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Baseline

Metals and pesticides in commercial bivalve mollusc production areas in the North and South Bays, Santa Catarina (Brazil)

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ABSTRACT

Concentrations of heavy metals were quantified in mussels *Perna perna* and Pacific oysters *Crassostrea gigas* in 28 cultivation sites in the North and South Bays, SC (Brazil). Concentrations of pesticides were also quantified in these bivalve, water and sediment samples collected in 14 cultivation sites on four occasions in the period October 2012–October 2013. Pesticides were not detected in any of the mussel, oyster, water or sediment samples. The South Bay was found to be generally more contaminated with As while the North Bay showed higher concentrations of Ni. Concentrations of Pb and Cd were below the limit of detection of the method (0.5 mg/kg) in all samples. Mussels accumulated more As and Ni than oysters, while the opposite was observed for Cu. Metal concentrations were below the maximum levels for foodstuffs specified in the Brazilian legislation.

Heavy metals are naturally ubiquitous in coastal aquatic environments through the slow release to the water column via weathering of rocks and sediments. These natural concentrations pose minimal threats to human and environmental health. However, in many parts of the world, metal levels from anthropogenic sources now exceed those from natural sources, particularly in industrial and urbanised catchments. Pesticides have become relatively more abundant in estuaries draining agricultural and urban land. Metals and pesticides accumulate in the tissues of bivalve molluscs at concentrations that can cause carcinogenic and mutagenic effects in consumers. The hazard is usually associated with long-term exposure as illnesses related to a single exposure (meal) are extremely rare (Jensen and Greenlees, 1997).

A good understanding of the sources of metals and pesticides released into aquatic environments and their baseline levels in water, bivalves and sediments is necessary for identifying appropriate pollution reduction programmes. It is also important to help inform aquaculture management plans and to protect public health. International guidance on hygiene controls for bivalves cultivated for human consumption places strong emphasis on monitoring of chemical hazards in growing waters because commercially used post-harvest purification treatments (depuration, relaying) are not effective in removing these substances from bivalve tissues (WHO and FAO, 2009).

The North and South Bays, on the coast of Santa Catarina, are the most important bivalve producing centres in Brazil. In 2012, these production areas generated a total of 17,150 t of bivalve molluscs, representing 70% of the total production in the country (Epagri, 2013). Production is focused on farming of brown mussels (*Perna perna*) and Pacific oysters (*Crassostrea gigas*) in longline systems. This locally important industry has coexisted with an expanding and lucrative tourism industry focused on water-based recreational activities, which has changed the landscape with large areas of the catchment near the city of Florianópolis and Santa Catarina Island now urbanised (Fig. 1). Despite growing concerns on the hygiene status of these bivalve mollusc production areas, very few studies have investigated the levels of metal and pesticide contamination in these bays. Souza et al. (2012) analysed concentrations of organochlorine pesticides in oyster and sediment samples from four sampling sites and found that only DDT and HCH were present in sediments and oysters at very low levels. Other organochlorine pesticides and PCBs were not present at concentrations above the limit of detection of the method. Saenz et al. (2010) tested Cr, V, Ni, Mn, Ag, As, Pb, Cd, Hg, Se and Cu in mussels and surface waters from two sites in the North bay and one site in the South Bay and found that all samples had concentrations below the maximum levels for foodstuffs specified in the national legislation. This study expands this knowledge by providing a more complete characterisation of the spatial and temporal variability of metal and pesticide contamination in the North and South Bays. The sampling programme focused on shellfish production areas that are vulnerable to contamination inputs from land-based sources.

Four sampling campaigns were conducted to understand if there are seasonal differences in contamination levels: 1st — 19–23/11/2012; 2nd

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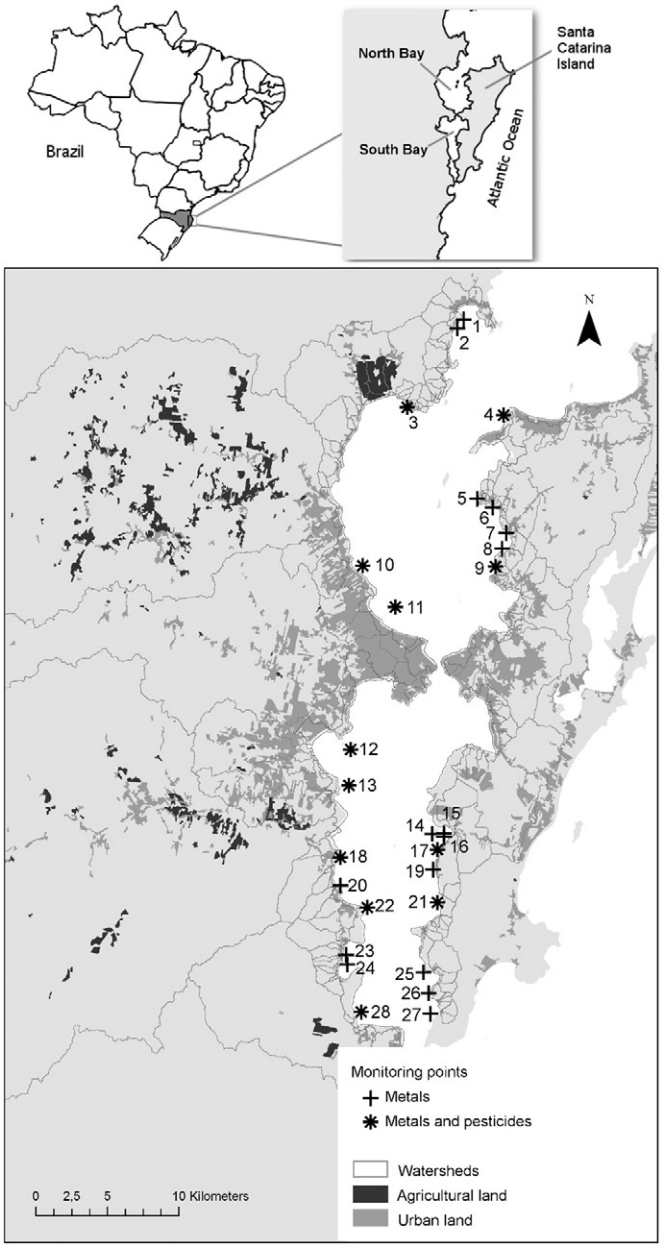

