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## Accumulation of Bio Debris and Its Relation with the Underwater Environment in the Estuary of Itanhaém River, São Paulo State

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### 1. Introduction

The following chapter presents some considerations regard to the interrelation between the bioclastic accumulations (plants and animals) in a coastal estuarine environment, and the influence of sub surface water in its preservation in the geological record. To it, the plants and zoo debris accumulations and the aquifers in the Itanhaém River basin, south coast of São Paulo State, Brazil were studied and characterized.

The estuary Itanhaém River is located on the southern coast of São Paulo State as part of Santos - Peruibe Quaternary Coastal Plain. It has characteristic of tropical environments, mainly by the exuberance of the Atlantic Rain Forest (Brazilian biome characterized by its high biodiversity which grows associated with the Brazilian coastal portion), largely in primary conditions of conservation, by the Forest of Restinga or dense ombrophyle forest of low altitudes (forest characterized by a high biodiversity that develops in sandy soils of the coastal regions of Brazil) also mostly in primary conditions for conservation and by the Mangrove, which is considered one of the most well protected area of the state.

The Coast of São Paulo has two climatic determiners that influence the dynamic of atmospheric water: (1) the line of the Tropic of Capricorn crosses the region, and (2) the presence of the Serra do Mar with altitudes (maximum of about 1000 meters) very close to the coast of the Atlantic Ocean, and covered by dense tropical vegetation, the Atlantic Forest. Thus, polar air masses and tropical, have interactivity with elements of the relief. The altitudes near the coast, the moisture of ocean evaporation, the evapotranspiration, the slope orientation are the factors responsible to make this region as one of the most humid in Brazil.

The characterization of climate dynamics is based on information from weather stations used in the regional analysis presented in Table 1.

The weather stations of São Paulo city was taken as a reference to the availability of climate information for long period to high altitudes. The station of the Research Center of the Itanhaém river (CPeRio), despite the short period of observation, is a complete station, situated in the Itanhaém river basin and was considered as a local reference.

Stations (name)	Period (years)	Latitude (degrees and Min.)	Longitude (degrees and Min.)	Altitude (m)
Santos	1961-1990	23°56'	45°20'	14
São Paulo	1961-1990	23°30'	46°37'	792
Ubatuba	1961-1990	24°26'	45° 06'	08
Paranaguá	1961-1990	25°31'	48°31'	05
Iguape	1977-1986	24°42'	47°33'	03
CPeRIO*	2002-2004	24°10'	46°47'	02

Table 1. Weather stations used for the study (the south coastal region of the state). \* Climate Station of the Research Center of Itanhaém River.

The Central and Southern coast region of São Paulo has average annual temperatures between 19.6 and 21.8 ° C. The highest values are found during January, February and March, while the lowest values are during June, July and August. The absolute maximum temperatures on record occurred in the summer and their values ranged between 39.0 and 40.0 ° C. The absolute minimum temperatures were recorded in the winter months and ranged from 2.4 to 6.4 ° C.

The rates of average annual total rainfall range between 1,932.2 and 2,080.8 mm. The rainiest quarter is January, February and March with rates accrued between 741.6 and 816.2 mm, making a percentage in relation to the total annual rates between 35.9 and 42.2%. The less rainy quarter is in June, July and August with combined rates between 271.9 and 283.0 mm, present in relation to the total annual rates ranging between 13.6 and 14.1%. The maximum daily rainfall recorded ranged between 206.7 and 289.9 mm.

The average values of atmospheric pressure range between 867.7 and 968.6 hPa. The highest values are observed in July (range between 917.2 and 1,018.8 hPa), while the lowest values are found in November (776.0 hPa) and February (1,009.9 hPa).

In the area, the total annual evaporation ranges from 736.9mm 968.6 mm. The maximum values occur in the summer with rates ranging between 83.4 and 93.3mm (January), while the lowest values are observed in winter, where rates range from 45.6 (June) and 70.4mm (July).

Annual insolation values range between 1,227.6 and 1,494.1 hours. Each month, the highest values are found in summer and range between 142.7 and 149.6 hours (January), while the lowest values are found in the spring and ranges between 73.0 and 88.7 hours (September).

The monthly average rates of cloudiness range between 6.3 and 6.4 tenths. The highest rates are found in late winter and spring, ranging between 6.1 and 7.3 tenths, while the lowest values are found in autumn / winter, ranging between 5.2 and 6.0 tenths.

The average annual rates of relative humidity range between 80.0 and 84.0%. The highest rates are observed in late summer with rates between 83.0 and autumn winter further south in the area, with rates of 86%, however, the lower values in the central portion, in winter, with a rate of 75%.

The hydrographic basin of the Itanhaém River is the second largest on the coast of the state of São Paulo, with an area of 930 km<sup>2</sup>, mostly located in the municipality of Itanhaém, in the southern coast of the state (Camargo et al., 2002; Ricardi-Branco et al., 2009, 2011). The Quaternary coastal plain of the Itanhaém is limited by the city of Peruibe to the southwest and the city of Mongaguá to the northeast, extending for some 50 km, it stretches 15-16 km to the west of the base of the Serra do Mar mountain range (Suguió and Martin, 1978;

Camargo et al., 2002; Amaral et al., 2006). The upper portion of the basin is contained within the Serra do Mar State Park with its sources well preserved. In the middle and lower portions of the basin, the anthropogenic influence is more intense. The main variations in the basin over time are thus the consequence of the patterns of variation of the tides and the intensity of the rain (Camargo et al., 2002). The tidal range is relatively low (less than 1 m, Giannini et al., 2009), but these microtides influence all of the river flowing across the narrow plain.

The main rivers draining the basin are the Itanhaém, formed by the junction of Branco and Preto rivers, and the Mambu, Aguapeú and Guaraú rivers, all tributaries of the Branco River. Studies have been conducted in Itanhaém, Preto and Branco rivers as described next. The Itanhaém river is formed by the confluence of Branco and Preto rivers, presenting estuarine features and drainage area of approximately 26 km<sup>2</sup> (Camargo et al., 2002). On its banks are still present the Restinga Forest and Mangrove Forest, as well as ornamental species introduced in recent years (e.g. *Terminalia*). Its course was modified in the first half of the twentieth century (the 40s) by opening a channel (artificial cut levees, joining two different points of the river after a meander), then about 1 m, now more than 100 meters wide. The opening of this artificial channel caused the abandonment of a portion of the meander, less active today and known as Acima River.

The Branco River originates in the Serra do Mar and runs much of its extension in the Precambrian terrains (Camargo et al., 2002) until it reaches the coastal plain. It is the largest river of the basin with 68 km in length. At its mouth there is a mixture of salt and fresh water under the influence of saline. In its margins are present the Atlantic Forest and the Restinga Forest, both considerably well preserved, as well as plantations (banana, cassava, etc.). Finally the Preto River has about 40 km long, originating in the Serra do Mar, although its greatest extent is located in the Quaternary plain (Camargo et al., 2002). It has little influence of salt water, mostly in its estuary with the Itanhaém River and its banks covered by the Atlantic and the Restinga Forests.

## 2. Bio debris taphonomy

### 2.1 Plant debris accumulations

Besides being a classical sedimentary environment of fossilization, the macro plant debris accumulations were studied in the middle and coastal portion for being the ones with best conditions for the biodebris accumulations. These accumulations were studied in detail by Ricardi-Branco et al. (2009, 2011) employing the original analytical methodologies for taphonomic studies. In addition, a systematic survey of the vegetation along the river basin was developed to draw comparisons with the leaves found in the accumulations. Despite the accumulation of plant debris are to be composed of leaves, twigs and fronds, preference was given to the study of angiosperm leaves, since they are the most abundant elements of the accumulations. The branches were small, often in the larger petioles. Finally, in the accumulations studied, none skeletal remains of invertebrates or vertebrates were found.

The survey was conducted during the years of 2002-2009, and were preferentially studied and / or accompanied with nine sites with leaves accumulations (Fig. 1), selected because they are in facies with the best potential for preservation and therefore fossilization. These accumulations are spatially distributed on the Quaternary plain as follows:

- in the levees in the interior of the plain on the banks of the Branco River (P1);
- in the middle portion of the plain in point bars - Inclined heterolithic structure desposits (IHS deposits) of the Preto River (P2 - P5);

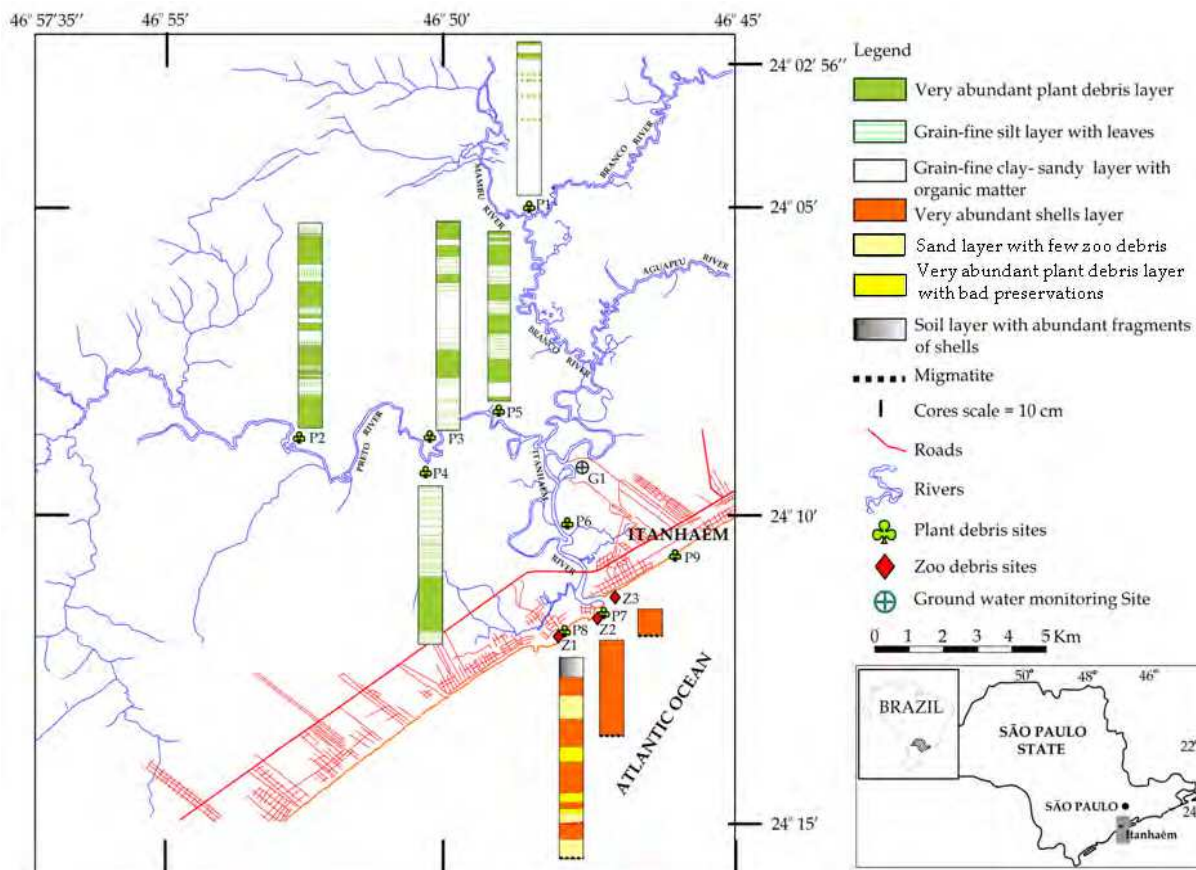


Fig. 1. Location map of the sites studied to plant debris (P1-P8) and to zoo debris (Z1-Z3). It was also plotted the cores developed to P1 to P5, in order to illustrate the constant presence of leaves packages in the margins of those rivers that drain the Itanhaém plain. The cores developed in Sites Z1 - Z3 show the studies to the shell accumulations collected in the coast of the basin.

