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Integrative assessment of coastal marine pollution in the Bay of Santander and the Upper Galician Rias

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ABSTRACT

Sediments from the Rias of A Coruña, Ferrol, Betanzos and Ares (n = 26) and the Bay of Santander (n = 11) were sampled in July 2012. The concentration of organic contaminants in sediment elutriates (CBs, PAHs, pesticides and personal care products) and sea urchin (*Paracentrotus lividus*) embryotoxicity were assessed. Relevant concentrations of organic pollutants were detected in the elutriates (ΣContaminants < 400 ng/L) but their interpretation in terms of the observed toxicity was not straightforward. A clear gradient of toxicity from the inner to the outer areas of the Bay of Santander was observed. Sediment elutriates from three stations situated close to the city of A Coruña showed moderate toxicity values, whereas sediment elutriates from the Rias of Ares and Betanzos showed no marked toxicity. Stations located close to the city of Ferrol showed moderate to high toxicity, which is indicative of a nearby source of contamination. On the contrary, the outer area of the Ria of Ferrol was classified as "Good" according to the calculated toxic units. These results allowed for an integrative assessment of the environmental quality of the studied areas.

1. Introduction

Current European legislation for the protection and conservation of the marine environment emphasizes the need to evaluate and keep within acceptable limits the environmental concentrations of contaminants, in order to take preventive measures to return impacted marine areas to good environmental status (Marine Strategy Framework Directive, MSFD, 2008/56/EC, Commission Decision 2010/477/EU). This environmental objective calls for the use of preventive tools that may allow the link between pollutant levels in the environment and their harmful effects on ecosystems to be established (Davies et al., 2012; OSPAR Commission, 2012).

Toxicity bioassays measure the effect caused by the exposure of test organisms, over a defined period, to different concentrations of one or more xenobiotics, at a given level of biological organization (Chapman and Long, 1983). For instance, the assessment of the biological effects of pollution in a complex matrix, such as sediment, usually involves the use of test organisms in the laboratory in order to predict ecosystem-level effects (Adams and Rowland, 2003). The rationale for using this type of biological tools to complement analytical chemistry techniques is that they present additional advantages such as detecting new contaminants for which no analytical techniques have yet been developed, providing an insight of the bioavailability of pollutants or integrating the toxic effects of different substances in the environment (His et al., 2000). The embryonic and larval stages of marine invertebrates are less tolerant to toxicants than adults (His et al., 2000; Marin et al., 1991) and embryo–larval bioassays, in particular with bivalves and sea urchins, have been used for decades for assessing and monitoring marine pollution (His et al., 1997; Kobayashi, 1981; Woelke, 1972).

Most anthropogenic chemicals introduced directly (by effluent treatment plants, accidental discharges, etc.) or indirectly (riverine inputs, surface runoff, atmospheric deposition, etc.) into the marine environment eventually accumulate in sediments (Burton et al., 2003). Marine sediments are preferred to seawater samples as a matrix for monitoring environmental quality, because the concentrations of hydrophobic pollutants are much higher and less variable in time and space than in seawater, reflecting in an integrated manner the pollution state in a given area (Bellas et al., 2011b; Power and Chapman, 1992). However, this matrix not only acts as a reservoir for contaminants, but also serves as a source of toxicants to marine fauna due to resuspension resulting from either natural (bioturbation and bio-irrigation, resuspension by storms, waves and tidal currents, diffusive fluxes, etc.) or anthropogenic (dredging, trawling) causes (Fichet et al., 1998; Long et al., 1996; Rial and Beiras, 2012). For these reasons, sediments are usually

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studied in marine pollution surveillance programs (European Union, 2010; OSPAR Commission, 2012; UNEP/MAP, 2011; USEPA, 2004).

Among the different types of procedures used to assess sediment toxicity (bulk sediment, pore-water, elutriate or extract assays), obtaining an elutriate has been recommended to simulate the maximum capacity of a sediment for releasing pollutants during a water-sediment resuspension event (e.g. storms, dredging episodes) (USEPA/USACE, 2004). The sea urchin embryo test with sediment elutriates represents a simple, cost-effective and sensitive technique, with an adequate level of standardization, and has been proposed by the International Council for the Exploration of the Sea (ICES) for routine use in the monitoring of coastal pollution (Beiras et al., 2012; Davies et al., 2012). Furthermore, the use of this biological tool has been established in the Spanish guidelines for the characterization of dredged material (CIEM, 2015) and is used as an indicator for the ongoing assessment of the MSFD descriptor 8 (*concentrations of contaminants are at levels not giving rise to pollution effects*) in Spain (Alemany et al., 2014). The characterization of sediment toxicity will offer an assessment of the adverse biological effects of the whole range of contaminants transferred from sediment to elutriate. The international monitoring programs only consider the analysis in representative matrices (biota and sediment) of a reduced group of pollutants due to their persistence and/or toxicity such as trace metals, organochlorinated compounds or polycyclic aromatic hydrocarbons. However, many other organic contaminants such as current-use pesticides, personal care products, pharmaceuticals or surfactants are present in the marine environment (Moreno-González et al., 2013; Moreno-González et al., 2015; Na et al., 2013; Pintado-Herrera et al., 2014, 2016; Tovar-Sánchez et al., 2013; Traverso-Soto et al., 2015). These substances are considered as contaminants of emerging concern due to their continuous input into the marine environment, particularly in coastal areas (Barceló, 2003). The presence and distribution of emerging organic contaminants (pharmaceuticals, personal care products and current-use pesticides) have been characterized in some Spanish coastal areas, such as the Catalonian coast (Ferrer et al., 1997; Kuster et al., 2008; Martínez and Barceló, 2001), the Bay of Cádiz (Pintado-Herrera et al., 2016), the Mar Menor lagoon and the Canary Islands (Camino-Sánchez et al., 2011). However, to the best of our knowledge these substances have not been studied in the North-Atlantic Spanish coast. PAHs and trace metals have been characterized in sediments from the Bay of Santander together with the bacteria *Vibrio fischeri* toxicity tests (Coz et al., 2008; Viguri et al., 2007) or the polychaete *Arenicola marina* (Ramos-Gómez et al., 2011c). Beiras et al. (2003) studied intertidal sediments taken in the Ria of A Coruña by chemical analysis (metals, PCBs) and bioassays (mussel, sea-urchin, ascidia and prawn). However, no previous toxicity tests have been performed using sea urchin embryos in the Bay of Santander or in the Artabrian Gulf, a coastal area formed by the Rias of A Coruña, Betanzos, Ares and Ferrol.

