 2000 to 2500 mm (CETESB, 1988).

According to the *Carta do Meio Ambiente da Baixada Santista* (environmental declaration

of *Baixada Santista*), the area of Cubatão is under the influence of subtropical, polar and equatorial continental air masses.

The transitions between winter and summer are very short, without autumn and spring. In turn, radiation-type thermal inversions are relatively frequent.

The movement of surface winds during the day is preferably SW to NE, favoring the transport and accumulation of pollutants in the valley. At night, the predominance of surface winds occurs in the NE-SW direction.

## MATERIALS AND METHODS

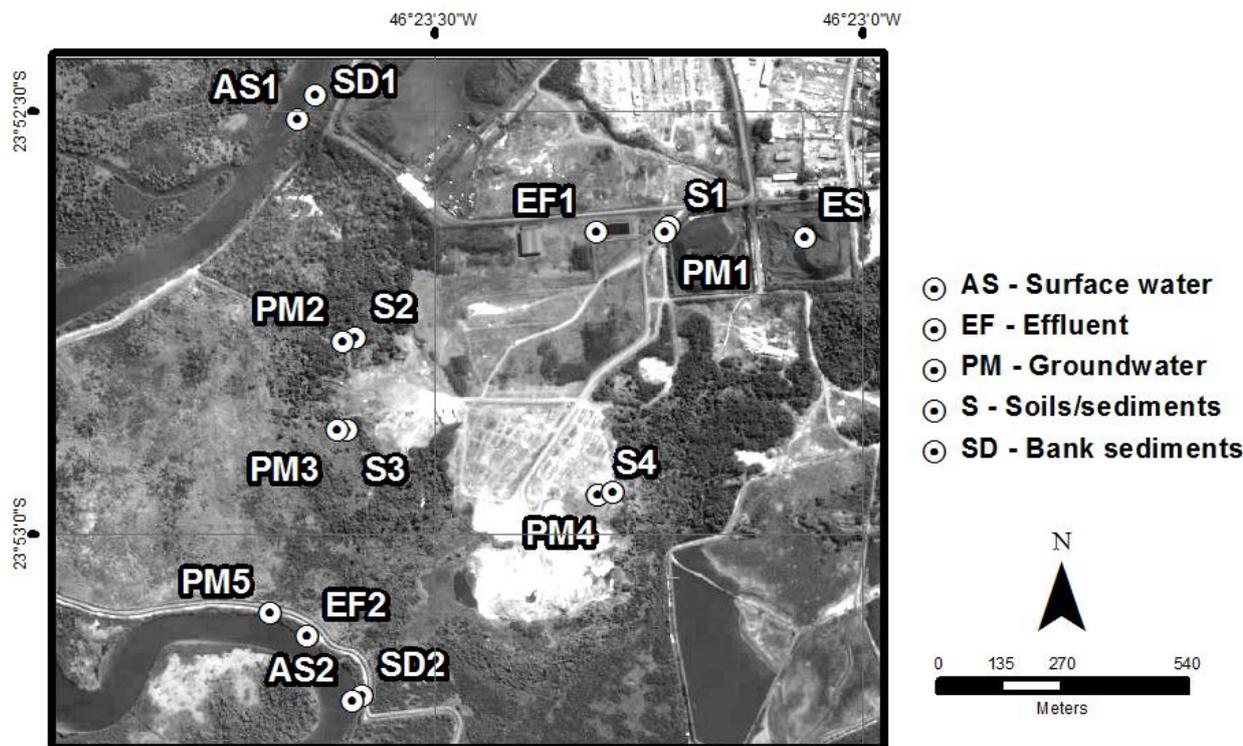
The study of the behavior of pollutant ions associated to the industrial landfill site of the steel plant involved field and laboratory work.