- in the lower portion of the plain within the Mangrove of the Itanhaém River (P6) and
- in the coastal portion (Sibratel beach - Poço de Anchieta - P8, Mouth of the Itanhaém River - P7 and Itanhaém - Suarão beach -P9). These were followed up and did not have a detailed study of their components, because they are very scattered and still, quickly fragmented by wave action.

With the purpose of carrying out the identification of angiosperm leaves, the methodology described by Ricardi-Branco et al. (2009) was applied. First, the leaves collect were included in morphotypes (Figs. 3, 4 and 5) and later compared to the leaves of plants collected on the banks of the study sites. The results of plant debris analysis clearly showed their differential distribution in the quaternary plain of the Itanhaém River. So within the plain (Branco River, Site P1), in the middle portion (Preto River, Sites P2-P5), and the low portion (Itanhaém River Site P6) the accumulation of leaves were characterized as parautochthonous, primarily reflecting the surrounding vegetation of the study sites. In the Preto and Branco rivers the species corresponded to the Restinga Forest, and in the Mangrove of the Itanhaém River the leaves corresponded to that forest, the latter being the least biodiverse accumulation of those studied. In the coastal portion (Itanhaém River Mouth, Site P7; Sibratel Beach, Site P8 and Suarão Beach/Itanhaém, Site P9), plant debris were characterized as allochthonous composed by various elements from the mainland and

from the ocean as well, and these were the only ones with plant and animal origins Ricardi-Branco et al. (2009).



Fig. 2. Sites of plant debris studies in the Itanhaém River Basin. 1, panoramic view of the Itanhaém River near its mouth; the arrow indicates the location of the Mangrove; 2 and 3, Site P1 overview and hand collection of leaves for study, 4 and 5, Preto River, meanders where layers of plant debris are deposited; 4 low tide and 5 high tide. 6 and 7, outcropping level of plant debris and 7 level of plant debris in core developed at P2.








Morphotype	C1 - B1	C2 - B2	C5 - B3	C6 - B4	Ac1 - B5	Ac2 - B6	P1 - B7
Venation	Campt	Campt	Campt	Campt	Acro	Acro	Parallelo
Leaf shape	Obovate	Elliptic	Elliptic	Oblong	Obovate	Elliptic / Ovate	Ovate / Oblong
Base Shape	Cuneate	Cuneate	Cuneate	Convex	Cuneate	Cuneate/Convex	Convex
Apex shape	Acuminate	Acuminate	Convex	Rounded	Convex	Straight	Straight
Margin shape	Entire	Entire	Entire	Entire	Entire	Entire	Entire
Quantity	160	121	7	140	25	72	5
Related family	Fabaceae ( <i>Inga</i> )	Lauraceae	Myrtaceae	Fabaceae ( <i>Senna</i> )	Melastomataceae	Melastomataceae	Poaceae
Image							

Fig. 3. Morphotypes of the Branco River and their botanical affinity. Site P1. Campt = camptodromous; Acro= Acrodromous and Parallelo = Parallelodromous.








Morphotype	C1-P1	C2-P2	C7-P3	C8-P4	C11-P5	Cr3-P6	P1-
Venation	Campt	Campt	Campt	Campt	Campt	Craspedo	Parallelo
Leaf shape	Elliptic	Elliptic	Oblong	Ovate	Elliptic	Elliptic	Elliptic
Base Shape	Complex	Cuneate	Cuneate	Complex	Convex	Convex	Cuneate
Apex shape	Straight	Convex	Convex	Acuminate	Convex	Acuminate	Straight
Margin shape	Entire	Entire	Entire	Entire	Entire	Crenate	Entire
Quantity	4	48	25	81	19	73	3
Related family	Lauraceae	Fabaceae ( <i>Inga</i> )	Rubiaceae	Fabaceae ( <i>Inga</i> )	Clusiaceae	Sapindaceae	Poaceae
Image							

Fig. 4. Morphotype of the Preto River and its botanical affinity. Site P2. Campt = camptodromous; and Parallelo = Parallelodromous.

At the same time, shallow cores were conducted with aluminum tubes of 7cm, manually buried during low tide up to 2m depth (Ricardi-Branco et al., 2009 , 2011), in three of the sites monitored for assembly of plant debris to follow the changes and evolution of the accumulations selected after the burying. The localities selected were: one on the margin of the Branco River inside the quaternary plain (P1), four on the margins of the Preto River in IHS deposits, in the middle portion of the basin (P2-P5) and the third in the mangroves in the lower portion of the plain. The best results regarding the preservation of the leaves were found in the cores of the Preto River (Fig. 1). The accumulations of plant debris along the meandering course of the Preto River to be characterized in greater detail with the aid of geophysical methods, were very frequent and associated with virtually all the meanders of the river (Fig. 4), featuring IHS deposits with an estuarine system with micro seas, where the monthly variations of the tide deposit thin laminated layers or tidal couplets the cause of variations in river level. So the more thick layers (around 20 cm) of plant debris observed in the study correspond to climatic events that defoliated the trees of the Restinga Forest (Ricardi-Branco et al., 2011).

Morphotipe	M1	M2
Venation	Campt	Campt
Leaf shape	Obovate	Elliptic
Base Shape	Cuneate	Convex
Apex shape	Convex	Convex
Margin shape	Entire	Entire
Quantity	8	30
Related family	Rizophoraceae ( <i>Rizophora</i> )	Combretaceae ( <i>Laguncularia</i> )

Fig. 5. Morphotype of the Itanhaém river and its botanical affinity. Site P6. Campt = camptodromous.

**2.2 Zoo debris accumulations**

From the second half of 2005 until the first half of 2006, natural deposits of zoo debris were characterized and described in the coastline portion of the Itanhaém River Basin (Zincone et al., 2007), showing the change in relative sea level during the late Holocene. These are the deposits where the presence of shell accumulations were detected (Fig. 1):



- Cibratel beach – beachrock of Poço de Anchieta (Site - Z1);
- Conchas beach in Costão de Paranambuco (Site - Z2) and
- the beach of Cabras Island located at a distance of approximately 140 m from the mainland (Site - Z3).

Pits were made in every site of the studied area up to the contact with the accumulations with the basement (Migmatite). The profiles were described and collected approximately 5 kg of each level has been taken to the laboratory for study and dating by C<sup>14</sup>.

Site - Z1. Cibratel beach - beachrock of Poço de Anchieta (24 ° 12 '05.1 "S / 46 ° 48' 41.3" W): consisting of composed zoo debris cemented accumulation with approximately 1.30 m depth (Table 2). This kind of accumulation can be considered a beachrock, chenier or conglomerates of beach, usually consisting of quartz grains bound by carbonate cement, located in the intertidal zones and containing biogenic intraclasts (Suguio, 1992, 2004).

Site - Z2. Conchas beach, (24 ° 11 '46.7 "S / 46 ° 48' 06.01"): the accumulation is associated with a small shore stuck on the left margin of the coast, situated between the walls of migmatites, that features 13 meters wide in low tide and 22.5 meters wide at the posterior border with the coast. During the sampling collect, excavations were conducted at three different points of this beach. The deposit of bioclats (mollusc shells) has 60 cm depth up to the base where it borders the migmatite.

Site Z3- Cabras Island (24 ° 11 '38.1 "S / 46 ° 47' 33.1" W): as the site is located on the Cabras Island at approximately 140m far from the Pescadores beach, the access occurs during low tide when the tide allows crossing the canal. In this place, three trenches were made in order to know the thickness of the shells deposit (Fig. 1 and tables 2 and 3).

The systematic composition of the deposits studied can be seen in Table 2. As the composition of sites Z1, Z2 and Z3 is very similar (Fig. 6).

Sites	Site - Z1	Site -Z2	Site Z3
Bioclats	Beachrock (Anchieta beach) (24°12'05.1" S / 46°48'41.3" W)	Conchas beach (24°11'46.7" S / 46°48'06.1" W)	Cabras island (24° 11'38.1" S / 46°47'33.1" W)
Molusca - Bivalvia	<i>Anachis</i> sp., <i>Perna perna</i> , <i>Tellina</i> sp., <i>Tivela</i> sp. and <i>Trachycardium</i> sp.	<i>Anadara</i> sp., <i>Macoma</i> sp., <i>Tivela</i> sp. and <i>Trachycardium</i> sp.	<i>Anadara</i> sp., <i>Brachidonte</i> sp., <i>Macra</i> sp., <i>Mytella</i> sp., <i>Ostrea</i> sp., <i>Perna perna</i> , <i>Pisania</i> sp., <i>Tivela</i> sp. and <i>Trachycardium</i> sp.
Molusca - Gastropoda	<i>Colissella</i> sp., <i>Diodora</i> sp., <i>Dorsanum</i> sp., <i>Hastula</i> sp., <i>Littorina</i> sp., <i>Olivancillaria</i> sp., <i>Thais</i> sp. and microgastropods	<i>Colissella</i> sp., <i>Crepidula</i> sp., <i>Hastula</i> sp., <i>Janthina</i> sp., <i>Littorina</i> sp., <i>Pisania</i> sp. e <i>Thais</i> sp. and microgastropods	<i>Colissella</i> sp., <i>Diodora</i> sp., <i>Hastula</i> sp., <i>Olivancillaria</i> sp., <i>Pisania</i> sp. and <i>Thais</i> sp.
Polychaeta -	Tubes	Tubes	Tubes
Artropoda	Chelae of crabs and barnacles	Chelae of crabs and barnacles	Chelae of crabs and barnacles
Vertebrata			Fish vertebrae
Fragments	Shells and sea urchin spines	Shells and sea urchin spines	Shells and sea urchin spines

Table 2. Systematic composition of the studied deposits with zooclats.



