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Dissolved and particulate metals dynamics in a human impacted estuary from the SW Atlantic

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In order to evaluate metal behavior in urban stressed estuaries, the distribution of major elements (Fe and Mn) and trace elements (Cd and Cu) between suspended particulate matter (SPM) and subsuperficial seawater in the Bahía Blanca Estuary, Argentina, was studied. Four different impacted areas were selected to study the spatial and temporal distribution of these metals in an estuary in continuous industrial development and where an environmental law was implemented to supervise industrial discharges in waters. Sampling was performed within intertidal areas. Physicochemical conditions usually influence the partitioning of metals between the dissolved and particulate fraction thus, salinity, pH, turbidity, temperature and dissolved oxygen were also measured.

Dissolved metals were analyzed with atomic absorption spectrophotometry (AAS) and the particulate fraction with inductively coupled plasma optical emission spectrometry (ICP OES). Metals concentration ranges, within the dissolved fraction (μg/L), were from below the method detection limit for all the elements to 4.7 in the case of Cd, 6.0 for Cu and 62 for Fe. Minimum and maximum values in the particulate fraction (μg/g, d.w.) were from below the method detection limit to 11 for Cd; from 24 to 220 for Cu and from 630 to 1500 for Mn. For Fe, concentrations ranged from 2.2 to 9.6 (%). The general order of the dissolved/particulate partition coefficients ($Log_{10}Kds$) for the studied metals, considering mean values, were: Fe (7.0) > Cu (4.2) > Cd (3.3).

The metals values as well as the physicochemical parameters showed temporal variations and many correlations were found among them. $Log_{10}Kd$ Fe values were the highest, highlighting its strong affinity for particles. Metals concentrations were sometimes higher than those from other polluted areas as well as from previous studies from the same estuary, which highlights the potential impact of these elements in the study area.

The concentrations of particulate metals achieved in the present work were in some cases of higher ranges than the previous from the same estuary and/or from other polluted estuarine environments. Thus, the environmental law that regulates the discharge of industrial waters appeared not to have a specific impact on the metals concentrations found. Moreover, human activities that surround the estuary and are in continue development should be considered as they might constitute a source of metals for the estuarine system.

1. Introduction

A wide majority of countries have a large percentage of their population (80–100%) living within 100 km of the coastline. Human burden on the coasts enhance pressure on these ecosystems through habitat conversion, infrastructure for manufacturing, transportation, energy processing, waste products disposal, among others (Martínez et al., 2007). Inputs of contaminants onto these

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environments have been intensified in the last years (Duarte and Caçador, 2012). Within coastal environments, the estuaries are recognized as dynamic and unique systems and of great economic importance. In addition, they are considered as filters of several inorganic and organic contaminants transported through rivers, streams, subterranean drainage and effluents, between others (Duarte and Caçador, 2012; Fu et al., 2013). Thus, estuaries play a key role in the transference of contaminants to the open sea, being these elements transformed, dissolved or/and sunk there (e.g. Lim et al., 2012), interacting with the biota and, discouraging human development along the coasts.

Among contaminants, metals are of particular concern as a result of their environmental persistence, biogeochemical recycling and human risk. Mobility and partitioning of metals within estuaries are dependent on several factors, e.g. pH, salinity, redox conditions, background levels, resuspension of sediment (due to dredging, tidal action, winds and storms), flocculation and coagulation of colloidal material and adsorption onto suspended particles (e.g., Zwolsman and Van Eck, 1999; Oursel et al., 2014). Metal partitioning is also highly influenced by the equilibrium of the metal between dissolved fraction and surface of suspended particles (Alquezar et al., 2007; Doig and Liber, 2007). Partition coefficients (Kds) have proved to be a convenient parameter to quantify and rank the relative strength of the association between individual contaminants and SPM. There are important differences, however, in the actual values of Kd between geographical areas which is related with the nature of the particle surface and physicochemical conditions (Owens et al., 1996).

There are many researches on metals in estuarine environments of the world, most of them studying their occurrence and distribution in the sediment fraction; However, to the best of our knowledge, in the last decade no more than 18 articles have dealt with heavy metals in the dissolved and particulate seawater fractions together (e.g., Audry et al., 2007; Jonas et al., 2010; Fu et al., 2013). Hence, it is worth evaluating metal concentrations in seawater as it is a particularly difficult matrix to study and since it is useful to make comparison with estuaries from other geographical areas of the world.

