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Identification of the toxic constituents of sediments in a Brazilian subtropical estuary

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ABSTRACT

Phase 1 of the TIE method was applied to samples of elutriates from sediments of the Itajaí-Açu estuary and adjacent coastal region in southern Brazil. Embryo-larval toxicity assays were used with the sea urchin *Arbacia lixula* in samples of raw elutriate, and treated with *Ulva fasciata*, EDTA and sodium thiosulfate. Inside the estuary, ammonia was responsible for more than 40% of the toxicity in both the dredged and undredged regions. A toxicity gradient was observed, between the estuary and the coastal region, with an increase in the importance of metals for the latter. Temporally, there is strong evidence of the influence of dredging and disposal of sediments in the contamination of the coastal dumping site. The results indicating that this area presents limitations in its saturation capacity. Chemical analysis indicated the metal Cu is probably responsible for the toxicity of the sediments observed, without the interference of ammonia.

1. Introduction

The Itajaí-Açu river is the longest river in Santa Catarina State (southern Brazil). It has a drainage area of 15,500 km^2, and the demographic density around its basin includes some 3000 industrial units, including textiles, metal-mechanics, fisheries, cold storage, paper and tanneries, as well as other smaller industries (Pereira Filho et al., 2003). Its estuary, besides receiving contributions of water, sediments and pollutants from the entire river basin, has the capacity to "neutralize" the majority of contaminants, like ammonium ($N-NH_4^+$), surfactants and total copper, through processes of adsorption and sedimentation (Rorig, 2005) leading to contamination of the sediment by organics and metals (Laitano and Resgalla Jr., 2000).

The port terminals of the towns of Itajaí and Navegantes (SC) are situated in the estuarine region of the Itajaí-Açu river. The port area is constantly dredged, to maintain the navigation channel (Schettini and Toldo Jr., 2006). Two types of dredging are used in this region: maintenance dredging, which is carried out fortnightly, and excavation dredging, which is conducted every three years. For the maintenance of the river access channel, the system used involves pumping water into the sediment, which is then carried away by the natural current towards the river mouth. For the excavation dredging, a suction dredger is used, which dumps the sediment in the coastal region adjacent to the river mouth.

Estuarine sediments have attracted the attention of ecotoxicological studies due to the integration and amplification of concentrations of anthropogenic chemical substances (Burton et al., 2001; Burton and Lamdrum, 2003; Cunha et al., 2007) and the release of these contaminants through dredging activities may present a risk to the environment. This can result in costly environmental problems that require a special approach for their management, including sampling and analysis of the sediments, interpretation of the results, and the establishment of guidelines and plans for corrective action (Mudroch et al., 1995).

Among the different techniques used to evaluate the quality of sediments, ecotoxicological assays associated with TIE (Toxicity Identification Evaluation) (USEPA, 2007) are powerful tools for identifying the major chemical groups present in environmental samples (Brack et al., 2000). Studies by Carr et al. (1996), Brack et al. (2000), Hunt et al. (2001) and Ho et al. (2002), using this approach, a wide range of compounds has been identified in sediments responsible for the toxicity, which can be linked to their sources of origin.

Through the standardized technique of short-term embryo–larval chronic toxicity tests on the sea urchin *Arbacia lixula*, the sediment quality in the lower estuary of the Itajaí-Açu river and adjacent coastal region was evaluated in this study, using the TIE method (Phase 1) to identify the chemical contaminants most likely to be responsible for the observed toxicity of the sediment.

2. Methods

2.1. Sediment sampling and collection

The study was carried out from November 2007 to June 2009, in the lower estuary of the Itajaí-Açu river, located in the north of

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Santa Catarina State, and the adjacent coastal region in southern Brazil. This region includes the port terminals of the towns of Itajaí and Navegantes and forms part of the environmental monitoring program of the area covered by the port of Itajaí.

The sampling events were carried out along two sections of the Itajaí-Açu river: regions upstream of the estuary and outside the area subject to dredging activity (Section 1) and regions under the influence of the maintenance and excavation dredging, including the port terminals and access channel to the port area (Section 2) (Fig. 1). In each section, samples were taken from the navigation channel and Itajaí and Navegantes river banks. The maintenance and excavation dredging are managed by the Itajaí Port Authority fortnightly and once every three years, respectively. The last excavation dredging was carried out from February to June 2009. The samples from the adjacent coastal area were obtained from a pumping site and two control sites located to the north and south of the river mouth.

The sediment samples were obtained using a Ponar-type bottom grab sampler, taking material only from the surface layer to a depth of 5 cm for the analysis. After the sample collection the sediments were divided up, packaged in plastic bags and kept cool at a temperature of 4 °C for subsequent sedimentological analysis and ecotoxicological and chemical assays, after preparing the elutriates. Of the sediment samples included in the Environmental Monitoring Program of the Area Covered by the Port of Itajaí, 58 (of a total of 88) were identified as toxic through prior toxicity tests and sent for analysis, applying the Toxicity Identification Evaluation (TIE) procedures.