Fig. 6. Zoo debris found in points Z1, Z2 and Z3. 1. *Trachycardium* sp.; 2, *Tivela* sp.; 3, *Perna perna*; 4, *Thais* sp.; 5, fragments of gastropods, 6, chelicerae crab, 7, tubes of polychaetes and 8, fragments of spines of sea urchins. Scale bar= 1, 2, 3, 4, 5 and 6 = 1 cm. 7 = 5mm e 8 = 0.5 mm

Regard to the taphonomy in points Z1, Z2 and Z3 the bioclasts (shells) are disconnected, densely packed and poorly chosen, since they vary in size and polymodal distribution, which does not observe a preferential orientation of bioclasts. The polymodal distribution indicates activity a turbulent flow during the formation of fossiliferous assemblage as in the case studied here where the waves remove the accumulations daily, the paleoecological fashion is polytypic (Holz & Simões, 2002). Regarding the presence of taphonomic signatures, the most obvious ones found were drilling marks by predation, mainly gastropods, and fragmented valves. These signatures were observed in the valves of mollusks collected at all study sites.

The age obtained for the beachrock (Table 3) indicates that although it is a deposit partially eroded and emerged, it reflects the environmental conditions during the deposition in intertidal zone (Angulo et al., 2002). On the other hand it is interesting to mention that as stated above, the composition in terms of bioclasts among sites Z1, Z2 and Z3, despite having different age composition is very similar, showing that at 1,185 cal yr BP the malacofauna of the Itanhaém coastal region was very similar to that currently inhabits the coast.

Age Sample/Depth (cm)	Conventional age ( <sup>14</sup> C years AP)	Calibrated Age (2 $\sigma$ ) (cal yr BP)	Historical Age (yr AD/BC)	Samples Numbers <sup>14</sup> Cena - USP
Z2 -Conchas beach 30 - 50	570+/- 70	510 - 665	766 - 1,024 AD	975 - CENA 547
Z1 - Anchieta Beach 92 - 98	1,130 +/- 70	930 - 1,185	1,286 - 1,442 AD	976 - CENA 549

Table 3. Ages obtained from deposits of shells Z1 and Z2.

### 3. River – Ground waters

#### 3.1 Regional aspects

The aquatic environment presents a great sensitivity in regions where the contacts between seawater and fresh water outflow are related. This estuarine environment that sustains unique living beings is a region that has developed under a dynamic that involves relief, tides, river flows and climate dynamics of masses of tropical and polar fronts.

The river belongs to the Southeast Atlantic Hydrographic Macro-region of Santos Coastline and has an area of 102.57 km<sup>2</sup>. The formation rivers, Branco River and Preto River, have areas of 411.66 km<sup>2</sup> and 426.46 km<sup>2</sup>, respectively. Yet, this report estimates of average flows for long period of 4.10 m<sup>3</sup>/s, 12.9 m<sup>3</sup>/s, 18.9 m<sup>3</sup>/s, and minimum flows (Q<sub>7,10</sub>) of 1.0 m<sup>3</sup>/s, 3.15 m<sup>3</sup>/s and 4.63 m<sup>3</sup>/s for the Itanhaém, Preto and Branco rivers, respectively (Comitê de Bacias Hidrográficas/ Baixada Santista [CBH-BS], 2000).

The region is influenced by the tide and consequent saline intrusion. According to Camargo et al. (2002) seawater at high tide penetrates through the river channel of the Itanhaém and Branco rivers, occurring predominantly in the lower river basin. The average values reported are of 2,252.6 ppm salinity in the Itanhaém River. The Branco River has a small influence of saline water with maximum records of 200.0 ppm salinity and no influence on the Preto River (average of 4.3 ppm and maximum value of 20.0 ppm). However, the influence of pressure of the tide is noticed in the entire length of the rivers mentioned, with the lifting and lowering of the water level. It is interesting to note the differences in the aquatic environments between rivers Itanhaém and Branco, and the Preto River. In the latter one, its water is dark attributed by the presence of organic matter. The clear water of the other rivers may be attributed to poor soils, the large slope of the terrain, turbulence and the small number of primary producers, consumers and decomposers (Camargo et al., 2002).

The contrast of the steep topography of the Serra do Mar and the coastal plain provide different aquifer systems with dynamics of complex flow and interactivity of groundwater. The Crystalline Aquifer System is mainly composed of granites, gneisses, migmatites, schists and phyllites, Açungui Group (granites and schists varied), the Embu Complex and Coastal Complex (heterogeneous migmatites), and eluvial - colluvium continental sediments, bordering such rocks and being their alteration products. It is characterized by its large regional extension, fractured, free to semi-confined, heterogeneous, discontinuous and anisotropic. In the study area are characterized by the Serra do Mar, the hills that exist in the plains, and in the subsurface with basement of the sediments deposited which makes up the Cenozoic Coastal System.

The Cenozoic Coastal System is composed by sands interbedding with clay and siltstone and characterized by having a limited extension, granular, free and semi-confined, discontinuous, heterogeneous and anisotropic, usually with shallow water level. It is

composed by Holocene sediments of Mangrove and swamp (sand and clay) by Santos Formation of fluvial sediments - lagoon (sand and clay), coastal marine sediments (sands), and reworked coastal marine sediments and coastal marine sediments (sands) of Cananéia Formation.

### 3.2 Groundwater monitoring

An area of six thousand square meters (6,000 m<sup>2</sup>) was selected for installation of eight monitoring wells for groundwater, located in the meander on the left bank of the Itanhaém River (Fig. 7), in order to understand the influence of tides on the river and in groundwater. Information from local people revealed the existence of at least three aquifers in this area: the first, superior, unconfined, with 7 meters deep; the second, confined between two clay layers, between 8 and 20 meters deep; and the third, below the clay layer from 20 meters deep.

Thus, monitoring wells were installed in the first two aquifers, four in the shallower aquifer and three in the second aquifer, whose main characteristics are shown in Table 4. Conductivity Hydraulic essays (slug tests) were made and the results and hydraulic conductivity (Hvorslev, 1951, as cited in Fetter, 2001) and transmissivity are presented in Table 4 and Fig. 7 shows the study area and location of the monitoring wells.

Monitoring wells	Coordinates Latitude/ Longitude	Topographic elevation (m)	Well depth (m)	K (m/s)	T (m <sup>2</sup> /s)	Aquifer
P-1	24° 8' 44" 46° 47' 10"	2.020	6	1.6 × 10 <sup>-4</sup>	8.8 × 10 <sup>-4</sup>	unconfined
P-2	24° 8' 43" 46° 47' 9"	1.854	6	1.6 × 10 <sup>-4</sup>	8.8 × 10 <sup>-4</sup>	unconfined
P-3	24° 8' 44" 46° 47' 9"	2.109	6	1.2 × 10 <sup>-4</sup>	6.6 × 10 <sup>-4</sup>	unconfined
P-4	24° 8' 44" 46° 47' 9"	2.005	6	1.3 × 10 <sup>-4</sup>	7.2 × 10 <sup>-4</sup>	unconfined
PII-1	24° 8' 44" 46° 47' 8"	2.261	21	1.8 × 10 <sup>-6</sup>	4.6 × 10 <sup>-6</sup>	confined
PII-2	24° 8' 45" 46° 47' 7"	1.926	21	5.1 × 10 <sup>-6</sup>	1.2 × 10 <sup>-5</sup>	confined
PII-3	24° 8' 45" 46° 47' 10"	1.452	21	1.8 × 10 <sup>-4</sup>	4.4 × 10 <sup>-4</sup>	(semi) confined

Table 4. Localization of monitoring wells. K - hydraulic conductivity (m/s); T - transmissivity (m<sup>2</sup>/s)

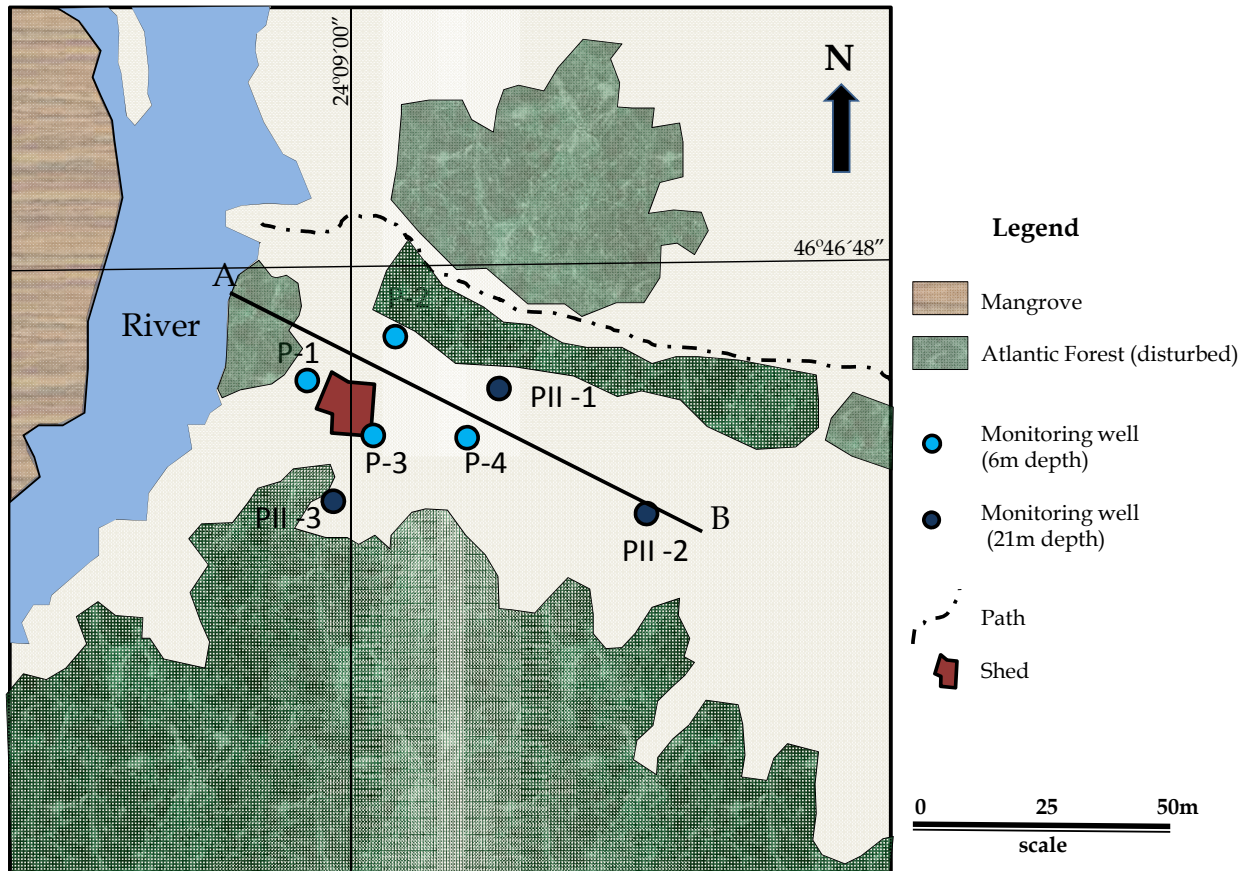


Fig. 7. Localization of monitoring wells and cross section (A - B) in the study area

The study area shows organic sandy soil in the upper portion, with fine-grained, and black color due to the presence of organic matter (up to half a meter deep). Then the soil becomes sandy with fine texture and a yellowish color (up to 1 meter deep), becoming dark gray after 2.5 meters deep. In the depth of 3.5 meters it presents light gray sand with the presence of plant debris to a depth of 7.0 meters. A 1- meter- thickness layer of silty clay is found in this interval, and between depths of 8 to 18.5 meters is found fine sand, with light gray color, but without the presence of plant debris. In the interval of 18.5 to 20 meters deep is found light gray fine sand with remains of calcareous shells. Finally, below 20 meters was found a silty clay layer, compact, with dark gray color (Fig. 8).

