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Organotin compounds in the Paranaguá Estuarine Complex, Paraná, Brazil: Evaluation of biological effects, surface sediment, and suspended particulate matter

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The input of organotin compounds (OTs) in marine coastal environments such as estuarine systems has been of great concern in recent decades, particularly because of their wide use as biocide components of antifouling paints, but also in industrial and agricultural activities surrounding these areas (Hoch, 2001).

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Although usually detected close to their emission source, OTs can also be carried along estuaries under dynamic-flow conditions (tides, currents), thus reaching remote regions far from the source of contamination (Buggy and Tobin, 2006). Physical estuarine processes such as the occurrence of a maximum turbidity zone (MTZ) or periodic channel dredging required by the intense shipping activity may create a risk to the environment, because of resuspension and transport of contaminated sediments through the water column (Hoch, 2001).

In Brazil, some studies of the occurrence of OTs in estuarine sediments have been conducted (Almeida et al., 2004; Felizzola et al., 2008; Fernandez et al., 2005; Godoi et al., 2003a,b). Biological effects of these compounds also have been demonstrated along the Brazilian coast (Castro et al., 2007a,b; Fernandez et al., 2005, 2007; Pinheiro et al., 2006). Nevertheless, there is a lack of data on the southeast coast of the country, particularly in harbour areas. Moreover, the study of as yet unexplored environmental matrices, such as SPM, provides important information about the transport and behaviour of OTs in estuarine systems, contributing to a better understanding of their environmental risks. This baseline report presents the development of imposex in molluscs, the occurrence of OTs in surface sediments and suspended particulate matter, and the resulting contamination levels in the Paranaguá Estuarine Complex (PEC), where shipping activity is intense. The results will aid in predicting potential environmental impacts on this important estuarine ecosystem.

The Paranaguá Estuarine Complex (PEC) is located on the southern coast of Brazil, (25°16′34″S; 48°17′42″W), in the northern part of the state of Paraná. It is composed of two main axes: north–south by Laranjeiras Bay, and east–west by Paranaguá Bay. The PEC system is highly dynamic due to the influence of a semi-daily tidal regimen and input from the shore. In addition to the marine influence, the estuary receives considerable freshwater input from several rivers, primarily in the rainy season (summer). The tide range can reach 2.2 m, and water renewal occurs approximately every 3.5 days. Two important harbours are installed in the area, Antonina and Paranaguá; the latter is one of the largest ports for grain exporting in Latin America, reaching more than 25 million tons of shiploads. Besides the harbour activities, an extensive fishery in the PEC forms the economic base of the local population. Several marinas are also located along the estuary, which is much frequented by leisure boats because of its abundant natural attractions and conservation areas.

Twenty samples of surface sediment were collected in July 2006, 17 along the main shipping channel (between Mel Island and Antonina Bay), and three samples from the northern part of the PEC in Itaqui, Benito, and Pinheiros bays (Fig. 1), with a bottom sampler. Salinity, pH, temperature, and redox potential were also measured. Samples were subsequently lyophilized, sieved (60 μm), and stored in glass flasks at low temperature until analysis. Samples of suspended particulate matter were collected in the MTZ (corresponding to locations 11, 12 and 13 in Fig. 1), at half-tide during two sampling campaigns (during neap and spring tides) in August 2006, and were identified with N (neap) or S (spring), followed by the number of the sample and B (bottom) or S (surface). Five liters of water from the surface and bottom layers were collected by means of a Niskin bottle sampler. Samples were taken every 2 h and stored in glass flasks under refrigeration (2–4 °C). After filtration on glass–fibre filters, these were stored in aluminum foil until analysis of the OTs. Seston content was evaluated through the difference between empty filters and those containing samples.

