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# Hydrological mixing and geochemical processes characterization in an estuarine/mangrove system using environmental tracers in Babitonga Bay (Santa Catarina, Brazil)

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**Abstract**

The hydrologic complex of Babitonga Bay (Brazil) forms a vast environmental complex where agriculture, shellfish farming, and industries coexist with a unique natural area of Atlantic rain forest and mangrove systems. The origin of different continental hydrological components, the environmental transition between saline and freshwaters, and the influence of the seasonality on Babitonga Bay waters are evaluated using isotopes and chemistry. End-member mixing analysis is used to explore hydrological processes in the bay. We show that a mixing of waters from different origins takes place in the bay modifying its chemical characteristics. Furthermore, biogeochemical processes related to well-developed mangrove systems are responsible for an efficient bromide uptake, which limit its use as a tracer as commonly used in non-biologically active environments. Seasonal behaviours are also distinguished from our datasets. The rainy season (April) provides a homogenization of the hydrological processes that is not seen after the dry season (October), when larger spatial differences appear and when the effects of biological processes on the bay hydrochemistry are more dynamic, or can be better recognized. Moreover, Cl/Br and stable isotopes of water molecule allow a neat definition of the hydrological and biogeochemical processes that control chemical composition in coastal and transition areas.


*Keywords:* Babitonga Bay; Estuarine; Mangrove; Halogens; Stable isotopes; Mixing processes

## 1. Introduction

Estuarine and transitional areas constitute natural reactors in which heterogeneous processes may affect the ecological equilibrium due to local changes in the sedimentation and in the biogeochemical processes and in the salinity conditions (Wolanski et al., 2007). Besides the natural sources, human inputs significantly contribute to the water chemistry. These include large volumes of poorly defined human wastes that are sometimes discharged directly or after treatment into rivers and bays. Besides the bulk effluents, anthropogenic sources also supply agricultural chemicals and off-products of industrial processes. Solid loads, anthropic pollutants, and variable water salinity control the environmental conditions of these areas. The distinction between the effects of natural and human sources in a bay's chemical processes is not always simple. Babitonga Bay (BB), one of the main estuarine formations with mangrove in the south of Brazil, is an excellent location to monitor and understand such processes.

In this paper, we present a multi-parameter approach, combined with classical hydrochemical and isotopic

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methods, to depict those biogeochemical processes. All of them are investigated according to the hydrogeological setting of the BB and its inland watershed which define the main controls on surface and groundwater, and finally upon the estuarine water quality. Our aim is to seek for a process-based model that describes the hydrochemical and nutrient functioning of bay and related lowland permeable catchments detecting, also, the effect of organic matter (OM) (natural and anthropical) in the bay.

Environmental tracers as halogens and stable isotopes are used in this research as they describe the movement of water through hydrological systems. Nevertheless, biogeochemical processes, considered as a whole in a bay environment, may even modify this behaviour and produce a change of their content.

For instance, chloride and bromide are generally used as tracers in complex environment, because their low chemical reactivity. As a consequence, the Cl/Br ratio is a conservative indicator for the origin and movement of natural waters (Fontes and Matray, 1993; Edmunds, 1996; Davis et al., 1998; Vengosh and Pankranov, 1998). The ratio in freshwaters is primarily controlled by the initial ratio in precipitation, which in coastal regions must have a value similar to that of seawater (Fontes and Matray, 1993), although water–rock interactions or human pressures may affect its original value. Halogens in rainfall result initially from physical processes that entrain atmospheric aerosols and control their size (Junge, 1972). Near coastal areas, the Cl/Br ratio also reflects the influence of ocean spray on local precipitation (Kaufmann et al., 1984; Long et al., 1993; Davis et al., 1998; Alcalá and Custodio, 2004). In the study area, this ratio remains relatively inert during transport above the Atlantic Forest and Serra do Mar, despite other atmospheric processes like continentality, elevation, and precipitation amount (Winchester and Duce, 1967; Brimblecombe, 1986; Goni et al., 2001).

