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ScienceDirect
Chemosphere 72 (2008) 826–835
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Integrative assessment of coastal pollution in a Ría coastal system (Galicia, NW Spain): Correspondence between sediment chemistry and toxicity

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Received 31 October 2007; received in revised form 12 February 2008; accepted 19 February 2008
Available online 2 April 2008

Abstract

Elutriate embryo-larval bioassays with sea-urchins (*Paracentrotus lividus*) and ascidians (*Ciona intestinalis*) were conducted concurrently with trace metal analyses as part of an integrative assessment of sediment pollution at Ría de Pontevedra (Galicia, NW Spain). High metal contents in sediments were found in localised areas from the inner part of the estuary indicating a clear anthropogenic influence. In particular, very high Cu, Zn and Pb levels were found at sites P2 and P3, which were also the most toxic to the embryo-larval bioassays. Sediment quality guidelines were used to help in the ecological interpretation of sediment chemistry data and to identify pollutants of concern. Cu and Zn in P3 were consistently above the effects range median (ERM) values, which seem to be good predictors of toxicity to sea-urchin and ascidian embryos. A toxic unit approach, based on published EC_{50} values and metal levels in elutriates, was used to assess the harmful ecological effects associated to sediment chemistry. Toxicity detected in P3 may be explained on the basis of the toxic unit model; however, the high toxicity detected at P2 may be attributable not only to the metals quantified in the analyses but also to unmeasured organic pollutants. Multidimensional scaling applied independently to the toxicology and chemistry data resulted in a good agreement between both types of configurations. Moreover, the Mantel test revealed a significant correlation ($r_M = 0.481$; $p = 0.019$) between metal concentrations and toxicity data profiles, supporting the correspondence between configurations.

Keywords: Sediment toxicity; Elutriate; *Paracentrotus lividus*; *Ciona intestinalis*; Trace metals; Embryo-larval bioassay

1. Introduction

Galicia (NW Iberian Peninsula) is considered by the European Union (EU) a region highly dependent on fisheries, where fishing (including shellfish), aquaculture and related activities account for 10% of Gross Internal Product (European Commission, 2007). The Galician Rías are highly productive estuaries of key economic, social and cultural value. Among the shellfish production of the Galician Rías stands out the marine mussel (*Mytilus galloprovincialis*) as the main cultivated species, with an annual production of more than 250000 metric tons (135×10^6 euros) which represents 20% of the world mussel production. Also, clams and cockles are relevant commercial species (Labarta, 2004). However, coastal regions are also densely populated areas subjected to the impact of urban and industrial development. For instance, more than 50% of the Galician population and the most important industrial areas of the region are located on the coast (INE, 2007), which causes a strong increment in the levels of potentially harmful chemical agents in the estuaries, giving rise to a decrease in the sediment and water quality and representing a serious threat for marine life. Within this socioeconomic framework, marine environment is rather unprotected. Although the economic relevance of the Galician coast prompted the development of a pioneer legislation at a national level that tries to protect aquatic

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doi:10.1016/j.chemosphere.2008.02.039

resources and cultures (Law for the Protection of Water Quality in Galician Rias, BOE num. 230, 25/9/2001; R.D. 345/1993 de 5 de Marzo, BOE num. 74, BOE num. 134), this is based on arbitrary levels of pollutants, and not on those that produce harmful effects on organisms.

Different international organisations and institutions with competence in environmental management (OSPAR Commission, 2000; ICES, 2003) identified the difficulty of establishing clear relationships between results of chemical assessment of pollution and the pollutant concentrations that may cause ecological damage, and consequently advocated the application of biological techniques to establish the link between pollutant levels and their harmful effects on living resources in order to fulfil the demands of the European legislation (Directive 2000/60/EC). Therefore, in view of the richness in marine resources of the Galician Rías and the potential uses of the coast which are incompatible with the sustained exploitation of those resources, we have conducted an integrative assessment of the coastal pollution in the Galician coast, focusing on Ría de Pontevedra, where we have previously found strong evidence of chemical pollution (Beiras et al., 2003a,b).