Fig. 1. Location of sampling sites in the North and South Bays, Santa Catarina, Brazil (27° 36'S; 48° 34'W; datum SAD 69).

— 20–27/02/2013; 3rd — 11–13/06/2013; 4th — 20/08–05/09/2013. In these campaigns, molluscs, water and sediment (upper 2 cm) were sampled from 14 sites in the North and South Bays and tested for pesticides. Mussels were sampled in the four campaigns; water was sampled (1 L sterile bottles at 1.5 m depth) in the first and second campaigns and sediment in the third and fourth ones. Oyster samples were also collected from points 10 and 12 (Fig. 1). Mussels (30 individuals/sample) were collected by hand from the cultivation ropes, rinsed with clean freshwater and placed in clean sampling bags. Sediment samples were collected using a Petersen Dredge and also placed in sampling bags. Upon collection, all samples were placed in coolboxes and transported to the laboratory for analyses. For detection and quantification of heavy metals, only mussels were sampled. Sampling was conducted from 28 sites in the North and South Bays. In five of these sites (points 7, 10, 12, 16 and 21), oyster samples were also taken to compare inter-species variation of metal contamination. The sampling procedure was similar to that described for pesticides.

Samples of bivalves and sediment were tested for a total of 196 pesticide compounds (including 19 organochlorines) (Table 1). Water samples were tested for 140 of these compounds. The metals analysed in the bivalves were As, Cd, Pb, Cu and Ni using analytical and quality control procedures described by the AOAC International (Association of Analytical Communities) (Horwitz and Latimer, 2005). All the testing laboratories were accredited for the methods by national competent authorities (heavy metals: LABCAL; pesticides: NFS — Bioensaios). Individual sample batches were checked against standard reference materials. Recovery rates for samples tested for metals were 90–110%.

None of the mussel, oyster, water and sediment samples had pesticide levels above the limit of detection (LoD) of the methods. The use of organochlorine pesticides in agriculture and livestock production has been prohibited by national legislation since 1985 (Ministério da Agricultura, Pecuária e Abastecimento, 1985). However, monitoring of chemicals in foodstuffs (fruits, vegetable, and cereal) in Brazil conducted by ANVISA has shown a relatively high percentage (36%) of samples with levels of pesticides above the statutory limits or detected biocides that are not allowed for use in Brazil (Agência Nacional de Vigilância Sanitária, 2013). Furthermore, although the production, export and import of DDT have been banned in Brazil since 2009 (Congresso Nacional, 2009), concentrations accumulated by benthic marine organisms remain high in parts of the country (Liebezeit et al., 2011). Different contamination profiles have been found however in shellfish production areas in catchments with different land uses (Galvao et al., 2012). The results obtained in this study indicate that despite the use of significant quantities of pesticides in Brazil, they are not a concern in the study area. The results also confirm the findings obtained by Souza et al. (2012) and indicate that the risk of human and ecological exposure to organochlorine pesticides in Florianópolis Bays is lower than that in other estuaries receiving higher volumes of discharges from industrial and urban areas on the coasts of Santa Catarina (Trevisan, 2008) and Rio de Janeiro (Galvao et al., 2012) or catchments with higher agricultural activity in São Paulo (da Silva et al., 2008).

The sampling programme for metals revealed that there is very little variation of contaminant levels in the bays. All samples tested for Pb and Cd had concentrations below the LoD (0.5 mg/kg). In mussels, median concentrations of As, Cu and Ni were 0.40, 0.82 and 0.68 mg/kg, respectively. In oysters, median concentrations for As, Cu and Ni were 0.20, 1.70 and 0.05 respectively (Table 2). Significant differences (Kruskal–Wallis H test, $p < 0.001$) were found in the concentrations of these three metals in mussels between sampling campaigns. The highest concentrations were detected in the first and third campaigns while the lower concentrations were found in the second and third campaigns. Arsenic concentrations showed a different seasonal pattern with high values also in the fourth campaign. No differences were found in the concentrations of metals in oysters between sampling campaigns ($p > 0.05$).

The concentrations of heavy metals in mussels obtained in this work were generally lower than those obtained by Saenz et al. (2010) with the exception of Cu whose levels showed a higher maximum concentration. The most striking differences were in relation to As, whose levels obtained by Saenz et al. were approximately ten times higher than those detected in this study. The study by Saenz et al. used mussels transferred from a commercial production area to other sites in the North and South Bays while the present study used locally produced shellfish in each of the sampling sites. Furthermore, the present study was conducted over a longer timeframe than that of Saenz et al. and therefore the differences observed could be attributed to seasonal variation in the abundance of this metal in the study site.

Concerning spatial variability, no differences were found in metal concentrations in either mussels or oysters between sampling points (Kruskal–Wallis H test; $p > 0.05$). Ni concentrations in mussels sampled from the North bay were generally higher than those from the South bay while the inverse pattern was observed for As (Fig. 2). A comparison of pooled results from all stations in the North bay and those from the