The study area is located in a mangrove ecosystem and has been used as a landfill disposal of steel industry waste for more than 30 years. For a better understanding of the characteristics of the solid material mixture of the mangrove/residues the words soil/sediment will be used when referring to the material collected in the landfill area. It is necessary to clarify that, while serving as substrates for the growth of typical mangrove vegetation, the waste material is composed of materials that has been discarded since the establishment of the steel plant in the region and used to cover almost the entire area. It is known that mangroves have a unique ability to adapt to stressful environments, and the occurrence of

this vegetation under the discarded material is evidence of its adaptive ability, which will be discussed in further studies.

The essential raw materials used to produce steel: iron ore (Mi), coal (CM), coke (CQ) and slag (ES) were sampled. Besides being disposed in the whole site of the company (former mangrove) for more than three decades as landfill material, the slag is reused in the manufacture of Portland cement and as railway track ballast.

Samples of soils/sediments associated to the monitoring wells (S1, S2, S3 and S4), bank sediments (Sd1 and Sd2), effluent from the landfill (EF1 and EF2) and samples of groundwater (PM1, PM2, PM3, PM4 and PM5) and surface water of the Piaçaguera River (As1 and As2) were collected in strategically selected points (Figure 1).



**Figure 1.** Location of sampling points in the industrial landfill.(Google 2007).

The landfill cell has a 1 m thick compacted clay bottom liner with a  $K=10^{-7}$   $\text{cm s}^{-1}$  degree of permeability. The second impermeable layer is a high density polyethylene geomembrane (HDPE). Above this layer, covering the entire area, there is a plastic geogrid for drainage, which, in turn, receives a new coating with HDPE geomembrane.

Surface soils/sediments of anthropogenic origin from the landfill (S1 to S4), associated to the monitoring wells (PM1 a PM4) were sampled.

Sediments Sd1 and Sd2 were sampled on the banks of Piaçaguera River, in the same sites of collection of surface water samples (As1 and As2).

The sludge (LD) deposited at the bottom of the effluent storage tank (EF1), which percolates the cell of the landfill, was also collected. This sludge is approximately 0.10 m thick, corresponding to a volume of 8 m<sup>3</sup>.

Solid samples (soils, sediments and waste were stored in plastic bags properly sealed and labeled for subsequent analytic treatments.

Measurements of pH and Eh were performed in situ, with glass electrodes and platinum combine (Multiline P3 – WTW brand) during the collection of water and effluent samples). Parameters such as temperature and electrical

conductivity were read with Multiline electrodes (P3/oxi/cond., WTW brand) and alkalinities were determined using a methodology described by Hypolito, et al.(2007, 2011).

Upon collection the samples were filtrated (millipore 0.45 $\mu\text{m}$ ), wrapped in plastic bottles, acidulated with HNO<sub>3</sub> to pH < 2, and some samples were kept without preservatives. All samples were kept in a thermal insulated box at 4°C.

EF1 and EF2 effluents were collected. The first effluents are generated in the cell of the landfill, drained and stored in a tank for treatment. The EF2 effluents that percolate the landfill site (EF2) are also drained, captured by underground pipes and discarded directly on the right bank of Piaçaguera River.

The samples of groundwater were collected from monitoring wells PM1 to PM5 drilled directly at strategic points of the landfill.

Finally, in the search for sampling points representative of the surface water of Piaçaguera River samples were collected at points near the landfill: one point upstream (As1) and another one downstream (As 2) within the limits of the landfill.

For the chemical and mineralogical characterizations, the solid samples were air

dried, the soil clods were loosened and broken and homogenized. Then, the samples were subjected to chemical analyzes of the major elements and to X-ray fluorescence (FRX) for trace elements, mineralogical analyzes by X-ray

diffraction (DFX), granulometric analyzes and Cationic Exchange Capacity (CTC).

In liquid samples, cations were analyzed by Atomic Absorption Spectrophotometry (Cg AA 7000 BC) and anions were analyzed by Liquid Chromatography (Dionex-2010i).

