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Radium isotope (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) distribution near Brazil's largest port, Paranaguá Bay, Brazil

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ABSTRACT

This work investigates the ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra isotope distribution in river, estuarine waters and sediments of the Paranaguá Estuarine Complex (PEC). The stratification of the Ra isotopes along water columns indicate differing natural sources. In sediments, the radium isotope activities was inversely proportional to the particle size. The highest concentrations of ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra in the water column were found in the bottom more saline waters and towards the inner of the estuary. These relatively high concentrations towards the bottom of the estuary may be attributed to the influence of tidally driven groundwater source and desorption from particles at the maximum turbidity zone. The apparent river water ages from the radium isotope ratios, ^{223}Ra/^{224}Ra and ^{223}Ra/^{228}Ra, indicate that the principal rivers that flow into the estuary have residence times from between 6 and 11 days.

Recently, there is a growing analytical applicability of measuring natural uranium and thorium decay series radioisotopes (de Oliveira et al., 2006; Huang et al., 2015; Lu et al., 2013). The outcome of such studies has contributed to a better understanding of the geological processes occurring on the Earth's crust, including sedimentation dynamics and water mass transport processes (Burnett et al., 2008; Sanders et al., 2011; Santos et al., 2008). However, to implement radionuclide tracer mass balance calculations baseline studies are needed.

Within the natural occurring ^{238}U, ^{235}U and ^{232}Th decay series are the radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra). The short lived radium isotopes, ^{223}Ra ($T_{1/2}$ 11.4 days), ^{224}Ra ($T_{1/2}$ 3.66 days) are continuously regenerated by the decay of their parent Th adsorbed on the sediment surface, or on aquifer particulate materials. Thus, Th isotopes continuously provide isotopes Ra short half -lives to salt water. In contrast, radioisotopes of long half-lives, ^{226}Ra (half-life 1600 years) and ^{228}Ra (half-life of 5.75 years) require a considerable time for regeneration. The differences in production rates lead to differences in the fluxes of each of these radionuclides to the coastal environment. The objective of this study was to examine the spatial distribution of the naturally occurring isotopes, ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra, in surface water and sediments along the Paranaguá Estuarine Complex (PEC).

The PEC is located in the southern coast of Brazil, 25°16′ and 25°34′ S and 48°17′ and 48°42′ W, occupying a total area of 612 km^2 (Fig. 1). The

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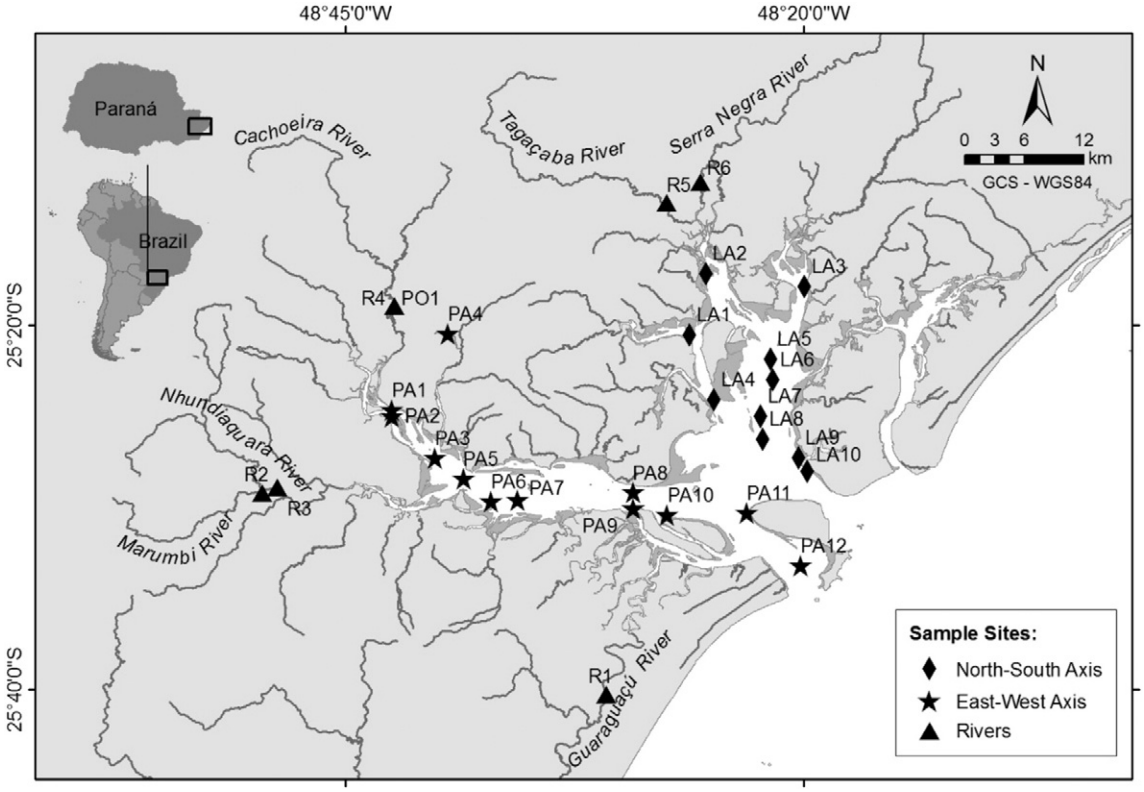

Fig. 1. Study sites along the Paranaguá Estuarine Complex, Southern Brazil.