Two aquifers were identified: (a) the shallowest, whose bottom is impervious is at 7 meters deep (silty clay) and (b) the confined aquifer located between two silty clay layers, and with a 12-meter- thickness. So the silty clay layers correspond to the aquifuges of the site.

The shallow aquifer, unconfined and homogeneous, presents hydraulic conductivity between  $1.6 \times 10^{-4}$  to  $1.2 \times 10^{-4}$  m/s (transmissivity between  $8.8 \times 10^{-4}$  and  $6.6 \times 10^{-4}$  m<sup>2</sup>/s). The deeper aquifer presents lower hydraulic conductivity, between  $4.6 \times 10^{-6}$  and  $1.2 \times 10^{-5}$  m/s (transmissivity between  $4.6 \times 10^{-6}$  and  $1.2 \times 10^{-5}$  m<sup>2</sup>/s). The PII-3 well presented values of K and T intermediate ( $1.8 \times 10^{-4}$  m/s to  $4.4 \times 10^{-4}$  m<sup>2</sup>/s) indicating the possibility of semi-confinement.

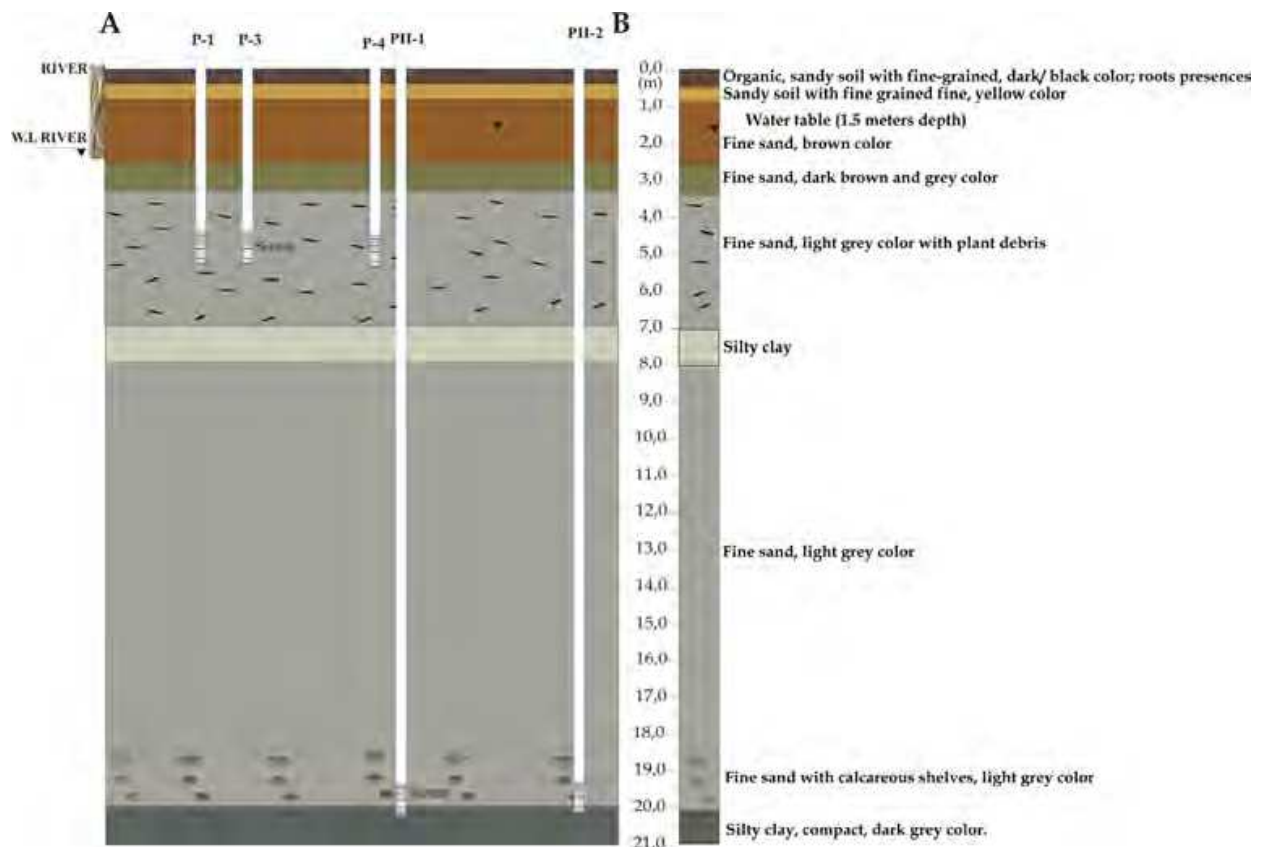


Fig. 8. Cross section (A – B) and geologic profile description (modified from Batista Filho, 2006)

### 3.3 Groundwater dynamics under tidal fluctuations

Two field campaigns were conducted to monitoring the dynamics of groundwater during the daily fluctuations of the tide. The first campaign was conducted between March-April 2005 (03/28 to 03/04/2005 - rainy season), and the second in August 2005 (08/20 to 08/26/2005 - less rainy season). The monitoring consisted of continuous measurements (every 30 minutes) of water levels from monitoring wells, pH and electrical conductivity (E.C.) during the fluctuation of the tide.

Table 5 shows the average results of monitoring of the river water (water level, pH, Eh and E.C.). The waters sampled during the rainy season are quite distinct from the waters of the less rainy period, as in the differences in tidal height variation as the values of pH, Eh and E.C.

The fluctuation measured of the level of river water is related to the location point of the tide gauge, located four kilometers from the Itanhaém river, downstream of the study area. The other physical-chemical parameters were measured in the study area, where the monitoring was conducted. The tide measured in CPeRio takes 1 hour and 30 minutes to reach the study area, through the river channel.

The differences of the variation in height of water level indicates a higher or lower influence of fresh water from the river (higher flow), combined with the fluctuation of the tide; in the rainy season there is a decrease in the difference between the maximum and minimum values of height. During the dry season, there is a reduction of river flow and consequently greater influence of the tides and greater height variation of the water level monitored.

RIVER	Water level (m) *		pH		Eh (mV)		E.C. (mS/m)	
	03/28 to 03/04/05 Rainy season	08/20 to 08/26/05 Less rainy season	03/28 to 04/04/05 Rainy season	08/20 to 08/26/05 Less rainy season	03/28 to 04/04/05 Rainy season	08/20 to 08/26/05 Less rainy season	03/28 to 04/04/05 Rainy season	08/20 to 08/26/05 Less rainy season
Average	0.51	0.74	7.5	6.4	224	260	27	827
Minimum	-0.19	-0.20	6.5	3.4	-169	182	10	186
Maximum	1.08	1.22	8.2	6.9	112	357	278	1100

Table 5. Average results (maximum and minimum) found in the monitoring of water level parameters, pH, Eh and E.C. of the river, from 03/28 to 03/04/2005 and 08/20 to 08/26/2005. \* Change the water level in CPeRio (located four kilometers from the study area).

During the rainy season (January to March), the waters are less acidic, reducing environment and lower concentrations of salts and less influence of seawater in the study area.

During the less rainy season (June to August), the waters become more acidic due to the increasing concentration of humic acids. There is the increase of the concentration of dissolved salts, the lower river flow and higher facility of inflow of sea water in the channel at great distances.

In both monitoring periods the accumulated rainfall was 18.8 mm in 03/28 to 03/04/2005 and 3.0 mm in 08/20 to 08/26/2005. The rains in the first monitoring occurred on 03/28/2005 (7.4 mm) and on 03/04/2005 (11.4 mm); in the second monitoring, the rainfall occurred on 08/21/2005 (0.2 mm), 08/23/2005 (0.2 mm), 08/24/2005 (0.8 mm), 08/25/2005 (1.6 mm) and 08/26/2005 (0.2 mm).

Potentiometric surface maps for the two aquifers, shallow and confined, were prepared at various times of the rise and fall of the tide. Monitoring the values of pH, Eh and E.C. were made in conjunction with measurements of water level.

Figures 9 to 12 presents three moments each monitored day representing the dynamics of groundwater in accordance with the fluctuations of the tide. The days selected, representative of each period (wet and dry) were 03/30/2005 and 08/20/2005, at the same times of water sampling for physical and chemical analysis.

The potentiometric surface maps of the day 03/30/2005 of the shallow aquifer at high tide presents S-N direction, SE- NW and W-E, with hydraulic head higher in PM 3, followed by a hydraulic head of PM 1 (Fig. 9). This flow pattern seems to indicate the pressure of high tide in the aquifer near the river in the opposite movement of freshwater into the river (effluent). During the falling tide and low tide the flow of groundwater toward the river has lower hydraulic gradients, but realize also that the flow directions of S-N and SW-NE are predominant. In the deep aquifer (Fig. 10) the direction of groundwater flow is the opposite (NE-SW and NE-SE), however, the distribution of hydraulic head at various times of tide fluctuations indicates vertical oscillations of the aquifer potentiometry. At high tide, the hydraulic gradient is higher and decreases with low tide.

On 08/20/2005 (Figs. 11 and 12) the movement of groundwater in the shallow aquifer has lower hydraulic gradient and the predominant SW-NE direction. The influence of the tides (high and low) in the groundwater is noted with the increase in hydraulic head at high tide. In the deep aquifer groundwater, the direction of water flow is NE-SW (toward the river).

The higher hydraulic head moves at high tide and at the beginning of the fall (Fig.12). In the deep aquifer, the groundwater flows toward the river (NE-SW), the hydraulic head increases with the rising tide and decrease during the fall of the tide.

The dynamics of groundwater flow in the shallow aquifer has a direct influence of fluctuations of the tide. In March 2005, the potentiometric maps presented a strong northeast flow direction that is intensified at high tide, with greater hydraulic gradients than at low tide. The same behavior is observed in August 2005. Yet the prevailing flow direction to the northeast, but with lower gradients. The hydraulic heads, however, present higher values in August than in March.

In the deep aquifer, the groundwater flow has a less variable behavior, flowing to the southwest toward the river. However, there is a shift in the area of higher hydraulic head from north to northeast.