## RESULTS AND DISCUSSIONS

The stability of the ionic components of natural waters is closely linked to and dependent on parameters such as pH, redox potential, electrical conductivity and alkalinity shown in Table 1.

The pH values of groundwater were practically constant, slightly acid, except for the sample of well PM 4 (pH 12,44) due to the nature of the materials associated, composed of slag deposited at the time of collection.

The strong smell of H<sub>2</sub>S in almost the entire landfill, though far from the preserved

mangrove, indicates the presence of sulfides, the main causes of reducing conditions of waters in the drilled wells.

The theoretical values of salinity, calculated by electrical conductivity, allow the classification of groundwater as salty (> 3000 mg dm<sup>-3</sup>) (CONAMA, 2005), characteristics of the mangrove ecosystem.

The conditions of pH monitoring wells indicate predominance of bicarbonate (HCO<sup>3-</sup>) except in well PM 4 where carbonates are stable (Hypolito et al., 2011).

**Table 1.** Chemical and physico-chemical parameters of effluents EF1 (treatment tank) and EF2 (water for disposal in Piaçaguera River), of Waters from monitoring wells (M1 to M5) and from Piaçaguera River (As1 – upstream and As2 - downstream).

Samples	pH	Eh (V)	T (°C)	CE (mS cm <sup>-1</sup> )	alkalinity (mg dm <sup>-3</sup> CaCO <sub>3</sub> )
EF1	9.74	0.02	22.30	0.22	30.00
EF2	6.79	0.03	22.60	8.26	43.00
PM1	6.85	-0.06	26.20	20.90	138.00
PM2	6.47	-0.33	24.30	23.50	13.00
PM3	6.78	-0.31	23.80	26.50	190.00
PM4	12.44	0.38	26.60	8.91	406.00
PM5	6.89	-0.08	24.40	18.30	150.00
As1	7.97	0.15	21.00	27.80	62.00
As2	7.31	-0.20	22.70	30.30	26.00

Regarding the samples of surface waters, it was found that the sample collected from Piaçaguera River, upstream of the landfill site (As1), the pH value was higher than that of the downstream sample (As2). However, the bicarbonate ion is the dominant form in these pH values. Both showed high electrical conductivity levels.

In sample As2 the redox potential indicated a reducing environment, characteristic imposed by the effluent generated in the landfill site and disposed directly in Piaçaguera river.

The effluents had different properties: The material discarded in Piaçaguera River (EF2) has lower pH because of the movement of liquid in close contact with the atmosphere and transfer of carbon dioxide from the atmosphere to the solution; acid pH favors the occurrence of higher concentrations of salts in solution, as evidenced by the higher value of electrical conductivity.

Analytical results of surface water, groundwater and effluent collected in the area of the industrial landfill site are shown in tables 2 and 3.

**Table 2.** Chemical analyzes of the cations of interest ( $\text{mg dm}^{-3}$ ) of the industrial landfill site: samples of effluents (EF), of monitoring wells (PM) and surface waters (As). The guiding values are also presented.

Analyte	EF1	EF2	PM1	PM2	PM3	PM4	PM5	As1	As2	CETESB <sup>1</sup>	Port.518 <sup>2</sup>	CONAMA <sup>3</sup>
Fe <sub>(t)</sub>	nd	0.04	nd	0.13	0.10	nd	nd	0.05	0.06	0.3	0.03	15
Mn <sup>2+</sup>	nd	1.17	0.96	0.12	0.60	nd	0.95	0.05	0.17	0.4	0	1
Cu <sup>2+</sup>	nd	nd	nd	nd	Nd	nd	nd	0.03	0.03	2	2	1
Pb <sup>2+</sup>	nd	0.21	0.18	0.1	0.33	0.19	0.18	0.03	0.41	0.01	0.01	0.5
Zn <sup>2+</sup>	nd	0.26	0.04	0.02	0.08	0.02	0.02	0.11	0.09	5	5	5

nd: undetected.

