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Biomonitoring of metals under the water framework directive: Detecting temporal trends and abrupt changes, in relation to the removal of pollution sources

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ABSTRACT

Temporal trends in metal concentrations, i.e. Ag, Cd, Cu, Cr, Hg, Ni, Pb and Zn, measured in soft tissues of *Mytilus galloprovincialis* mussels and *Crassostrea gigas* oysters collected from estuarine waters within the Basque Country (Bay of Biscay), have been investigated to determine if actions undertaken have improved the environmental quality of rivers and estuaries. Data compiled between 1990 and 2010 have been analysed statistically, applying the Mann–Kendall and the Mann–Whitney–Wilcoxon tests. Moreover, in those cases with significant trends, the Kolmogorov–Zurbenko Adaptive (KZA) filter was applied to detect abrupt changes. Results showed significant decreasing trends for some metals, i.e. Ni, Cu, Pb and Zn, and differences between medians. Trend lines showed abrupt changes occurring between 1998 and 2002. Therefore, observed downward trends were related to increased wastewater treatment and diversions of discharges to ocean, implemented mainly during 2000–2002.

1. Introduction

It has been long recognised that human activities, such as the industrial processing of ores or discharge of urban and industrial waste water, result in metal pollution within the coastal environment which can damage further human health (Clark, 2001). In particular, estuaries and coastal zones near large population centres are of concern (Chase et al., 2001; Kljakovic-Gašpic et al., 2006).

At European level, the Water Framework Directive (WFD; Directive 2000/60/EC; EC, 2000) was adopted in 2000, in order to protect, conserve and manage continental, estuarine and coastal waters. Together with the WFD, Directive 2008/105/EC (EC, 2008) on environmental quality standards (EQSs) gives the legal basis for the monitoring of priority substances in sediment and biota, as they are considered important matrices for the monitoring of certain substances with significant potential for accumulation. In this sense, monitoring should provide sufficient data for a reliable long-term trend analysis of priority substances. Since the aim of monitoring is to ensure that existing levels of contamination will not significantly increase, this data become essential in long-term impacts assessment of anthropogenic activity and measures taken to restore aquatic systems (EC, 2008).

Biomonitors, in fact, as they accumulate contaminants in proportion to bioavailability, can be used to measure the relative contamination of coastal environments (e.g. Phillips and Rainbow, 1993). Moreover, the accumulated concentrations are time-integrated measures of the exposure of the biomonitor to all sources of bioavailable forms of the contaminant, over a previous time period (e.g. Phillips and Rainbow, 1993; Rainbow, 1995).

Therefore, in the last decades, many monitoring networks which include biomonitors (i.e. mussels or oysters) have been developed world-wide, such as the Mussel Watch Project in the USA (Kimbrough et al., 2008; O'Connor and Lauenstein, 2006), the *Réseau d'observation de la contamination chimique* (ROCCH; Observation of the chemical contamination of the coastline) in France (until 2008 known as *Réseau National d'Observation de la qualité du milieu marin*, RNO) (Claisse, 1989; IFREMER, 2011), the Asian-Pacific Mussel Watch (Monirith et al., 2003), or the Spanish Monitoring Programme (Besada et al., 2011). Their main objective is to determine the spatial and temporal distributions of chemical pollutants, as well as identify potential pollution sources, with the general aim of evaluating the state of the coastal environment (Besada et al., 2008; Chase et al., 2001; Kimbrough et al., 2008).

Along the Basque coast (Bay of Biscay; Fig. 1), the Department of Environment, Territorial Planning, Agriculture and Fishing of the Basque Government and the Basque Water Agency have monitored contaminants in molluscs by means of the *Water Quality Monitoring and Control Network for Mollusc Culture and Shellfishing* (hereafter, MQM), since 1990 (Borja et al., 2004b; Franco et al., 2002), and the *Littoral Water Quality Monitoring and Control Network* (hereafter, LQM), since 1994 (Borja et al., 2004a), respectively. Waters and sediments of Basque estuaries and coast have been also

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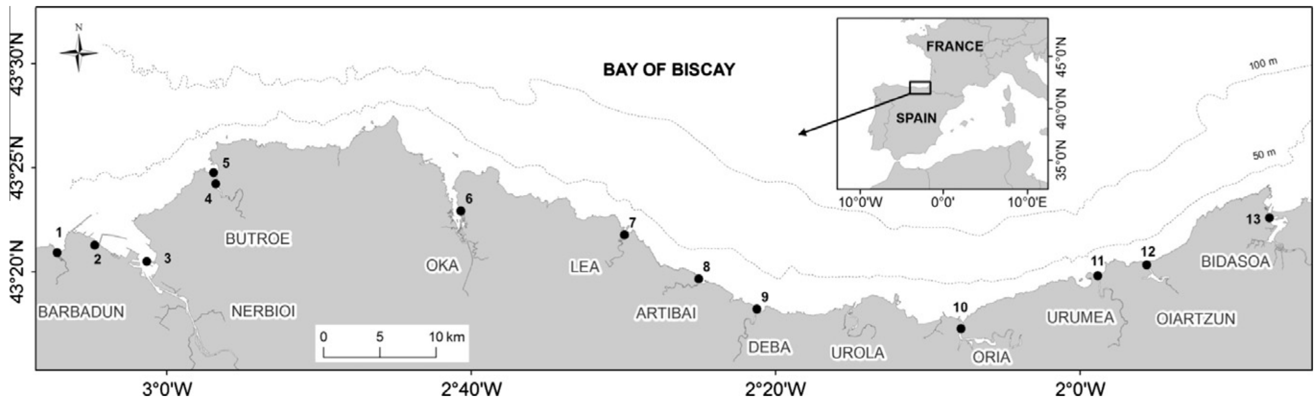

Fig. 1. Location of sampling sites within the Basque Country.

monitored within the LQM (Belzunce et al., 2004a,b) and results have shown major improvements in the water and sediment quality, since 1995 (Tueros et al., 2009).