The major direction northeast flow of groundwater in the shallow aquifer is consistent with the situation of the river channel of the Itanhaém river, which greatly influences the movement of groundwater. In the case of deep aquifer the behavior is different and has SW direction toward the river. There is influence of the tide, but to a lesser extent than the shallow aquifer.

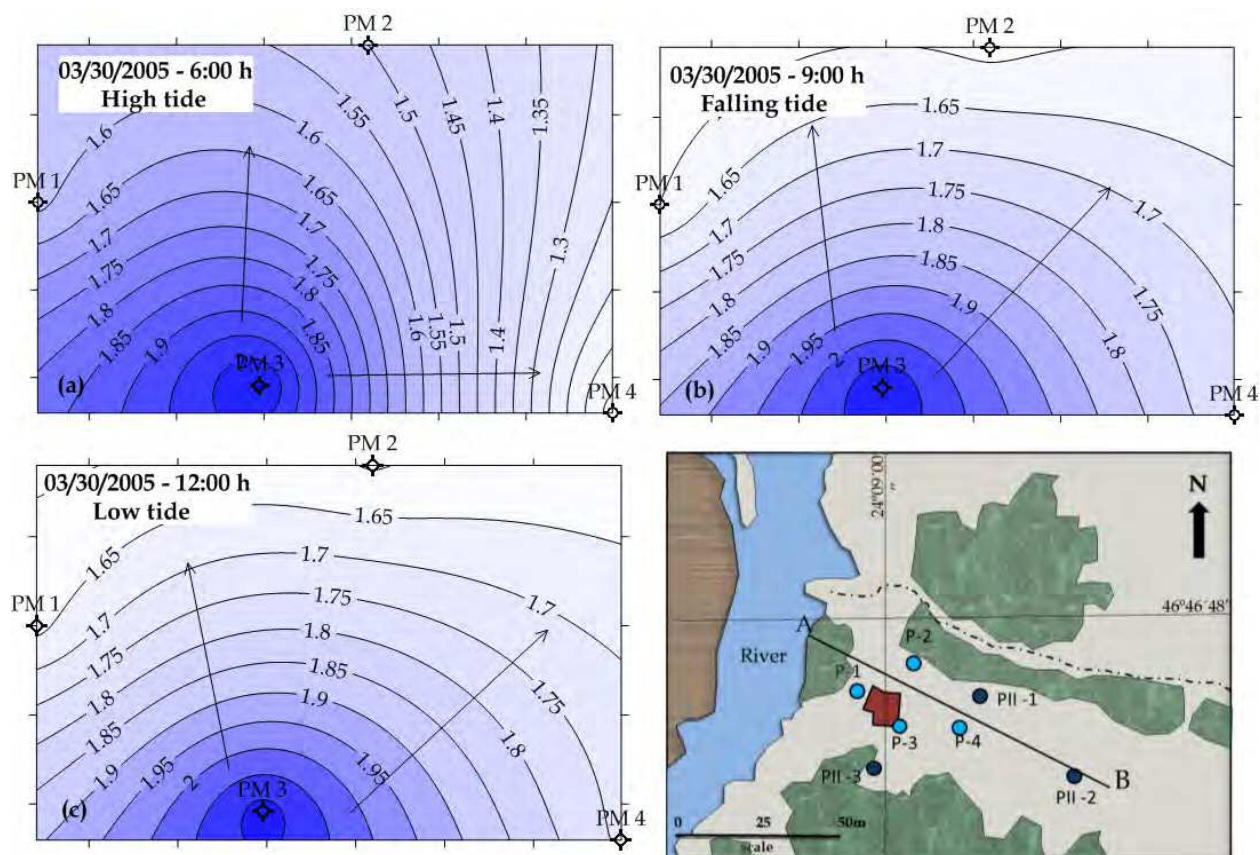


Fig. 9. Potentiometric surface maps representing groundwater flows in the following fluctuations: (a) high tide; (b) falling tide and (c) low tide - Shallow Aquifer (03/30/2005).



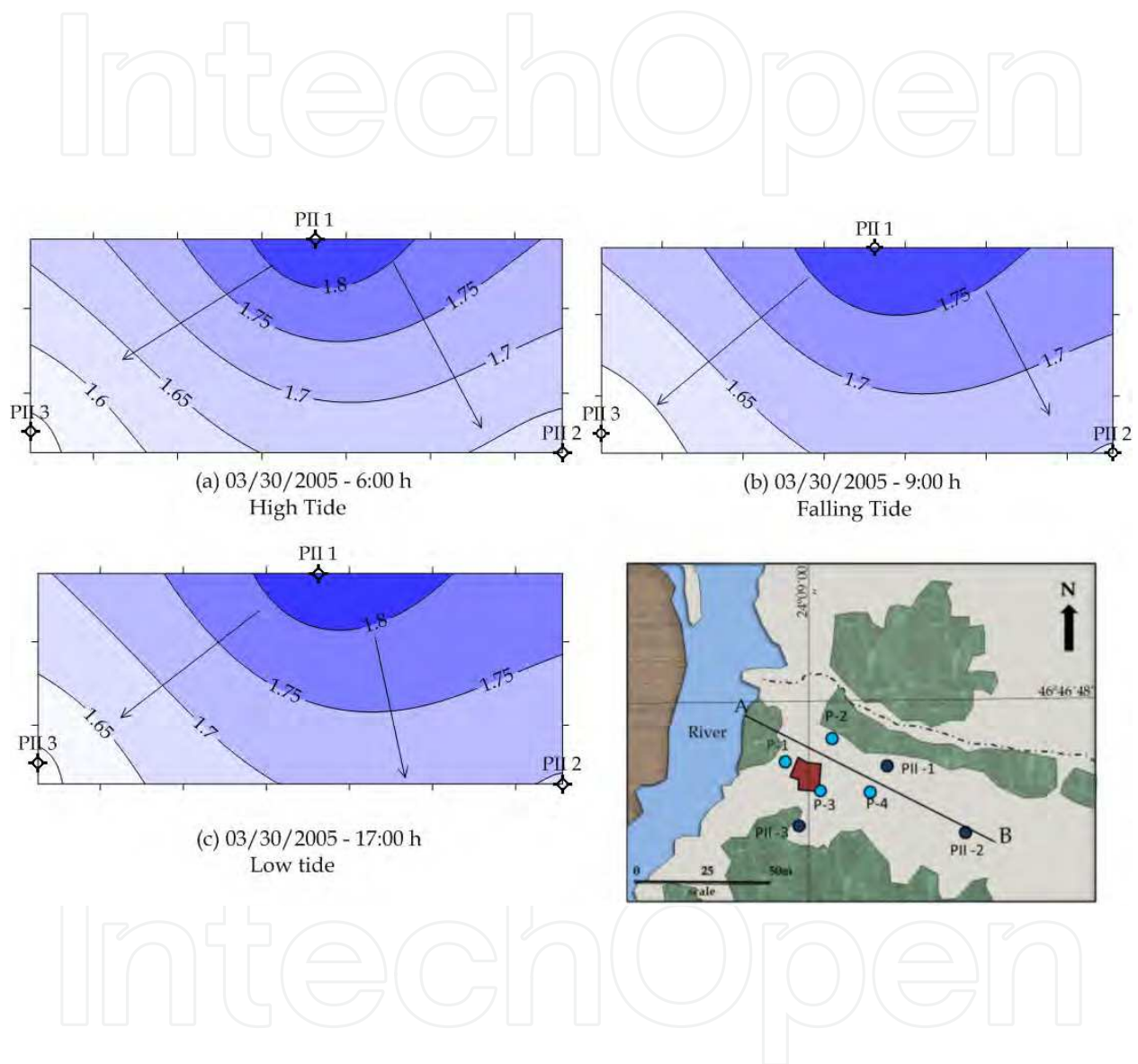


Fig. 10. Potentiometric surface maps representing groundwater flows in the following fluctuations: (a) high tide; (b) falling tide and (c) low tide - Deep Aquifer (03/30/2005).

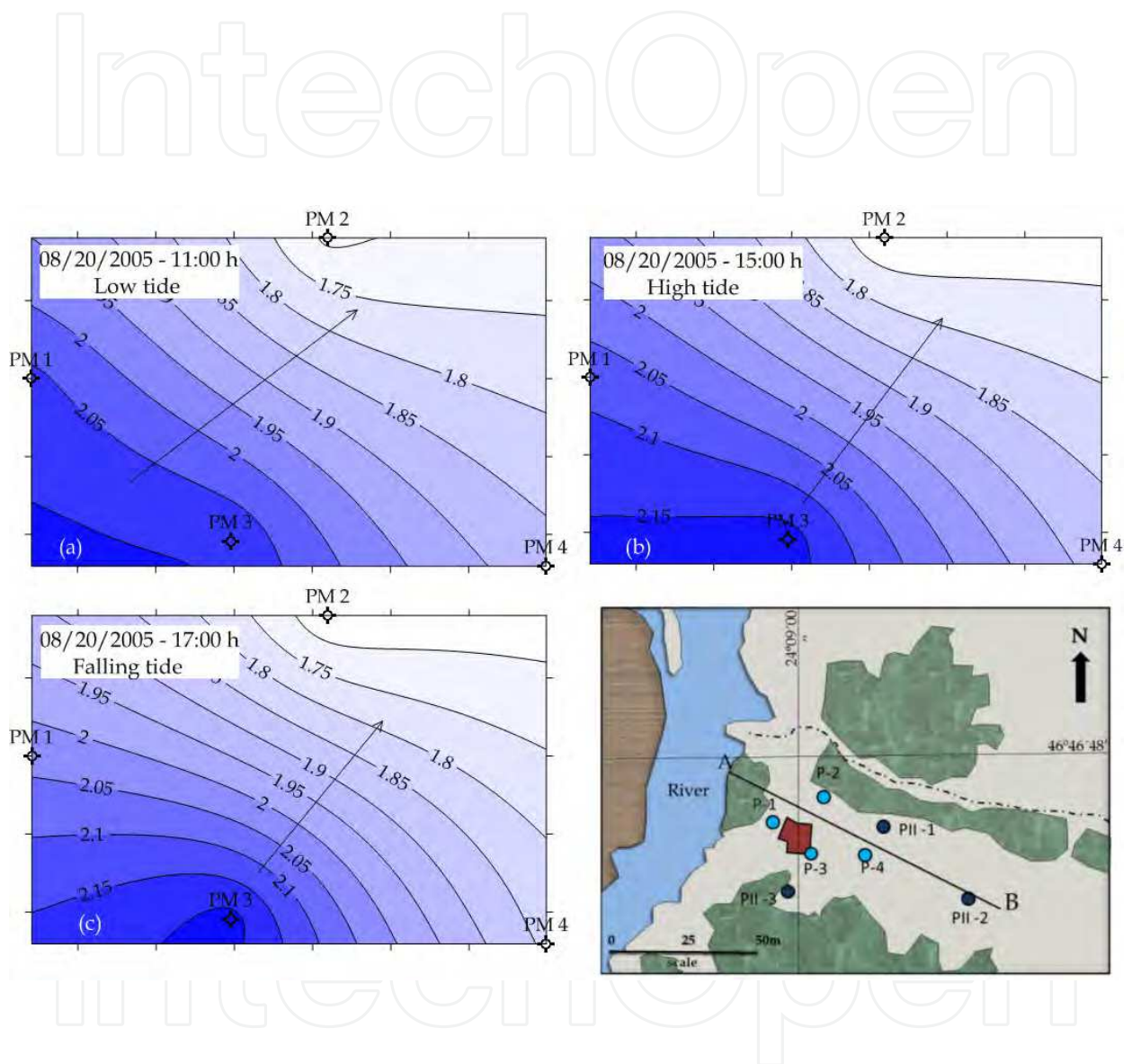


Fig. 11. Potentiometric surface maps representing groundwater flows in the following fluctuations: (a) low tide; (b) high tide and (c) falling tide - Shallow Aquifer (08/20/2005).