The Bahía Blanca estuary (BBE), a coastal environment in Argentina, is of great economical and biological value. Important industries, cities and harbors are in continuous developing. However, few articles studied metal concentrations (i.e. Cd, Cu, Fe and Mn) in the waters of this system, working with either one or all the metals in the dissolved (Ferrer et al., 2000; Botté et al., 2007, 2008) or the particulate fraction (Fernández Severini et al., 2013). Both compartments together were evaluated four times (Andrade et al., 2000; Ferrer et al., 2003; Botté, 2005; Fernández Severini et al., 2009) and only in one case (Fernández Severini et al., 2009) the interaction between metals was analyzed, with samples taken from the subtidal area. In the present work, sampling was performed within intertidal areas, known as important sites within an estuary (Wood and Widdows, 2002; Feng et al., 2004; Botté et al., 2007), which could be used as proxies for monitoring metal concentrations in a more immediate way.

The present work is the first record of these four metals distribution together, in the particulate and dissolved fraction, after the enforcement of an environmental law supervising industrial discharges in this estuarine waters (Law: 12257, 2007). It is also a contribution to the knowledge of metal concentrations in an estuary with a continuous industrial development. By 2002, the industrial area surrounding the petrochemical center embraced only 9 industries while nowadays includes more than 135 industries, within an area of 136 ha (Sznaiberg, 2012). Physicochemical parameters were also evaluated to determine possible influences on metal partitioning. In addition, the study includes the first registers for two sampling sites, with recognizable "biological pollution" originated by sewage discharges on these ecosystems (Pierini et al., 2012; Spetter et al., 2015).

2. Materials and methods

2.1. Study area

The BBE (Fig. 1) is the second largest estuary of Argentina, South America, located in the south-east coast of the country, between 38°45′ and 35°10′S and 61°45′ and 62°30′W. It is a mesotidal estuary, which drains an area of 2300 km^2 of a very complex system of channels. It is northwestern–southeastern directed, with the Canal Principal (60 km long) as the main navigation channel (Perillo and Piccolo, 1999). The BBE has a semidiurnal tidal regime with a mean amplitude that varies between 3.5 and 2.2 m at the head and mouth of the estuary, respectively (Perillo and Piccolo, 1991). Winds are mainly from northwest and north with a medium velocity of 24 km per hour (Piccolo, 2008). The inner zone has been regarded as turbid with an annual mean of particulate suspended matter of 78 mg/L (Guinder et al., 2009). Sediments are mainly represented by silts and clays, while towards the mouth, the estuary becomes characterized by sandy sediments (Gelos et al., 2004). The BBE has few minor freshwater contributors, producing localized spots of lower salinity but with marine conditions prevailing. The Sauce Chico river, with a mean discharge of 150,000 m^3/day and the Naposta Grande stream, with a mean of 91,000 m^3/day, are the major contributors to the freshwater superficial drainage net (Limbozzi and Leitao, 2008). Additionally, the BBE receives other freshwater inputs through continental runoff, sewage discharges and harbor-related operations (Botté et al., 2010).

Two cities are established adjacent to the estuary, Bahía Blanca (350,000 inhabitants) and Punta Alta (60,000 inhabitants), generating urban sewage discharges of almost 84,000 m^3/day that reaches the estuary without appropriate treatment (CTE, 2003). One of the most important deep-water port systems of Argentina is located on the northern coast of the BBE, contributing with the mobilization of thousands of tons of sediment from deepening and maintenance activities of the navigation channels. Industries from a petrochemical center are located in the harbor area, which main ports are Puerto Galván and Ingeniero White. The latter comprises a dock for coastal fishing boats and an area for loading grain (Limbozzi and Leitào, 2008). Water discharges of this harbor area have a mean of 22,000 m^3/day (CTE, 2012), with some type of treatment before reaching the estuary. Spills originated from harbor actions in Puerto Rosales port, near Punta Alta city, also reach the estuary. Cattle and agricultural activities are well developed in the area, especially in the upper part of the Naposta Grande stream and the Sauce Chico river (Limbozzi and Leitao, 2008) adding different types of contaminants to the water courses. The BBE, hence, undergoes intense human-induced disturbances related to urban and industrial developments in the area (Botté et al., 2007; Fernández Severini et al., 2009).

2.2. Sampling sites

Four sites, from the head to the mouth of the estuary, were selected representing locations with presumable different anthropogenic impact (Fig. 1).

Almirante Brown (AB) is the closest to the head of the estuary, with the Maldonado stream coming from across Bahía Blanca city and draining next to the sampling site. It is located next to an urban effluent discharge that began to operate in 2008 with an estimated release of 4800 m^3/day (Streitenberger and Baldini, 2010). This area was also an ancient municipal dump until 1992 but still receives