Improvements in the sensitivity and accuracy of analytical techniques has made it possible to determine many organic pollutants in marine matrices at very low concentrations using specific or multi-residue methods. In this sense, stir bar sorptive extraction (SBSE) is suitable for apolar compounds (log Kow > 2), proving its usefulness as a multi-residue method for seawater sample analysis. In fact, different analytical procedures have been proposed for the determination of several groups of organic pollutants in seawater by SBSE coupled to gas chromatography–mass spectrometry (GC/MS) in recent years (Moreno-González et al., 2013; Pérez-Carrera et al., 2007; Sánchez-Avila et al., 2010), showing limits of quantification of only a few ng/L. Consequently this multi-residue method can also be applied to elutriates in order to determine simultaneously regulated and emerging organic pollutants at environmental concentrations.

The aim of this work was to: a) describe spatial patterns of the more readily bioavailable fraction of pollutants in coastal sediments by chemical analyses of elutriates and sea urchin toxicity bioassays, and b) to link chemical analyses and toxicity to sea urchin embryos.

2. Material and methods

2.1. Sediment sampling

Sampling was conducted in two areas from the N-NW Iberian Peninsula, namely the Upper Galician Rias (A Coruña, Betanzos, Ares and Ferrol) and the Bay of Santander (Fig. 1). Eleven stations of the Bay of Santander were sampled aboard the research vessel B/O José María Navaz from 3rd to 5th July 2012 and twenty-six samples were taken from 11th to 12th July 2012 in the Upper Galician Rias (Fig. 1). Sediments were collected with a box-corer (10 × 16 cm), the surface layer (first 2–3 cm depth) being immediately sampled and stored at 4 °C in the dark.

The main rivers in the study areas are the River Mero in the Ria of A Coruña, with a mean river discharge (Qm) of 3.67 m^3/s, the rivers Mendo (Qm = 3.04 m^3/s) and Mandeo (Qm = 10.41 m^3/s) in the Ria of Betanzos, the River Eume (Qm = 23.82 m^3/s) in the Ria of Ares, the rivers Xubia (Qm = 4.58 m^3/s) and Belelle (Qm = 3.02 m^3/s) in the Ria of Ferrol and the River Miera (Qm = 5.24 m^3/s) in the Bay of Santander (Confederación Hidrográfica del Cantábrico, 2017; Xunta de Galicia, 2016). The percentage of fine particles (<63 μm) in the sediments presents values below 25% in the Ria of A Coruña, 10–60% in that of Betanzos, 30–60% in that of Ares, 5–50% in that of Ferrol and 5–70% in the Bay of Santander (Pérez, 2016).

Urban, agricultural and industrial activities that take place on the margins of the Upper Galician Rias and the Bay of Santander generate chemical substances that can reach the marine environment through fluvial and atmospheric pathways, although most substances are released directly into the marine environment either deliberately (urban and industrial effluents, dredging, cleaning of boat tanks or out-of-pipe dumping) or accidentally. Total traffic in the main ports of the study areas was (figures for the year 2014): 11.96×10^6, 7.56×10^6 and 5.32×10^6 metric tons, for A Coruña, Ferrol and Santander, respectively (Ministerio de Fomento, 2016). The main industrial activity in A Coruña is petroleum refining, but other industries include the manufacture of aluminum and metal products. In fact, the inner part of the estuary (known as the Ria of O Burgo) presents very high levels of hydrocarbons, mainly due to chronic oil pollution, a situation which has been aggravated by several oil spills (Soriano et al., 2006). The Ria of Ferrol is home to large-scale shipbuilding and port activities that give rise to the introduction of different pollutants in the inner part of the estuary, including hydrocarbons, polychlorinated biphenyls, polybrominated diphenyl ethers or metals (Bellas et al., 2014). The margins of the Bay of Santander host a wide range of industrial activities, including iron and steel casting, metal processing, shipbuilding, chemical and pharmaceutical industries or wood processing, as well as intense port activity and a large population nucleus. These activities mainly affect the inner zone of the bay, which receives the majority of fluvial inputs and has a low rate of water renewal.

2.2. Elutriate preparation

Sediments were transported and kept refrigerated at 4 °C. Sediment elutriates and bioassays were performed within one week after sampling finished. Elutriates were obtained by rotatory mixing of 100 g of sediment and 500 mL of control 1 μm filtered seawater (FSW) at 60 rpm for 30 min in polypropylene flasks, and overnight decantation at 20 °C (Beiras, 2002). The liquid phase (elutriate) was siphoned into a separate beaker and then aerated for 10 min to eliminate any potential toxicity caused by H_2S. Temperature, salinity, pH and dissolved oxygen were recorded prior to the bioassays. The presence of H_2S was checked with Aquaquant tests (detection limit: 0.1 mg/L) (Merck KGaA, Germany). Elutriates were filtered through GF/F filters (0.7 μm, 47 mm) and frozen for further chemical analyses.

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