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Integrative assessment of coastal pollution: Development and evaluation of sediment quality criteria from chemical contamination and ecotoxicological data

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ABSTRACT

Elutriate embryo-larval bioassays with sea-urchins (*Paracentrotus lividus*) were conducted concurrently with chemical analyses of sediments and biota as part of an integrative assessment of pollution in highly productive coastal regions. High metal contents and organic compounds in sediments and mussels were found in localised areas from the inner part of the estuaries indicating a clear anthropogenic influence. In particular, average maximum concentrations of 2803 mg Cu/kg dw, 776 mg Pb/kg dw, 2.5 mg Hg/kg dw and 5803 μg $\sum_7$PAHs/kg dw were measured in sediments from the most polluted sites. Significant correlations were observed between sediment chemistry and toxicity bioassays. Moreover, the Mantel test revealed a significant correlation (r_M=0.80; $p<0.01$) between sediment pollutant concentrations and toxicity data profiles. In addition, sediment quality criteria were used to help in the ecological interpretation of sediment chemistry data and to identify pollutants of concern. The toxicity bioassays identified polluted sites and quantified the level of toxicity, providing a cost-effective tool to complement the routine chemical monitoring currently conducted in European coastal waters with ecologically relevant information. This is in line with the recent European legislation that advocates the use of biological tools with the ultimate aim of protecting marine resources from anthropogenic substances that will affect their sensitive early life stages.

1. Introduction

Environmental pollution has been traditionally assessed by means of chemical analysis of a list of individual compounds on different environmental matrices. However, the chemical monitoring of marine pollution does not allow the detection of all potential pollutants entering the marine environment and their transformation products (e.g. Zhadan et al., 1992; His et al., 1999). Moreover, there is no simple direct relationship between the pollutant concentrations and their ecological risk, since the presence of contaminants does not necessarily mean that they are bioavailable and, therefore, that they may cause toxic effects on living organisms (Long et al., 1995; His et al., 1999; Beiras et al., 2003a, b). Current European legislation for the protection of the marine environment (Directives 2000/60/EC and 2008/56/EC) places emphasis on the ecosystem assessment rather than the amount of chemicals identified in the laboratory. Also, different international organisations and institutions with competence in environmental management (e.g. OSPAR Commission, 2000; ICES, 2003) identified the difficulty of establishing clear relationships between results of chemical monitoring 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. Attempts to fill this gap lead to the proposal of biological responses at different levels of organisation, from molecular biomarkers to community indices, with particular attention to ecotoxicological bioassays. Marine invertebrate embryo-larval bioassays, are well-known biological techniques among those frequently used in coastal monitoring because of their sensitivity, ecological relevance, cost-effectiveness and rapid response (e.g. Kobayashi, 1971, 1991; Bougis et al., 1979; Vashchenko and Zhadan, 1993; Carr et al., 1996).

Galicia (NW Iberian Peninsula) is considered by the EU a region highly dependent on fisheries, where fishing, aquaculture and related activities account for 10% of the Gross Internal Product. However, these highly productive coastal regions are also densely populated areas subjected to the impact of urban and industrial development, which causes a strong increment in the levels of potentially harmful chemical agents in the estuaries, representing

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a serious threat for marine life. In view of the richness in marine resources of the Galician Rias and the potential uses of the coast, which are incompatible with the sustained exploitation of those resources, we have been developing integrated tools with which to assess coastal pollution that included embryo-larval bioassays, concurrently with chemical analyses of sediments and biota, for the past ten years (e.g. Beiras et al., 2003a, b; Fernández et al., 2008; Bellas et al., 2008).

On the basis of this information we aim now at linking the chemical contamination and the ecotoxicological data sets with the objective of deriving empirical guidelines suitable for the management of these productive ecosystems. Sediment quality criteria (SQC), or guidelines, are numerical values useful to interpret the significance of chemical concentrations in sediments, identify contaminants of concern and prioritize areas for regulation or restoration (MacDonald et al., 1996 and citations therein). In North-America, empirical SQC have been developed from comprehensive local data sets (Long et al., 1995; MacDonald et al., 1996). In this context, it is necessary to carry out site-specific assessments to determine if allochtonous SQC are applicable to that particular site (Long et al., 2006).

2. Materials and methods

A multiyear data set, including sediment chemistry and ecotoxicological bioassays with sea-urchin embryos, was generated from the investigative monitoring of marine pollution conducted in small-scale surveys along the Galician Rias (NW Iberian Peninsula) for the past ten years (Table 1). Details on the field sampling methods were provided elsewhere (Beiras et al., 2003a, b). Only chemicals for which international environmental quality criteria were available (ERL, effects range low/ERM, effects range median and TEL, threshold effects level/PEL, probable-effects level) were included in the data set. For consistency, only those locations where the sediment chemistry data included at least Pb, Cu, Zn, Cr, Ni, Phe, Fla, Pyr, BaA, Chr, BaP and DahA were selected. In addition, sediment concentrations of Hg, Cd, Ant and PCBs (polychlorinated biphenyls) were available for most of the selected locations.

Table 1
Locations sampled in the investigative surveys conducted in the Galician Rias.