The extraction of OTs from surface sediments, as well as from SPM, was carried out following the method proposed by Godoi et al. (2003a). Two grams of dry sediment or small pieces of a filter containing SPM were transferred to a test tube where the extraction procedure was performed with three portions of a 10:4 toluene/acetic-acid mixture in ultrasonic bath. In both cases, tripropyltin (TPrT) and tricyclohexyltin (TCyT) were added as surrogates. For derivatization, 3 mL of Grignard reagent was added to 2 mL of the extract. The organic phase was cleaned through an Al_2O_3 column with hexane as eluent. Final extracts were concentrated to 2 mL with N_2 and TeBT corresponding to 200 ng g^{-1} was added as the injection standard.

Extracts were analyzed by gas chromatography with pulsed-flame photometric detection (PFPD) using a DB5 column (5% phenyl-methylpolysiloxan) and helium as carrier gas. Quality control was carried out with blanks, treated the same way as the samples. The accuracy and precision of the method were checked using PACS-2 marine sediment reference material (National Research Council of Canada, Ottawa, Canada), and the results were in good agreement with the certified values.

Samples of 25–30 sexually mature specimens of the oyster drill *Stramonita haemastoma* were collected at ten sites in Paranaguá

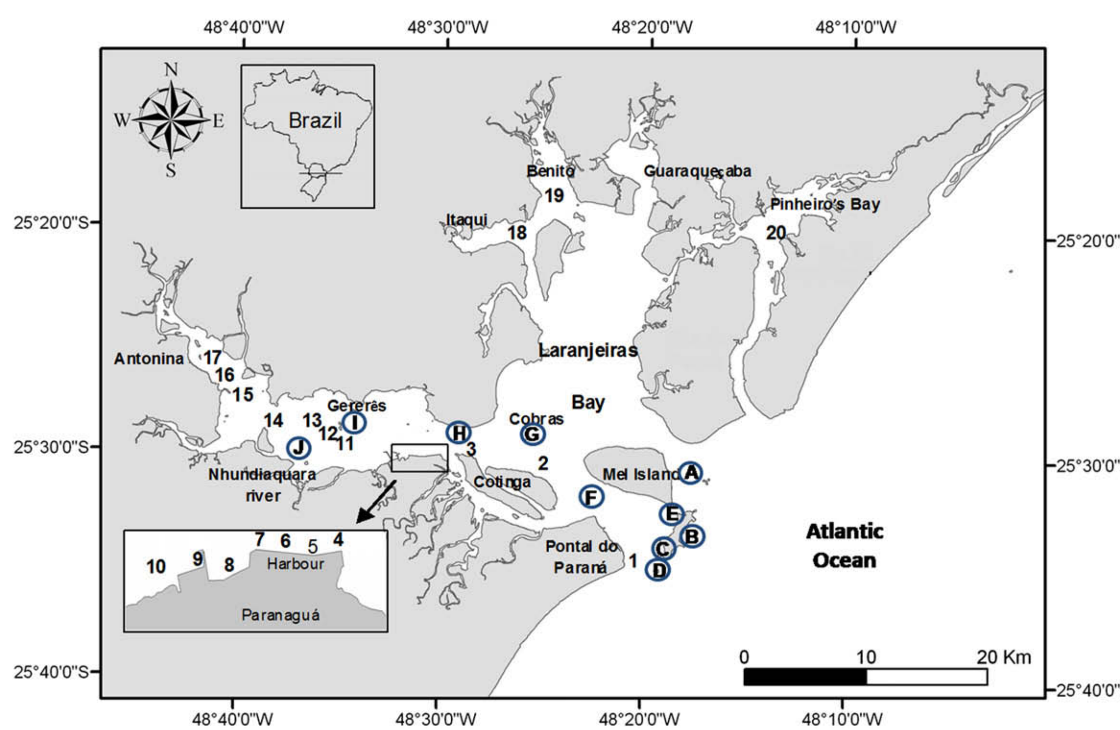

Fig. 1. Surface-sediment (1–20) and biomonitoring stations (A–J) sampling points in the Paranaguá Estuarine Complex (PEC), Brazil.