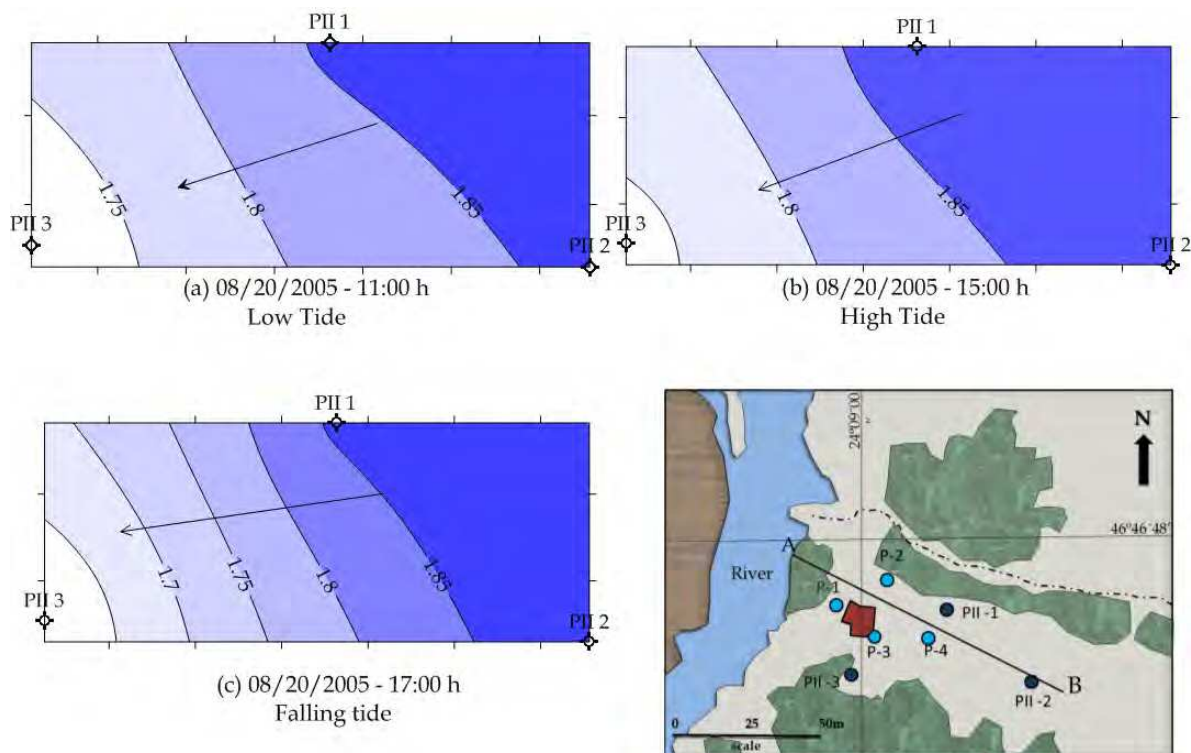


Fig. 12. Potentiometric surface maps representing groundwater flows in the following fluctuations: (a) high tide; (b) falling tide and (c) low tide - Deep Aquifer (03/30/2005).

### 3.4 Hydrochemistry

Samples of river water and groundwater were collected at different times of oscillation of the diurnal tide to study the variations of physical and chemical composition. The parameters pH, Eh and E.C. were determined by portable field equipment *in loco*, and  $\text{HCO}_3^-$  by titrations. The chemical analysis  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{N-NO}_3^-$ ,  $\text{N-NO}_2^-$ ,  $\text{SO}_4^{2-}$  e  $\text{PO}_4^{2-}$  and  $\text{PO}_4^{2-}$  were performed by ion chromatography and the elements Na, K, Si, Mg, Ca, Sr, Co, Mn, Cu, Zn, Pb, Al, Ba, Cd, Ni, Fe and Cr by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry).

The test results are presented in tables 6 and 7. The elements Cd, Co, Cr, Cu, Ni and Pb showed no concentrations above the detection limit of the equipment.

In 03/30/2005 the river presented alkaline pH (7.5 to 7.8) and Eh between 227 and 259 mV. The values of E.C. in this period ranged between 12 and 13 mS/m. In general, low concentrations are presented for all elements analyzed. The element zinc is not present in these waters, and the concentrations of phosphate and barium are very low. The waters have low concentrations of calcium (average of 4.4 mg/L), magnesium (2.2 mg/L), sodium (13.4 mg/L), potassium (1.8 mg/L), fluoride (0.05 mg/L) chloride (23.5 mg/L), sulfate (3.78 mg/L), nitrate (0.26 mg/L) and bicarbonate (16.9 mg/L). The concentrations of elements between the different moments of the tide almost did not change with the fluctuation of the tide in the river in the study area.

The waters of the shallow aquifer had acid pH (between 4.8 and 7.3, average 5.4), Eh between 222 and 271 mV and low E.C. values (between 7 and 8 mS/m). The concentrations of all elements of water from each well hardly varied over the period monitored, however the well PM-2 showed higher concentrations of calcium ions and bicarbonate and lower concentrations

of potassium and sulfate in relation to other wells (PM-1, PM-3 and PM-4). In general, calcium ions, magnesium, sodium and potassium ranged from 1.1 to 4.0 mg/L, 0.4 to 0.8 mg/L, 5.5 to 8.3 mg/L and 0.8 to 2.8 mg/L, respectively. Bicarbonate concentrations ranged from 6.7 to 10.1 mg/L, sulfate between 4.8 and 8.3 mg/L, and chloride between 11 and 13 mg/L. There is presence of fluoride (up to 0.06 mg/L), bromide (from 0.46 to 0.88 mg/L), aluminum (0.082-0.400 mg/L), barium (0.017-0.042 mg/L), iron (0.20 to 0.93 mg/L), manganese (0.009 to 0.017 mg/L), strontium (0.016-0.044 mg/L) and zinc (up to 0.009 mg/L).

The water of the deep aquifer is more mineralized with E.C. between 57 and 270 mS/m, alkaline pH (between 6.6 to 7.5), and lower Eh (from 129 to 187 mV). However, there is significant variation in concentrations among the water of the wells (PMII-1, and PMII-2 and PMII-3). The waters of the well-PMII-1 had E.C. of 270 mS/m, followed by the waters of PMII-2, E.C. between 79 and 95 mS/m, and PMII-3 with E.C. of 58 mS/m. It is notorious the concentration of sodium and bicarbonate in these waters (between 58 and 501 mg/L, and 322 and 1,152 mg/L, respectively), as well as chloride (40 to 260 mg/L). Among the elements of lower concentrations are the fluoride (between 0.17 and 0.45 mg/L), bromide (between 0.10 and 2.23 mg/L). The concentrations of calcium, magnesium and potassium ranged from 25.0 to 39.9 mg/L, 10.3 to 41.5 mg/L, and 8.4 to 41.2 mg/L, respectively. Sulfate, nitrate and phosphate presented low concentrations of up to 2.8 mg/L, from 3.30 to 21.90 mg/L and up to 2.61 mg/L respectively. Other elements like aluminum and barium showed negligible concentrations; iron, manganese, strontium and zinc presented variations between 0.02 to 0.43 mg/L, 0.006 to 0.091 mg/L, and absent to 0.056 mg/L, respectively. The three wells in the deep aquifer presented distinct compositional aspects, while the lowest mineralized water was in PMII-3 and the one with highest concentration water was in PMII-1. The water of the shallowest aquifer had lower concentrations of chemical elements and higher compositional homogeneity in relation to the deepest aquifer. The river water had low concentrations of elements and less reduced environment. The monitoring in this period showed a predominance of fresh water in the estuary at that location, since the river flow had a strong contribution of rainwater from the entire drain area of the basin.

According to the monitoring of August (08/20/2005), the groundwater analyzed presented low compositional variation in relation to the monitoring results of March (03/30/2005). However, the river water presented high mineralization, with E.C. between 860 to 1,100 mS/m, acidic pH (6.5 and 6.8) and Eh from 240 to 289 mV. The surface water had low calcium concentration (between 5.6 and 7.4 mg/L), magnesium (23.26 and 16.90 mg/L) and potassium (between 6.93 and 9.76 mg/L), and high concentrations of sodium (between 151.5 and 192.4 mg/L). Regarding the anions, the concentrations vary as follows: bicarbonate, between 35.58 and 39.04 mg/L, sulfate, 362.4 and 470.6 mg/L, chloride, between 2,654.4 and 3,446.3 mg/L. There is an absence of phosphate, nitrite, fluoride, barium and zinc. Nitrate occurs at concentrations between 0.986 and 1.243 mg/L.

The waters of the shallow aquifer presented more acidic pH than in the first monitoring (4.2 to 4.8), with Eh values between 254 to 341 mV and E.C. between 6 and 10 mS/m. Elements of calcium, magnesium, sodium and potassium concentrations presented between 1.5 and 3.8 mg/L, 0.71 to 1.19 mg/L, 6.4 to 9.2 mg/L and 0.84 and 4.14 mg/L. Bicarbonate (between 4.9 and 17.1 mg/L), sulfate (4.5 to 13.2 mg/L), chloride (9.1 to 15.0 mg/L) presented at low concentrations, and absence of nitrate and nitrite. Fluoride (0.02 mg/L) occurs only in the first and second sampling of PM-1. The other elements such as bromide, aluminum, barium,

iron, manganese, zinc and strontium in their respective concentration ranges: 0.35 to 0.52 mg/L, 0.248 to 0.513 mg/L, 0.021 to 0.062 mg/L, 0.421 to 0.934 mg/L, 0.011 to 0.025 mg/L, 0.023 to 0.047 mg/L and 0.009 to 0.025 mg/L.