<sup>1</sup>: Groundwater guiding values and principles of intervention in the State of São Paulo – CETESB (2005);

<sup>2</sup>: Maximum guiding values allowed established by Ordinance 518 – Brazilian Ministry of Health;

<sup>3</sup>: Maximum value allowed for effluent discharges in water bodies. CONAMA Resolution No 430/2011.

**Table 3.** Analytical data from anions of interest ( $\text{mg dm}^{-3}$ ) in the industrial landfill site: effluents (EF), monitoring wells (PM) and surface water (As).

Analyte	EF1	EF2	PM1	PM2	PM3	PM4	PM5	As1	As2
Cl <sup>-</sup>	30.47	1548.60	3960.60	2597.30	5515.50	495.74	2719.70	7280.60	7383.60
SO <sub>4</sub> <sup>2-</sup>	12.87	1625.00	1.06	193.11	70.14	9.48	8.64	1131.70	17.25

The concentrations of metal ions of interest in this study, such as iron, manganese, copper, lead and zinc were low, yet at levels above the reference values, with potential risks to human health.

In the wells, the high concentrations of chloride and sulfate are due to seawater, and sulfate as a product of sulfur oxidation in the steel making process.

Sediment grain size analyzes (granulometry) of samples from the banks of Piaçaguera River were performed and the predominance of silt fraction (silt clay (Sd1)) and sandy silt (Sd2) (Sheppard, 1954).

Mangrove soils are influenced by physical processes such as transport of coarse particles by traction and suspension of clay and silt particles that sediment by mechanical action of tidal currents (ebb and flow) (Ferreira, 2006).

According to Ukpong (1997), the predominance of silt fraction is common in tidal and distribution channels (channels that distribute water) and active deposition of sediments transported by water. In these sites, due to daytime flooding, tidal force is mild and current speed is low.

The solid materials of the landfill site were analyzed by X-ray diffraction in the laboratories of GMG, IGc-USP and identified as major constituents: quartz, kaolinite, illite and hematite of natural origin and predominance of sulfates and carbonate minerals from products used in the metallurgical industry.

IEC analyzes were conducted at Escola Superior de Agricultura Luiz de Queirós. The results are shown in Table 4.

**Table 4.** Data on Ion Exchange Capacity (IEC) and Organic Matter (OM) of the sediments.

Sample	CTC ( $\text{cmol}_c \text{ kg}^{-1}$ )	MO ( $\text{g dm}^{-3}$ )
Sd1	166.00	40.00
Sd2	240.00	32.00

The high levels of CTC mean a high cation exchange capacity. However, since the area is located in a mangrove region, the influence of sodium (cumulative and/or deposited) on the exchangeable soil/sediment complex, with no direct relationship with the clays should be considered.

X-ray fluorescence (GMG/IGc-USP laboratory) was used to determine the chemical properties of the materials. The raw materials used to produce steel were analyzed: coal (CM), coke (CQ) and iron ore (Mi). Byproducts generated in steel production were also analyzed: slag (ES), material deposited in the landfill cell (R1), sludge (LD) associated to the

effluent of the landfill; soils/sediments (S1 to S4) associated to the monitoring wells installed in the area, as well as samples of sediments (Sd1 and Sd2) along the banks of Piaçaguera River.

Chemical analyzes of major and trace constituents of raw material are presented in Table 5.

**Table 5.** Chemical analyses of major and minor constituents of the raw materials used in steel production.

Major elements (%)			
Analyte	CM	CQ	Mi
SiO <sub>2</sub>	31.44	0.03	1.34
Al <sub>2</sub> O <sub>3</sub>	15.51	0.01	0.98
MgO	2.11	nd	0.06
CaO	1.96	0.02	0.06
Na <sub>2</sub> O	1.30	nd	0.07
K <sub>2</sub> O	2.11	nd	0.10
P <sub>2</sub> O <sub>5</sub>	0.78	nd	0.01
Fe <sub>2</sub> O <sub>3</sub>	9.47	0.02	95.38
MnO	0.42	nd	0.01
Trace elements (mg kg <sup>-1</sup> )			
Cu	46.00	13.00	nd
Pb	46.00	14.00	70.00
Zn	31.00	18.00	31.00
S	3590.00	7960.00	130.00

Analytical results of metal ions from solid samples show considerable concentrations of pollutant ions such as iron, manganese, copper, lead and zinc.