2.2. Grain-size analysis of the sediment

The samples were analyzed to determine the predominant grain-size fractions, and the results were processed applying the method of moments (Folk and Ward, 1957). The samples were washed to remove the salts, then dried in an oven at 60 °C. The organic matter content was determined by the hydrogen peroxide (H_2O_2) method and for the carbonates the hydrochloric acid (HCl) method was used, both at concentrations of 30%. For the grain-size fractions, a 0.062 mm sieve was used to separate the coarse fraction (diameter >0.062 mm) and the fine fraction (diameter <0.062 mm) was determined by pipetting. The coarse fraction was separated by a battery of sieves based on the Wentworth (1922) grade scale, and the pipetting followed the recommendations of Suguio (1973).

2.3. Preparation of the elutriates

According to the USEPA (1998) guidelines for the preparation of elutriates, the sediments were mixed with maintenance seawater at a proportion of 1:4. The mixture was then homogenized with a mechanical stirrer for 30 min and left to stand overnight to decant. The supernatant samples were then filtered through a Whatmann® (GF/F) fiberglass filter and stored in amber glass bottles at 4 °C for the subsequent toxicity tests and metal determinations. Where necessary, the salinity was adjusted to 30 by adding brine.

2.4. Determination of ammonium (NH_4^+) and ammonia (NH_3)

After the preparation of the elutriates, the ammonium (NH_4^+) analysis was performed using a MERCK Spectroquant® kit, and the complex color was determined using a BioTek® microplate reader at a wavelength of 690 nm. The un-ionized ammonia (NH_3) was estimated based on the pH, temperature and salinity characteristics of the elutriate, according to the Reis and Mendonça (2009).

2.5. Toxicity tests

The toxicity tests, considering the embryo–larval development of the sea urchin *A. lixula*, followed the methodology described in technical standard NBR15350 (2006). Adults of *A. lixula* were collected in Penha (town on the north coast of Santa Catarina State/Brazil) and after acclimatization in a laboratory, the animals were submitted to an electrical discharge (0.35 A and 30 W) from an ICEL PS4100 electrical source to obtain the gametes. The eggs, obtained by *in vitro* fertilization, were exposed to the samples, maintaining controls containing seawater, under controlled temperature conditions (25 °C) and a 12:12 h light/dark cycle for

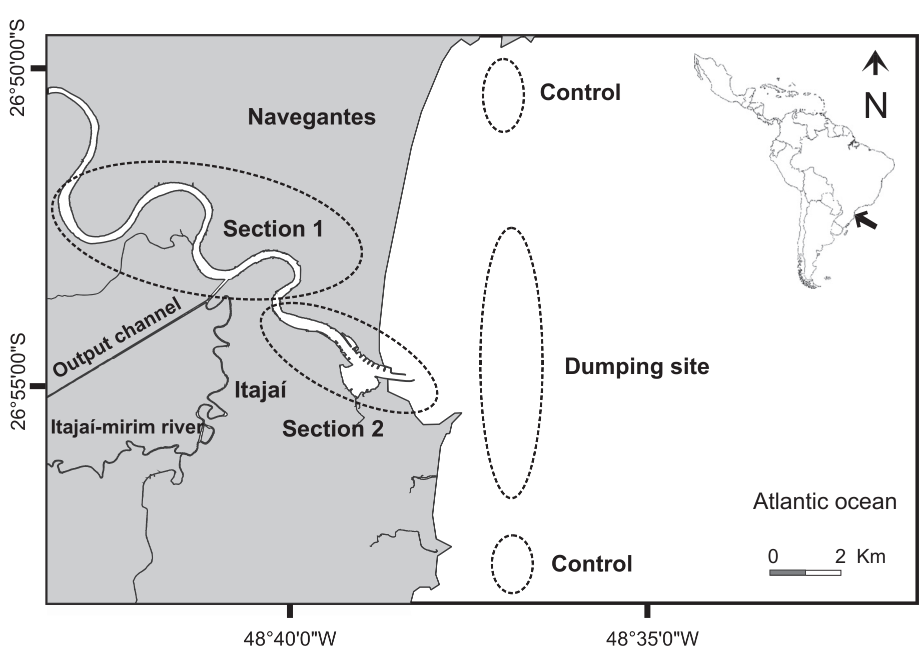

Fig. 1. Area of study with the estuary of the river Itajaí-Açu river in southern Brazil and Sections 1 without dredging and 2 with dredging, and the coastal region adjacent to the confluence of the Itajaí-Açu river, used as the dumping site area, and two control points.