Therefore, the objective of this research is to know if environmental quality improvement, observed previously in waters and sediments of the Basque coast, are also detected in biomonitors (mussels and oysters), after wastewater treatment within estuarine catchments. Hence, two hypotheses were investigated: (i) as progressive wastewater treatment actions have been undertaken, a decreasing trend in metal concentrations in the soft tissues of biomonitors should be detected and (ii) as the wastewater treatment was completed mostly by 2000–2002, an abrupt change in the concentration should be detected around that period.

2. Materials and methods

2.1. Study area

The Basque Country is characterised by sedimentary rocks, with a higher proportion of sandstones and lutites in the eastern part of the region, with more marls and limestones towards the west (Pascual et al., 2004). Most of the estuaries and coastal areas have been affected historically, to some degree, by urban and industrial wastes and/or mineral ores; of special relevance are Zn, Pb and Fe (Cearreta et al., 2000, 2004, 2002). In fact, some of these metals have been highly concentrated in mollusc species (Borja et al., 2004b; Franco et al., 2002).

2.2. Pollution sources

The exploitation of abundant iron ore has led to early industrial development in the Basque Country, since the mid-19th Century, together with an increase in human population and port facilities (Borja et al., 2006a; Cearreta et al., 2004). Such development has resulted in high urban and industrial wastewater discharges within the estuaries and along the coast, consisting mainly of organic matter, nutrients, metal and organic compound discharges. Hence, these aquatic systems have received high nutrient and pollutants loads up until the end of the 1990s (Borja et al., 2006b; Cearreta et al., 2004). Consequently, Borja et al. (2006a), applying the DPSIR (Driver, Pressure, State, Impact, Response) approach, considered population density and industry as the main drivers producing the most impacting pressures (water and sediment pollution, intertidal losses and shoreline reinforcement) within the Basque Country.

In turn, closure of the iron mines and steel companies (mainly in the 1990s), together with the implementation of positive actions or measures to restore degraded aquatic systems, has led to an overall improvement in the water quality in the estuaries and coastal areas (García-Barcina et al., 2006; Pascual et al., 2012). Those actions include diversion or removal of the most polluting discharges, implementation of wastewater treatment programmes (at catchment and estuarine levels, including wastewater treatment plants) and diversion of wastewater discharges to coastal areas. Most of these programmes were completed by 2000–2002. Such information, together with relevant new information obtained within the present study, is summarised in terms of estuary, in Table 1.

According to the information gathered in the study carried out by Borja et al. (2006a), the overall pressure (considered as the mean pressure calculated by applying a relative rating to each identified pressure; for additional details see Borja et al., 2006) on the Nerbioi and Oiartzun estuaries was considered as high; on the Deba, Urola and Bidasoa, as moderate; and on the remaining estuaries, as low. In fact, although new actions have been taken since then, this classification is valid to have an overall view of the Basque coast and to identify the most negatively-impacted estuaries.

2.3. Mollusc sampling and preparation

Mussels (*Mytilus galloprovincialis*) and oysters (*Crassostrea gigas*) data, were obtained between 1990 and 2010 within the framework of two projects: (1) the MQM (1990–2007) and (2) the LWM (1994–2010); there were a total of 27 sites sampled within the estuaries along the Basque coast, throughout the year. As seasonal environmental changes affect the bioaccumulation process of metals in molluscs (Besada et al., 2008; O'Connor, 1996, 1998), only sites with the longest time-series for a season were selected. This season corresponded to autumn, when mussels of the study area are in the post-spawning and resting stages (Ortiz-Zarragoitia and Cajaraville, 2010; Ortiz-Zarragoitia et al., 2011). On the other hand, metal bioaccumulation in molluscs differs also between species, when a particular metal is considered (e.g. Kimbrough et al., 2008). Consequently, in those sampling stations where the two considered species (mussel and oyster) had been sampled alternately, data of one of them (the one with the highest number of data) were selected for the analysis. Therefore, only 13 out of the 27 sites sampled in these monitoring programs fulfilled these two conditions (Fig. 1; Figs. S1–S4, SM). Data considered in this study were compared to the background levels of metals in mussels and oysters within the Basque Country (Solaun et al., 2012). Background ranges for autumn are presented in Table 2.

Each data point represented a pool of around 50 wild mussels between 35 and 45 mm in length, or 30 oysters between 55 and 85 mm in length. These were collected at the intertidal zone of each sampling site and transported wet to the laboratory. There, the molluscs were kept for 24 h in seawater from the collection site, for depuration, since tissue analysis can be influenced by