The deep aquifer presented slightly acidic to neutral water (6.7 and 7.2), Eh between 109 and 196 mV, and EC 49 and 230 mV. As in the shallow aquifer, the waters of the deep aquifer did not show significant compositional differences between one period and another. The concentrations of calcium, magnesium, sodium and potassium presented respective values of 23.6 and 49.0 mg/L, 12.28 and 44.49 mg/L, 54.3 to 442.4 mg/L, 302.56 and 1,073.6 mg/L. High concentrations of bicarbonate (302.6 and 1,073.6 mg/L) and chloride (38.0 and 262.0 mg/L) are also present, as well as phosphate (2.86 and 30.90 mg/L). There is no presence of barium, and low concentrations of nitrate and zinc (occurring on average concentration of 0.045 mg/L in PMII-1). There is nitrite concentration up to 60.0 mg/L. Other elements such as fluoride, bromide, aluminum, iron, manganese, strontium and zinc occurred in the respective concentrations: 0.17 and 0.41 mg/L, 0.85 and 4.16 mg/L, 0.008 and 0.017 mg/L, 0.267 and 0.519 mg/L, from 0.037 to 0.145 mg/L, 0.278 and 0.287 mg/L, and absent at 0.049 mg/L.

The Piper Plot (Fig. 13) shows the compositions of the water analyzed and monitored in the river in the shallow aquifer, and in the deep aquifer. The chemical groundwater type does not change with the fluctuations of the tide.

The river water presents Na-Cl water type, typical of marine waters, although in the sample of 03/30/2005 waters have mixed behavior in relation to the sampling results of 08/20/2005, which are predominantly Na-Cl water type.

The waters of the shallow aquifer had mixed composition, Na-Cl-SO<sub>4</sub> water types.

The waters of the deep aquifer had Na-HCO<sub>3</sub> water type, and high concentrations. However, there are samples of Ca-HCO<sub>3</sub> water type. The presence of bicarbonate may result from the calcite dissolution, present in the organic matter but also on the shells found in this aquifer. The increased presence of sodium in these coastal environments over calcium may indicate exchange of bases where calcium can be adsorbed and sodium released, resulting Na-HCO<sub>3</sub> water type. It happens when fresh water flushes salts that are in the aquifer (Appelo & Postma, 2007).

The fraction of seawater ( $f_{sea}$ ) was calculated using the chloride concentration of the water sample. The chloride molar relation from the sample with the chloride from the sea water results in the contribution of salinity in fresh water (Appelo & Postma, 2007).

It is assumed that chloride is a conservative parameter and its only contribution is the sea water. Thus, Equation 1 was used.

$$f_{sea} = m_{Cl^-, sample} / 566 \text{ (mmol/L)} \quad (1)$$

$f_{sea}$  - fraction of seawater

$m_{Cl^-, sample}$  - concentration of Cl<sup>-</sup> (mmol/L)

566 mmol/L - concentration of 35‰ (grams of salt per kilogram) seawater

The results of  $f_{sea}$  of the waters from the shallow aquifer ranged between 0.05 and 0.07%.

$f_{sea}$  of the waters from the deep aquifer ranged from 0.20 to 1.29%, and the waters of PMII-1 are those with the highest rate.

There was no variation in these rates in groundwater in the daily tidal fluctuations.

The river water presented variations in the fraction. The waters on 03/30/2005 showed low values, 0.11 and 0.12. On 08/20/2005, the waters had rates of 13.2, 17.2 and 16.1%, indicating influence of seawater into the river in the study area.

03/30/2005	pH	E.C. (mS/m)	Eh (mV)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	HCO <sub>3</sub> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	(mg/L)	PO <sub>4</sub> <sup>3-</sup> (mg/L)	NO <sub>3</sub> (mg/L)	(mg/L)	Al (mg/L)	Ba (mg/L)	Fe (mg/L)	Mn (mg/L)	Sr (mg/L)	Zn (mg/L)
PM-I (6:00 h)	5.0	8	252	1.6	0.8	6.8	2.7	6.7	7.6	13	< 0.05	< 0.013	0.02	0.62	0.230	0.60	0.017	0.021	0.005
PM-I (9:00 h)	4.9	8	271	1.6	0.8	6.6	2.8	6.7	7.8	15	< 0.05	0.043	0.02	0.88	0.210	0.53	0.015	0.020	< 0.005
PM-I (12:00 h)	5.0	8	269	1.5	0.8	6.0	2.7	6.7	8.2	13	< 0.05	< 0.013	0.06	0.52	0.180	0.034	0.013	0.018	0.005
PM-II (6:00 h)	5.3	7	233	4.0	0.7	6.0	0.8	10.1	5.0	11	< 0.05	< 0.013	0.01	0.47	0.190	0.017	0.009	0.043	< 0.005
PM-II (9:00 h)	5.1	8	245	3.9	0.7	5.5	0.9	10.1	5.1	11	< 0.05	< 0.013	0.02	0.46	0.082	0.014	0.008	0.044	< 0.005
PM-II (12:00 h)	5.3	8	256	4.1	0.8	6.8	0.8	10.1	4.8	11	< 0.05	< 0.013	0.03	0.49	0.220	0.017	0.008	0.044	0.005
PM-3 (6:00 h)	4.9	8	248	1.5	0.7	6.6	2.0	6.7	8.3	12	< 0.05	< 0.013	< 0.001	0.57	0.270	0.65	0.015	0.021	0.007
PM-3 (9:00 h)	4.8	8	256	1.6	0.7	6.8	1.9	6.7	7.8	12	< 0.05	< 0.013	0.02	0.52	0.270	0.59	0.013	0.021	< 0.005
PM-3 (12:00 h)	5.2	7	280	1.6	0.6	6.1	1.7	6.7	6.2	11	< 0.05	< 0.013	< 0.001	0.59	0.270	0.54	0.012	0.020	< 0.005
PM-4 (6:00 h)	7.3	8	222	1.2	0.4	7.3	1.3	6.7	6.4	13	< 0.05	< 0.013	0.02	0.69	0.360	0.92	0.011	0.016	0.005
PM-4 (9:00 h)	5.7	8	227	1.1	0.4	8.3	1.3	6.7	6.5	13	< 0.05	< 0.013	0.03	0.76	0.400	0.93	0.011	0.016	0.009
PM-4 (12:00 h)	6.5	8	228	1.2	0.5	7.7	1.3	6.7	6.4	13	< 0.05	< 0.013	< 0.001	0.74	0.390	0.92	0.010	0.016	0.005
PMII-1 (6:00 h)	7.2	270	170	25.1	39.0	440.0	32.2	1102.9	< 0.01	245	18.60	< 0.013	0.37	0.65	< 0.010	< 0.0005	0.43	0.240	0.056
PMII-1 (9:00 h)	7.1	270	175	25.0	41.1	501.0	41.2	1151.7	0.9	259	19.50	< 0.013	0.45	1.01	< 0.010	< 0.0005	0.41	0.240	0.049
PMII-1 (12:00 h)	7.2	270	187	24.4	41.5	473.0	35.8	1132.2	2.8	260	21.90	2.61	0.33	2.23	< 0.010	< 0.0005	0.38	0.240	0.044
PMII-2 (6:00 h)	7.5	81	147	22.6	14.7	121.0	14.0	409.9	1.3	64	3.60	0.09	0.29	1.01	< 0.010	< 0.0005	0.02	0.170	< 0.005
PMII-2 (9:00 h)	7.5	79	163	25.9	18.4	118.0	14.3	429.4	< 0.01	67	5.40	< 0.013	0.30	0.18	< 0.010	< 0.0005	0.04	0.180	< 0.005
PMII-2 (12:00 h)	7.5	95	161	28.1	21.1	165.0	15.6	507.5	1.8	85	8.10	0.043	0.31	2.31	< 0.010	< 0.0005	0.05	0.200	< 0.005
PMII-3 (6:00 h)	6.7	58	129	39.9	10.3	59.4	8.5	327.0	0.4	40	3.30	< 0.013	0.17	< 0.005	< 0.010	< 0.0005	0.31	0.230	< 0.005
PMII-3 (9:00 h)	6.7	58	138	39.5	10.6	58.9	8.4	322.1	1.6	40	3.60	< 0.013	0.17	0.10	< 0.010	< 0.0005	0.32	0.091	< 0.005
PMII-3 (12:00 h)	6.6	57	147	39.0	10.4	58.0	8.5	331.8	1.6	40	3.30	< 0.013	0.17	0.10	< 0.010	< 0.0005	0.30	0.074	< 0.005
River (6:00 h)	7.6	12	259	4.7	2.2	12.6	1.8	16.8	3.8	21	0.17	0.26	0.05	0.24	0.260	0.006	1.09	0.058	< 0.005
River (9:00 h)	7.8	13	233	3.8	2.2	13.9	1.8	16.8	3.5	25	< 0.05	0.26	0.05	0.23	0.230	0.008	0.77	0.032	< 0.005
River (12:00 h)	7.5	12	227	4.7	2.3	13.7	1.9	16.8	4.0	24	< 0.05	0.26	0.05	0.35	0.150	0.004	0.89	0.037	< 0.005

Table 6. River and ground water compositions under tidal fluctuations in the study area (03/30/2005)

