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Ecological effects of contaminated sediments following a decade of no industrial effluents emissions: The Sediment Quality Triad approach

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ABSTRACT

Sediments contaminated by industrial effluents a decade after the emissions were stopped were statistically compared to sediments from reference channels, using the Sediment Quality Triad approach. The metals and metalloid concentrations, mainly Hg and As, increased towards the upper part of a contaminated channel, where the industrial discharge was located. A bioaccumulation assay with *Scrobicularia plana* showed the highest bioaccumulation and mortality in the most contaminated sediments and bioaccumulation strongly correlated with the sediments metals and metalloid concentrations. The resident macroinvertebrate community also showed significant differences between the contaminated and reference channels, in the upper areas, where the community was most affected. All three elements of the quality triad rejected the null hypothesis and indicated that despite the emissions ceasing in 2004, sediments remain contaminated by high levels of metals and metalloid, leading to bioaccumulation and with severe community level consequences.

1. Introduction

Estuaries are among the most productive ecosystems on earth. They are important for many species and constitute preferential areas for the reproduction and growth of several aquatic species, some with high economic value (among others, McLusky and Elliott, 2004). They have long been the sites of large urban and industrial settlements and intensive agriculture upstream, all of which are sources of pressures to surface water bodies (Ferreira et al., 2004; Chapman et al., 2013). The Ria de Aveiro, Western Portugal, is no exception since it has received industrial discharges from the Estarreja Chemical Complex (CQE), which began operating in the 1930s with the production of fertilizers, mineral acids, chlorine and soda, plastics, aromatics and other products. Until 1975, industrial effluents containing organic compound, metals and metalloids, such as mercury, arsenic, zinc, lead, aluminum, cadmium, copper, vanadium and iron were discharged into artificial channels and then into the Estarreja Channel. This produced highly contaminated superficial sediments in the upper areas of the Estarreja Channel (Costa and Jesus-Rydin, 2001; Lucas et al., 1986; Hall et al., 1985; Monterroso et al., 2003; Pereira et al., 1998a, 2009). After 1975, the effluents were discharged directly by pipes into the Estarreja Channel. In 1994, mercury emissions were reduced to regulatory levels (50 μg L^{-1}, the limit value for discharges from chlor-alkali electrolysis industry in accordance with the European Directive 82/176/EEC, 1982) and then emissions ceased in 2002. In 2004 the effluents discharged into the Estarreja Channel were channelled to a multi-municipality sanitation system (SIMRIA) and ocean outfall, thus removing all sewage and industrial effluent discharges from the Ria de Aveiro.

Sediments represent, quantitatively, the major compartment for metal storage in aquatic environments and, consequently, a potential source to interstitial waters and the infauna living in direct contact with the sediments (Chapman et al., 1998; Simpson and Batley, 2007; Luoma and Rainbow, 2011). Macrobenthic organisms and communities are a key component of coastal ecosystems, playing an important role in detritus decomposition, nutrient cycling, and energy flow to higher trophic levels and due to their life-history characteristics, have frequently been used to evaluate the impact of both anthropogenic and natural disturbances in the estuarine environment (Gray and Elliott, 2009). Due to their relatively long lifespan, sedentary lifestyle and consequent incapacity to avoid unfavorable conditions, benthic communities integrate contaminant impacts over time and permit discriminating between episodic and chronic disturbances (Reiss and Kröncke, 2005; Reiss et al., 2006; Dauvin et al., 2007; Elliott and Quintino, 2007; Ward et al., 2013). Their taxonomic diversity produces communities with organisms having a wide range of response/tolerance to environmental stressors (Dauer, 1993; McLusky and Elliott, 2004).

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Although the total metal concentrations in sediments indicate contamination, such measures do not necessarily predict the toxicity of these contaminants to aquatic organisms. The ecotoxicological risk induced by contaminated sediments will depend on metal availability as well as of the ability of living organisms to assimilate those (Amiard et al., 2007; Campana et al., 2012). The relationship between metal accumulation and the feeding behavior of the benthic organisms influences the bioavailability of different metals in the aquatic environment (Monperrus et al., 2005).

This study uses the Sediment Quality Triad (SQT) approach (Long and Chapman, 1985) to analyze the ecological effects of contaminated sediments associated with the industrial chemical effluents discharged in the Estarreja Channel, a decade after the emissions ceased. This approach has been used in marine, estuarine and freshwater environments (e.g., Chapman et al., 1987; Quintino et al., 1995, 2001; Canfield et al., 1996; Delvalls et al., 1998; Carr et al., 2000; Hollert et al., 2002; Khim and Hong, 2014) and integrates the sediment chemistry, sediment toxicity or bioaccumulation assays and resident benthic communities (Chapman, 1986, 1989, 1990). This study compared SQT descriptors analyzed in samples from the impacted (Estarreja) and reference channels (Salreu and Canelas), under the null hypothesis of no significant differences associated with the sediment contamination. The SQT descriptors included sediment metal and metalloids concentrations, their bioaccumulation in the bivalve *Scrobicularia plana* exposed to the test sediments under controlled laboratory conditions and the resident macrofauna benthic community species composition and abundance.