Sediments are commonly used as environmental matrices in monitoring programmes because they act as major reservoirs of persistent pollutants in coastal and estuarine systems, at concentrations orders of magnitude above those in water and constituting complex mixtures of chemicals that may eventually be available to organisms (Campbell and Tessier, 1991; Förstner and Salomons, 1991; Fichet et al., 1998; Bellas et al., 2007). Currently, integrative approaches including not only sediment chemistry but also toxicity tests with early life stages of marine organisms, which respond to the bioavailable fraction of pollutants, are advocated (Long et al., 1995; His et al., 1999; Beiras et al., 2003a,b). The embryonic and larval stages of marine invertebrates are less tolerant to toxicants than adults (e.g., Connor, 1972; Marin et al., 1991; Ringwood, 1991) and, if the fitness of a species depends on its performance through successive developmental stages, it seems natural to use the most sensitive step in its life history to evaluate the environmental quality (Stebbing et al., 1980). The embryo-larval bioassays, in particular with bivalves and sea-urchins, have been used for decades as sensitive, simple, and reliable tools for assessing and monitoring marine pollution (Woelke, 1972; Kobayashi, 1981; His et al., 1997).

In the present study we implemented an integrative approach based on chemical analyses of sediments from sampling sites in Ría de Pontevedra and embryo-larval liquid-phase bioassays with the sea-urchin *Paracentrotus lividus* (Lamarck, 1816) and the ascidian *Ciona intestinalis* (Linnaeus, 1767) as biological tools for the assessment of marine pollution. *P. lividus* is a large sea-urchin (up to 7 cm diameter) which is widely distributed throughout the Mediterranean Sea and European Atlantic coast (Hayward and Ryland, 1990; Boudouresque and Verlaque, 2001). This species occurs in rocky shores down to a maximum depth of 150 m (Besteiro and Urgorri, 1988), and plays key ecological roles in the functioning and structure of benthic assemblages (Hayward and Ryland, 1990). Also, in some European countries (France, Spain, Italy, Ireland, Portugal and Croatia) *P. lividus* is exploited for its high valued gonads (Boudouresque and Verlaque, 2001). *C. intestinalis* is probably the most studied and cosmopolitan species of ascidian (Berrill, 1947). This solitary ascidian occurs in dense aggregations down to 500 m depth and is usually the dominant space occupier playing an important role in the ecosystem as a filter-feeder (Dybern, 1965).

The main goals of this study were to reveal patterns in sediment coastal pollution and to compare and establish relationships between toxicity and chemical analyses of sediments and elutriates in Ría de Pontevedra. This integrated approach will permit to understand which sediment pollutants may be contributing to the toxicity in the estuary.

2. Materials and methods

2.1. Sampling and environmental parameters

Twelve intertidal and eight subtidal stations from Ría de Pontevedra (Galicia, NW Spain) were sampled during spring and summer 2002. Sites are located at the inner part of the estuary where the highest environmental hazard was detected in previous studies (Beiras et al., 2003a,b). General environmental parameters (surface water temperature, salinity, pH, dissolved oxygen and redox potential at 1, 3 and 5 cm in the sediment) were recorded *in situ* by means of electrodes. Biological oxygen demand (BOD_5) and phosphate levels were measured in triplicate water samples according to standard methods (APHA–AWWA–WPCF, 1992).

Triplicate samples of intertidal sediments collected at each site were used concurrently for toxicity testing and chemical analysis of trace metals. The surface layer (4 cm) of the intertidal sediments was collected with wooden spatulas at low tide within the vertices of a 3 m side triangle, placed into sealed polyethylene bags and carried to the laboratory on ice. In addition, subtidal sediments were sampled at eight stations with a Box corer for toxicity testing and chemical analysis of trace metals.

Samples intended for chemical analyses were stored at −20 °C, whilst samples for bioassays were stored at 4 °C in the dark for less than 3 days until use. Organic matter content was estimated as loss on ignition by drying the sediment at 80 °C until constant weight and incineration in furnace at 450 °C overnight. Fine fraction (% dry weight) was obtained by sieving at 0.063 mm (Restch, AS2000 model). All glassware was washed with diluted HNO_3 and rinsed with distilled water.

2.2. Analysis of metals in sediments and elutriates

Analysis of trace metals (V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Ba and Pb) in sediments was carried out by X-ray fluorescence (Siemens SRS 3000), after grinding the