Samples of soils/sediments (S1 to S4) associated to the monitoring wells together with

the sample of sediments from the banks of Piaçaguera River (Sd1 and Sd2) have high levels of pollutant metal ions (Table 6) that can be considered potential sources of these elements for surface and groundwater in the study area.

**Table 6.** Chemical analyzes of samples of soils/sediments (S1 to S4) associated to monitoring wells and sediments from the banks of Piaçaguera River (Sd1 and Sd2).

analyte	S1	S2	S3	S4	Sd1	Sd2
Major elements (%)						
SiO <sub>2</sub>	29.21	6.69	27.12	12.70	49.35	18.54
Al <sub>2</sub> O <sub>3</sub>	4.64	1.07	9.33	4.69	13.43	5.47
Fe <sub>2</sub> O <sub>3</sub>	26.09	67.17	7.76	28.68	7.40	23.04
MnO	2.11	0.89	1.86	5.22	0.15	4.13
MgO	3.35	0.64	7.48	8.46	1.44	6.12
CaO	13.88	4.23	40.85	33.80	6.60	28.68
Na <sub>2</sub> O	0.02	0.03	0.02	nd	0.63	0.20
K <sub>2</sub> O	0.61	0.10	0.39	0.02	2.15	0.56
P <sub>2</sub> O <sub>5</sub>	0.44	0.16	0.33	1.10	0.61	1.29
Trace elements (mg kg <sup>-1</sup> )						
Cu	31.00	45.00	11.00	18.00	13.00	77.00
Pb	75.00	429.00	10.00	7.00	26.00	51.00
S	740.00	1690.00	1660.00	1540.00	2150.00	3910.00
Zn	115.00	6764.00	19.00	24.00	66.00	372.00

nd: undetected

The pH of the medium is adjusted by hydrolysis of the sulfides of iron (III) that generate respectively hydroxyl (OH<sup>-</sup>) and hydronium (H<sub>3</sub>O<sup>+</sup>).

Manganese appears as stable hydrated Mn<sup>2+</sup> ions in a wide range of Eh-pH (Hypolito, 1980; Stumm & Morgan, 1998).

The samples of soils/sediments also show different availabilities of metal ions depending on the mineralogical properties and associated waste.

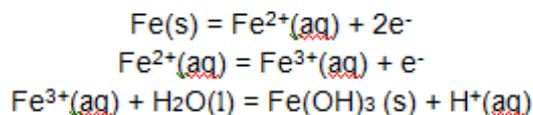
The samples of soils/sediments associated to monitoring wells PM-01 and PM-04, (S1 and S4, respectively), and the sample of sediment from the banks of Piaçaguera River collected downstream of the landfill (Sd2) also have concentrations of manganese ions higher than those in the referred list.

Sodium relates to marine sediments and is associated to chlorides, sulfates and carbonates, forming readily soluble salts. Its concentration is affected by the adsorption capacity of this element on the active surface of colloids.

Under natural conditions, potassium is easily affected by exchange of bases and is adsorbed in a manner that is not easily reversible way by the clays being formed that will be part of its structure, which clearly distinguishes it from sodium. For this reason, despite the abundance of potassium in many rocks, natural waters have much less potassium than sodium, except

in very dilute solutions (Custódio & Lhamas, 1986).

Most waste is metal iron. However, in the presence of O<sub>2</sub> from air or dissolved in water, it oxidizes producing Fe<sup>2+</sup>, and then to Fe<sup>3+</sup> that hydrolyzes (Equation 1):



The precipitation of iron, which can lead to the formation of oxide/hydroxide, explains its relatively low levels in leach solutions.