2. Material and methods

2.1. Study area

The Ria de Aveiro is located on the NW coast of Portugal, between 40°38′N and 40°57′N, and is characterized by extensive intertidal mud and sand flats, salt marshes and islands. The study was conducted in three small channels, Estarreja, Canelas and Salreu, discharging to the Laranjo Bay, in the central area of the Ria (Fig. 1). The Estarreja Channel received continuous industrial discharges for decades which produced an environmental contamination gradient (Pereira et al., 1998a,b). The Canelas and Salreu Channels were reference sites, representing largely uncontaminated channels. For the bioaccumulation assays, control sediment was also collected at the mouth of the Mira Channel, from where the specimens of *S. plana* used in the assay were also collected (cf. Fig. 1).

2.2. Field and laboratory procedures

The sediment samples for this study were collected in 2011 and 2013. In 2011, the sediment concentrations of Hg, Cr, Ni, Cu, As, Cd, Zn and Pb and the benthic macroinvertebrate communities were studied along the impacted and the reference channels. In 2013 the sediment contamination analyses and the macrofauna study were repeated and a bioaccumulation assay with the bivalve *S. plana* was set up in order to assess the bioavailability and accumulation of the sediment contaminants. In view of the results obtained in 2011, the sampling effort in 2013 was concentrated in the four areas located along the impacted channel and in the upstream areas of the reference channels.

2.2.1. Sampling, sediment baseline and contamination descriptors and macrofauna communities

Sediment samples for the macrofauna study in the Estarreja, Salreu and Canelas Channels in April 2011 were collected in four areas per channel, with two sites per area and four replicates per site, totaling 96 replicates, 32 per channel (Fig. 1). Each sample was collected with a 0.01 m^2 hand-held corer and placed separately in a plastic container, brought to the laboratory, washed through a 0.5 mm mesh sieve and the residue preserved in 70% ethanol. Benthic macroinvertebrates were hand-sorted and identified using binocular stereoscopic and optical microscopes to species level whenever possible. For each site a species/taxa list with the respective abundance was prepared.

An extra sediment sample per site was collected for grain-size, organic matter and metal and metalloid analyses. The sediment grain-size was analyzed by wet and dry sieving, following Quintino et al. (1989). The fines fraction (particles with diameter < 0.063 mm) was wet sieved through a 0.063 mm mesh screen. The sand (particles with diameter from 0.063 mm to 2 mm) and the gravel fractions (particles with diameter above 2 mm) were dry sieved through a nest of sieves spaced at 1ϕ interval ($\phi = -\log_2$ the particle diameter expressed in mm).

The sediment samples for the total organic matter analysis were kept at −20 °C. After thawing, the samples were oven dried at 60 °C for 24 h and ground. Total organic matter concentration (TOM) was obtained by loss on ignition, as the percent weight loss in 1 g of dried sediment, after combustion at 450 °C for 5 h (Kristensen and Anderson, 1987).

Total mercury (Hg), chromium (Cr), nickel (Ni), copper (Cu), arsenic (As), cadmium (Cd), zinc (Zn) and lead (Pb) were analyzed by an accredited laboratory. For Hg, Cr, Ni, Cu, As, Cd, Zn and Pb quantification, 2 g of homogenized air dried sediment were digested overnight (±18 h) at 115 °C with 10 ml of 65% HNO_3 (Suprapur, Merck) in digestion Teflon bombs (sealed chambers). To prevent the loss of metals and metalloids by volatilisation, chambers were only opened when completely cooled. The cooled digest was made up to 25 ml with 1 M HNO_3. After a 20× dilution, the concentrations of Cr, Ni, Cu, As, Cd, Pb and Hg were determined by inductively coupled plasma mass spectrometry (*ICP-MS*) following the laboratory internal standard method ISO 17294 and the concentration of Zn was measured by inductively coupled plasma atomic emission spectroscopy (*ICP-AES*), according to the standard method ISO 11885.

In order to measure salinity over a tidal cycle, bottom water samples were collected simultaneously every 30 min during a period of 12 h, at three sites per channel, (sites Ea–Ec in Estarreja, Ca–Cc in Canelas and Sa–Sc in Salreu, Fig. 1).

In April 2013, sediment metal and metalloid analyses were repeated and a bioaccumulation assay was carried out in order to test the bioavailability of the sediment contaminants and their effect in the survival of the test bivalve *S. plana*. Taking into account the results from 2011, the sampling effort in 2013 was concentrated to the four areas of the Estarreja Channel and the most upstream area of the reference channels, Canelas and Salreu. The number of replicate samples per site was increased in order to increase statistical hypothesis power. For the bioaccumulation assay, a control sediment was also sampled in the Mira Channel, near the mouth of the Ria de Aveiro, from where the specimens of *S. plana* used in the assay were collected (Fig. 1). This bivalve is a long-lived facultative surface deposit feeder and suspension feeder (Kamermans, 1994). The natural habitat of this species ranges from muddy to sandy sediments, with a wide salinity range (4–30) and geographical distribution (Byrne and O'Halloran, 2001). It has a lifespan of 5 years, annual recruitment and growth rate of approx. 1 cm y^{-1} in S Europe (Verdelhos et al., 2005). This species has been previously used both in biomonitoring programs (Cheggour et al., 2005; Anajjar et al., 2008) and toxicity tests (Byrne and O'Halloran, 2001; García-Luque et al., 2004; Pérez et al., 2004; Riba et al., 2004).

For the bioaccumulation assay, four sediment replicates per area were collected with a plastic spatula, placed in separate