Studies in continental and urban areas demonstrate, on the contrary, a lower Cl/Br ratio in precipitation (Slanina et al., 1982; Vengosh and Pankranov, 1998). This relatively low Cl/Br ratio was attributed to a contribution of bromine (Vengosh and Pankranov, 1998; Davis et al., 2001), showing the effects of human pressures on natural processes. However, significant assimilation of bromide by green plants and peat deposits is presently well documented (Lundstrom and Olin, 1986; Vengosh and Pankranov, 1998; Whitmer et al., 2000; Hammer et al., 2005). Bromide is assimilated like adsorbable organic bromine (AOBr), following seasonal cycles (Putschew et al., 2003). Actually in wetlands, lakes, and lagoon, in late summer during periods of rapid plant growth, bromide concentrations assimilated in OM are higher than those during the rest of the year (Whitmer et al., 2000; Carpenter et al., 2003; Hammer et al., 2005). The non-conservative behaviour of bromide is caused by the strong preference for $Br^-$ over $Cl^-$ by the plants and by photosynthetic bacteria, or by better chemical interactions between organic matrixes (Blodau and Moore, 2002).

Furthermore, stable isotopes of the water molecule ($\delta^{18}O$ and $\delta D$) are also appropriate tracers to depict surface and groundwater flow lines and recharge areas (Clark and Fritz, 1997; Kendall and McDonnell, 1998). Both of them, halogens and stable isotopes are studied using end-member mixing analysis to describe the influence of different water inputs into the saline BB water, as well as the occurrence of biogeochemical processes in this particular environment.

## 2. Site environment description

The estuarine system of BB covers an area of 1400 km$^2$, including the last great south hemisphere's mangrove ecosystem (130 km$^2$; Fig. 1). The complex is located northeast of Joinville, the most industrialized and urbanized city of Santa Catarina State. The bay's drainage basin (26°02′–26°28′S and 48°28′–48°50′W) forms a vast environment, where agriculture and shellfish farming as well as a broad spectrum of industries, like textile, ''metal-mechanical'', foundries, etc., coexist with a unique natural area of Atlantic Forest. The BB is connected to the Atlantic Ocean via an opening of 1850 m and presents a salt-wedge circulation system. A significant tide oscillation brings an appreciable water renewal to whole ecosystem. Tides are mixed with semidiurnal dominance and diurnal inequalities (Truccolo and Schettini, 1999). Non-linear effects result in the amplification of the astronomical constituents towards the interior of the bay, presenting a hypersynchronous behaviour. The mean tidal amplitudes in BB range from 0.14 m during neap tides to 1.53 m during spring tides (FEMAR, 2000).

The region is characterized by a humid subtropical climate with a rainfall average of 2000 mm/year. It presents two differentiated seasons: summer (from November to April) and winter (from May to October). During summer, weather is characterized by high temperature and humidity, with intense precipitation. During winter, the influence of polar air masses brings a decline of temperature and precipitation in the region.

Geomorphological analysis reveals large differences in lithology and structure, including the occurrence of well-developed Quaternary formations. The basin and range topography of the region generates pronounced altimetric contrasts. The whole Babitonga basin is characterized by four geological domains: granites and a complex Paleozoic tectonic basement; molasses; associated vulcanites; and sedimentary deposits from the Quaternary. It is divided in four hydrographic watersheds: Cachoeira, Palmital, Cubatão, and Parati.

The Cachoeira River basin has an area of 84.82 km$^2$, completely located in the urban area of Joinville, and it runs out to Saguaçu Lagoon. There is no accurate information about the Cachoeira River discharge, roughly estimated as 3–5 m$^3$/s. Water quality is very low due to pollution from domestic and industrials effluents. Only 16.40% of the domestic sewages receive partial water treatment. Nevertheless, the largest chemical pollution of