Name	Ria	Site	Location (N–W)	Years
Ponte romana	O Burgo	C1	43°18.983′–8°21.500′	1998
Perillo	O Burgo	C2	43°19.800′–8°22.333′	1998
Bamio	Arousa	A1	42°38.417′–8°45.617′	1997–1999
Fangueira	Arousa	A2	42°37.500′–8°46.167′	1997–1999, 2008
Carril	Arousa	A3	42°37.000′–8°46.483′	1997–1999
Catoira-1	Arousa	CT1	42°40.013′–8°43.853′	2008
Catoira-2	Arousa	CT2	42°40.087′–8°43.956′	2008
Catoira-3	Arousa	CT3	42°40.176′–8°44.015′	2008
Ponte autopista	Pontevedra	P1	42°25.950′–8°38.900′	1997–2002
Lourizán	Pontevedra	P15	42°24.867′–8°40.417′	2001–2002
Praceres	Pontevedra	P2	42°24.483′–8°40.950′	1997–2002
Marín	Pontevedra	P3	42°24.417′–8°41.283′	1997–2002
Portocelo	Pontevedra	P35	42°23.383′–8°42.933′	2001–2002
Combarro-porto	Pontevedra	P4	42°25.850′–8°42.117′	2000–2002
Combarro-praia	Pontevedra	P5	42°26.050′–8°42.050′	2000–2002
Fábrica	Pontevedra	P6	42°26.267′–8°41.417′	2000–2002
Praia do polvorín	Pontevedra	P7	42°25.267′–8°40.383′	2000–2002
Lourido	Pontevedra	P8	42°25.550′–8°40.033′	2000–2002
Lourido-punta	Pontevedra	P85	42°25.467′–8°39.967′	2001–2002
Poio	Pontevedra	P9	42°25.550′–8°39.283′	2000–2002
Portela	Vigo	V1	42°17.350′–8°37.467′	1997–1999
Ponte do tren	Vigo	V2	42°17.200′–8°37.983′	1997–1999
Soutelo	Vigo	V3	42°17.417′–8°38.417′	1997–1999
Redondela	Vigo	RE	42°17.350′–8°38.080′	2004–2006
Moaña	Vigo	MO	42°16.080′–8°44.380′	2004–2006
A Guía	Vigo	AG	42°15.500′–8°42.630′	2004–2006
Cangas	Vigo	CA	42°14.580′–8°46.950′	2004–2006
Bouzas-a	Vigo	VB	42°13.850′–8°44.500′	2005–2006
Náutico-a	Vigo	VN	42°14.490′–8°43.390′	2005–2006
Baiona	Vigo	BA	42°7.330′–8°50.410′	2004
Bouzas-b	Vigo	VI1	42°13.983′–8°45.033′	2007
Bouzas-c	Vigo	VI2	42°13.567′–8°44.717′	2007
Porto pesqueiro	Vigo	VI3	42°14.367′–8°43.950′	2007
Náutico-b	Vigo	VI4	42°14.517′–8°43.283′	2007
Teis	Vigo	VI5	42°15.117′–8°42.467′	2007

2.1. Chemical analyses and calculation of the chemical pollution index (CPI).

The methodology used for the chemical determinations was detailed elsewhere (Beiras et al., 2002, 2003a, b; Nieto et al., 2006).

The Hg in sediments (fraction <2 mm) and mussels was determined by cold-vapour atomic absorption spectrometry (AAS) coupled to a Flow Injection system, after digestion with a mixture of HNO_3 and H_2SO_4. The Cd was determined in sediments by graphite furnace AAS after digestion with a mixture of HNO_3–HCl–HF and neutralization of the excess of HF with HBO_3. For the analyses of the remaining elements (As, Cr, Cu, Ni, Pb, Zn) sediments were ground in an agate mill down to a grain size <200 μm and quantitative analysis was carried out by X-ray fluorescence. Mussel samples were digested with HNO_3 in teflon digestion vessels by means of a microwave oven. Cd, Cr, Cu, Ni, Pb and Zn were determined by inductive coupled plasma optical emission spectrometry (ICP-OES).

For the analysis of PCBs (IUPAC numbers 28, 52, 101, 118, 138, 153 and 180, considered as priority marine pollutants by international agencies) sediments were extracted by Soxhlet with a mixture of pentane–dichloromethane (1:1 vol.). The extracts were purified in an alumina column, eluted with pentane, and fractionated in a silica gel column sequentially eluted with iso-octane and iso-octane/diethylether. In addition, sulphides were previously eliminated from sediment samples by adding an aqueous solution of sodium sulphite and tetrabutylammonium. The purified extracts were analysed by gas chromatography with electron capture detector (GC-ECD) using capillary columns (50 m, 0.22 mm i.d. and 0.33 μm film) and N_2 as carrier gas.

PAH in sediment and mussels were extracted by Soxhlet with a mixture of *n*-hexane and acetone. A subsequent clean-up by solid phase extraction in an alumina column eluted with *n*-hexane was carried out. The solvent was replaced by acetonitrile and the extract was determined by HPLC with fluorimetric detection. The elution was performed with water and methanol in a Grace Vydac 201TP54 C_{18} column (4.6×250 mm, 5 μm particle size) and the excitation and emission wavelengths were programmed for detection.

For each chemical concentration in the sediment, contamination factors (CF) were calculated as

$$CF = \log(C/C_{crit})$$

where C is the measured concentration and C_{crit} is the sediment quality criteria (SQC): the TEL for PAH and the ERL for the other pollutants (Long et al., 1995; MacDonald et al., 1996). The chemical pollution index (CPI) for each site was the mean CF for all the chemicals analysed, which conveniently takes positive values when pollutants exceed on average the quality criteria and negative values otherwise.

2.2. The sea-urchin embryo test (SET)

Elutriates for the embryo tests were obtained by mixing 100 g of sediment and 500 mL of control seawater during 30 min