PEC is comprised of two main drainage basins, the east-west axis is formed by Paranaguá and Antonina bays with an average depth of 5.4 m, and the north-south axis - with an average depth of 2.7 m covers the Laranjeiras Bay (Lana et al., 2001). The spring tide in PEC ranges from 1.7 m to 2.7 m (Marone et al., 2005). The rivers Cachoeira and Nhundiaquara are the major tributaries to the PEC (Lana et al., 2001) of the east-west axis of the PEC - present average flows of 21.13 and 15.88 $m^3\ s^{-1}$, respectively (Lana et al., 2001; Marone et al., 2005).

The sampling campaign for this work was carried out from 18 to 21 March 2013, covering a total of 28 sampling stations (Fig. 1). The sampling points were distributed in transects along the main salinity gradient of each axis, during low tide. Salinity was measured in the field by a refractometer (ATAGO) and CTD (JFE Compact), as well as the turbidity, temperature and depth. Samples were taken from Guaraguaçu Rivers (R1), Sacred (R2), Nhundiaquara (R3), Cachoeira (R4), Tagaçaba (R5) and Serra Negra (R6). A sample from an artesian well near the Rio Cachoeira was also sampled (Fig. 1).

To measure the Ra isotopes activities in water, approximately 60 L of water were pumped, then filtered in situ (average flow rate of 1 L min^{-1}), by means of acrylic fibers impregnated with manganese dioxide (Moore, 2008; Moore and Arnold, 1996). At each sampling station, near 500 g of sediments from rivers and PEC were collected with a Petit Ponar. The ^{224}Ra and ^{223}Ra activities in surface and bottom water samples of the rivers and estuary were determined by a delayed coincidence system (RaDeCC sys) (Moore and Arnold, 1996). The ^{224}Ra, ^{228}Ra and ^{226}Ra water and sedimentary measurements were performed by high-resolution gamma spectrometry, after being sealed for over 21 days before measuring (Smoak et al., 2012). The ^{226}Ra and ^{228}Ra activity concentrations were then determined through their daughters ^{214}Pb and ^{214}Bi, and ^{228}Ac, respectively (Godoy et al., 1994; Moore, 1983, 1984).

The depths along the estuary ranged from 1.2 to 11.9 m, from the inner to the mouth of the estuary. Water temperature showed little variation, ranging between 21 and 25 °C along the sampling stations. The salinity fluctuated significantly along estuary, ranging from 0.04 ppt at the innermost point (PA1) to 29.15 ppt towards the mouth of the estuary (PA12) (Fig. 2). The salinity was generally higher along the bottom (Fig. 2), likely triggered by denser water currents at the beginning of the flood tide. The highest turbidity in surface water, 54.71 FTU, was detected at the point LA6, while lowest turbidity was found towards the mouth of the estuary (PA12) 2.55 FTU (Fig. 3).

The sediment radium isotope concentrations showed a general decrease from the rivers to the mouth of the estuary (Figs. 4, 5 and 6). In general, the highest and lowest activities were found in Nhundiaquara (R3) and Guaraguaçu (R2) Rivers, respectively. It should be noted that the headwaters of these rivers originate from the Serra do Mar Mountain range, except for the Guaraguaçu River, which originates from springs on the coastal plain and is the river with lowest sediment radium isotope concentrations. In the sediments, it is apparent that the radium isotope concentrations are a function of grain size as the ^{224}Ra, ^{226}Ra and ^{228}Ra activities were inversely proportional to the sediment particle size and driven by the Serra do Mar. geology (Lamuar et al., 2004). Even though there are not many studies in which to compare our findings, the ^{226}Ra results in this work are similar to what was found in the surface sediments in earlier studies (Sanders et al., 2006; Sanders et al., 2012).

It is proposed that the diffusion potential of Ra isotopes is enhanced in fine sediments (Stieglitz et al., 2013). However the water concentrations did not follow a specific pattern that could be attributed to grain size. Indeed, the distribution of the ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra are likely driven by a range of sources (Carroll et al., 1993; Stieglitz et al., 2013). This is because estuarine systems present multiple potential secondary activity sources (end members), such as rivers, tidal channels, mangroves, coastal waters and groundwater discharge (Santos et al., 2010; Smoak et al., 2012; Stieglitz et al., 2013). Although activity distributions in sediment and water surface did not follow the same patterns, the concurrent influence of diffusion in the sediment-water interface on Ra isotopes activities in the water column cannot be discarded, as the aqueous matrix is also affected by tidal factors, wind and river discharge