Lead predominates in metallic form, and can also react to form sulfides, sulfates, oxides and carbonates.

The reaction of water on waste produces hydroxides, carbonates and even Pb<sup>2+</sup> despite the fact that these are poorly soluble compounds.

Copper and zinc are associated to waste as metal alloys, and their availability depends on the pH of the medium.

## CONCLUSION

The main sources of pollution in the study area consist of waste rich in iron, manganese, and to a lesser extent in lead, copper, zinc, amorphous materials and sulfur compounds.

The original solid material consists of mixed metal sulfides and oxides.

In the landfill site, metallic iron from the waste materials exposed to weathering processes oxidizes producing iron (II) and iron (III). The latter is hydrolyzed becoming hydroxide, and subsequently loses water and is converted into various oxides/hydroxides. Hydrolysis of iron (III) occurs with production of H<sup>+</sup> markedly lowering pH.

Other important components are sulfur compounds, especially sulfides, which have reducing properties. They oxidize, become sulfates, facilitating the formation of iron in a lower oxidation degree such as iron (II), more mobile. Sulfides also undergo hydrolysis. However, unlike iron (III), reaction with water increases pH. The high concentration of sulfur compounds, from the mangrove environment itself, as well as from impurities of the ores, was detected by the presence of hydrogen

sulfide gas, easily identified by the strong smell throughout the area.

The presence of manganese, the third most abundant element, is related to reactions involving oxidation of iron and sulfides, which stabilize the element in its most soluble form, manganese (II).

Lead, zinc and copper under the prevailing pH conditions are mainly in insoluble form as sulfides, oxides, hydroxides, carbonates and even in solution as simple or complex ions.

In all the monitoring wells except PM4, bicarbonate is the dominant form of dissolved inorganic carbon, and, thus, electrical conductivity levels are high. In waters with pH higher than 10.0, such as in well PM4, the carbonate ion is the dominant species with low electrical conductivity levels, indicating precipitation of metal ions in the form of carbonate and/or oxides/hydroxides.

The chemical and physico-chemical data of groundwater associated with collection points for solid materials indicate low ionic mobility, which, however, due to environmental conditions, intermittently provide pollutant ions

to the environment. The ionic behavior is mainly due to factors pH and Eh of the solid/solution system.

Although the environment of the study area had an average pH level close to 8.0, which facilitates the formation of slightly soluble compounds, due to reducing conditions, the mobility of ions such as iron (II) and manganese (II) is facilitated. Given the low levels of these ions in the waters of the wells, it can be concluded that pH is the dominant parameter that confers stability to the newly formed insoluble products. This fact is demonstrated by the comparison of analytical data of the solutions and mud from the effluent tank from the cells and drainage solutions of the landfill. These solutions exposed only to rain water, with a pH higher than 9, have precipitates that contain carbonates, oxides/hydroxides of aluminium, iron, copper, lead, and the solution in equilibrium with these solids has practically no ions of heavy metals.

An accumulation of washed away waste material deposited in the landfill was detected

on the banks of Piaçaguera River, and the ionic contribution to the river was demonstrated by chemical analyzes of sediments on the banks and of waters collected upstream and downstream, within the landfill.

Despite their different characteristics, the results indicate the contribution of each material in the landfill, whose stability is a function of the environmental conditions, represent potential hazard with risk of bioaccumulation of contaminants in the bodies, exposing the local human population to the consumption of fish, crustaceans and related products unfit for consumption due to pollution load.

Since changes in pH on the ecosystem studied are one of the main factors that regulate ionic migration, one of the possible ways to remedy/mitigate this situation can be maintenance of pH values above 8,00. Thus, it would be advisable to construct a permeable reactive barrier formed by limestone, within the landfill, on the right bank of Piaçaguera River.

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