08/20/2005	pH	E.C. (mS/m)	Eh (mV)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	HCO <sub>3</sub> <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	PO <sub>4</sub> <sup>3-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	NO <sub>2</sub> <sup>-</sup> (mg/L)	F <sup>-</sup> (mg/L)	Br <sup>-</sup> (mg/L)	Al (mg/L)	Ba (mg/L)	Fe (mg/L)	Mn (mg/L)	Sr (mg/L)	Zn (mg/L)
PMI (11:00 h)	4.8	10	287	1.8	1.19	7.8	2.96	8.5	6.9	13.8	< 0.05	< 0.013	< 0.017	0.02	0.36	0.285	0.062	0.934	0.025	0.026	0.022
PMI (15:00 h)	4.5	7	308	1.8	1.16	7.7	4.14	7.3	8.5	13.0	< 0.05	< 0.013	< 0.017	0.02	0.47	0.304	0.055	0.748	0.021	0.025	0.020
PMI (17:00 h)	4.4	8	315	1.6	1.00	7.4	2.88	7.3	8.8	13.1	< 0.05	< 0.013	< 0.017	< 0.001	0.35	0.308	0.053	0.737	0.020	0.024	0.015
PM2 (11:00 h)	4.7	7	342	3.5	0.88	6.4	0.95	14.6	4.6	9.1	0.22	< 0.013	< 0.017	< 0.001	0.37	0.248	0.023	0.588	0.013	0.047	0.013
PM2 (15:00 h)	4.8	6	341	3.6	0.85	6.4	0.84	17.1	4.5	9.5	< 0.05	< 0.013	< 0.017	< 0.001	0.37	0.251	0.021	0.421	0.011	0.046	0.009
PM2 (17:00 h)	4.8	6	299	3.8	0.85	6.5	0.87	17.1	4.6	9.6	< 0.05	< 0.013	< 0.017	< 0.001	0.39	0.251	0.021	0.430	0.011	0.047	0.011
PM4 (11:00 h)	4.2	9	266	1.5	0.71	9.2	1.50	4.9	13.2	14.4	< 0.05	< 0.013	< 0.017	< 0.001	0.50	0.533	0.058	1.367	0.018	0.023	0.025
PM4 (15:00 h)	4.3	8	265	1.5	0.72	9.1	1.45	5.5	12.5	14.8	< 0.05	< 0.013	< 0.017	< 0.001	0.52	0.513	0.054	1.357	0.018	0.023	0.019
PM4 (17:00 h)	4.4	9	254	1.5	0.74	9.2	1.45	5.5	12.4	15.0	< 0.05	< 0.013	< 0.017	< 0.001	0.51	0.496	0.054	1.360	0.017	0.023	0.017
PMII-1 (11:00 h)	7.1	230	135	23.9	44.49	439.0	29.93	1073.6	< 0.01	258.6	30.21	< 0.013	58.62	0.41	3.50	0.012	< 0.006	0.519	0.039	0.278	0.049
PMII-1 (15:00 h)	7.1	230	134	23.6	44.30	435.4	29.99	1073.6	< 0.01	260.1	29.94	< 0.013	< 0.017	0.41	4.16	0.017	< 0.006	0.509	0.037	0.280	0.042
PMII-1 (17:00 h)	7.2	230	109	24.1	43.08	442.4	30.20	1073.6	< 0.01	262.0	30.90	< 0.013	60.00	0.34	3.99	0.015	< 0.006	0.500	0.038	0.285	0.044
PMII-3 (11:00 h)	6.7	49	196	49.0	12.28	55.5	9.36	302.6	0.1	38.0	2.86	< 0.013	15.17	0.17	0.93	0.008	< 0.006	0.267	0.143	0.281	< 0.01
PMII-3 (15:00 h)	6.6	49	190	46.8	12.35	54.3	9.36	302.6	0.1	38.7	2.89	0.013	15.86	0.17	1.82	0.009	< 0.006	0.361	0.142	0.278	< 0.01
PMII-3 (17:00 h)	6.9	49	150	45.3	12.40	55.0	9.37	312.3	0.1	38.7	2.90	< 0.013	15.52	0.17	0.85	0.005	< 0.006	0.282	0.145	0.287	< 0.01
River (11:40 h)	6.5	860	240	5.6	16.90	151.5	6.93	35.4	362.4	2654.4	< 0.05	0.986	< 0.017	< 0.001	9.80	0.007	< 0.006	0.046	0.007	0.114	< 0.01
River (16:10 h)	6.5	1100	289	7.4	23.26	192.4	9.76	39.0	470.6	3446.3	< 0.05	1.243	< 0.017	< 0.001	12.89	0.008	< 0.006	0.016	0.009	0.151	< 0.01
River (18:15 h)	6.8	1000	256	7.0	22.28	187.2	9.52	39.0	451.0	3333.3	< 0.05	1.113	< 0.017	< 0.001	11.16	0.006	< 0.006	0.014	0.008	0.146	< 0.01

Table 7. River and ground water compositions under tidal fluctuations in the study area (08/20/2005)

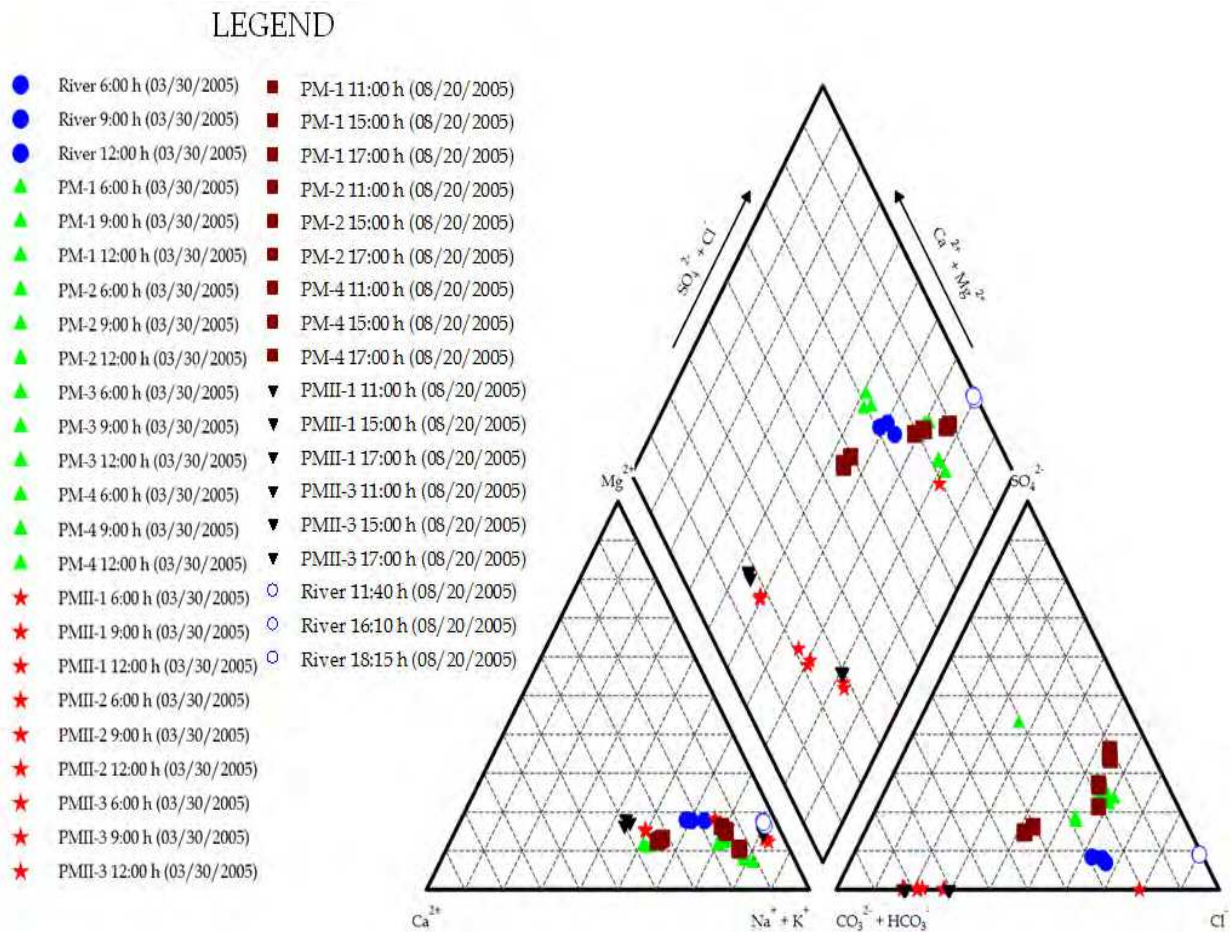


Fig. 13. Piper plot showing compositions of river water and groundwater from shallow and deep aquifers

### 3.5 Groundwater dynamic and the tide influence

The waters of the shallow and deep aquifers do not suffer direct interference of tides and saline intrusion that enters by the river channel. However, the potentiometric surface of the shallow aquifer has groundwater flow direction from SW to NE, or the river to the inland area of study, both in the rainy season (represented by day 03/30/2005) as during dry season (08/20/2005). During the rainy season, the river flows are high and the daily tide has less influence on the dynamics of groundwater, due to a lower pressure of the tide (the flow direction of the river to the mouth is predominant). However, in the less rainy period, one notices the presence of more saline waters in the river, and an influence of saline intrusion in relation to the fresh waters of the river as the river flows are lower. Thus, the potentiometry of the water in the shallow aquifer can be related to this dynamic. The daily fluctuation of the tide makes the potentiometry of the water in the shallow aquifer, both vertically and laterally.

The waters of the deep aquifer have the flow towards NE-SW, toward the river with lateral variations between one period and another, and vertical (especially during the rainy season).

The waters of the shallow and deep aquifer almost do not suffer the influence by tidal changes and seasonal climate. The waters of the shallow aquifer have low mineralization,



are acidic and less reduced, have mixed composition, Na-Cl-SO<sub>4</sub> water type, and are similar to the composition of the river water.

The waters of the deep aquifer already show compositional differences, and are characterized as Na-HCO<sub>3</sub> water type and Ca-Na-HCO<sub>3</sub> water type. These waters have calcium and bicarbonate resulting from the dissolution of calcite from the shells and organic matter in the geological formation. In contact with saline waters, there is ion exchange with sodium and change to Na-HCO<sub>3</sub> water type.

The waters of the aquifer do not have significant contribution from the sea water. However, the river waters suffer significant compositional changes between the rainy and less rainy period. During the rainy season the waters are slightly mineralized, although in the dry season, there is an increase of dissolved salts in the waters of the river and its composition becomes typical of sea water (Na-Cl water type).

#### 4. Final considerations

The preservation of plant and zoo debris accumulations is directly related to the sediment and aquatic environments. These characteristics have in turn influenced by the dynamic seasonal climate variations and the tides throughout the Quaternary plain of the Itanhaém River.

Along the estuary there are two clear taphonomy trends differentiated by the joint action of the depositional and aquatic environments. The Preto River has a low oxygen content and a high humic acid content, low salinity and higher stability in the chemical composition of water, due to little influence of the saline intrusion. These factors joined to low energy of the river present an ideal location for the preservation of plant biomass that is deposited in the IHS deposits. However, the preservation of zoo debris is minimal, since the skeletons of carbonate composition are easily dissolved in these conditions.

On the other hand, the Itanhaém and Branco rivers show a greater variability in hydrodynamics and in chemical composition. This variation may be a result of: (1) the Branco river rises in the Serra do Mar in steep areas and its journey through the Quaternary plain is shorter than the Preto River, a fact that favors greater water oxygenation; (2) Branco River presents greater flow than the Preto River, softening the chemical characteristics of the Preto River in the Itanhaém River, and finally (3) the Itanhaém River also receives the direct influence of the saline intrusion.

So the rivers Preto, Branco and Itanhaém have high variability in their dynamics, chemical and sedimentological characteristics that are reflected in the nature of bio debris accumulations.

Unlike the waters of rivers, sub aquatic environment have no significant compositional changes, however, there is influence of tidal oscillations in the groundwater flow dynamics. The potentiometry of the shallow aquifer has a strong influence on the daily fluctuation of the tide; however, it was not observed compositional changes, not with seasonality.

In the shallow aquifer, the waters have the same water type of the river waters in the rainy season. However, in the less rainy period, the composition is maintained and the river becomes more saline. The more acidic and oxidizing environment of groundwater are favorable to the preservation of logs rich in lignin. Yet in the waters of the deep aquifer, carbonate skeletons are preserved, since the water is more basic and saline.

These unique features of the sea water are the conditions that preserve the shells in the coastal assemblies of zoo debris.

The integrated and multidisciplinary studies are important tools in studying environment and paleoenvironmental, also contributing to better understand the processes that can lead or not to the preservation of fossil records. The aquatic environment where the records are being fossilized or suffering the epigenesis is crucial to the preservation of fossils or not.

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