Continental Shelf Research 31 (2011) 457–465

Contents lists available at ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

Monitoring of heavy metals in wild mussels (*Mytilus galloprovincialis*) from the Spanish North-Atlantic coast

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ARTICLE INFO

Article history:
Received 3 December 2009
Received in revised form
24 March 2010
Accepted 23 April 2010
Available online 20 May 2010

Keywords:
Coastal pollution
Wild mussels
Heavy metals
Spain
Galicia

ABSTRACT

Concentrations of five heavy metals (Hg, Cd, Pb, Cu and Zn) were determined in tissues of wild mussels (*Mytilus galloprovincialis*) collected at 41 stations located on the Spanish Atlantic and Northern coasts to assess the levels and spatial distribution of metals in the environment. This study, performed in 2005, constituted a contribution to the last international OSPAR pollution monitoring survey. A pool of mussel soft tissue was prepared using 50 or more individuals, representing the size range present at the sampling points. Quantification was carried out after a nitric acid digestion by atomic absorption spectrometry, AAS (Cd and Pb by electrothermal AAS; Cu and Zn by flame AAS; and total mercury by the cold vapour technique). The quality of the chemical analyses was assessed by interlaboratory exercises carried out on a regular basis. In general, the levels of the metals were higher for the Northern region than for the Atlantic one (except for a sampling site close to Vigo, one of the main Galician industrial areas). Some Galician sampling points (Atlantic coast, NW of Spain) located far from human inputs showed high Cd concentrations, which were attributed to the annual upwelling processes in this region. The levels of Cu increased from Northwest to East, whereas Zn concentrations were very homogeneous throughout the two studied geographical regions. These results were confirmed using multivariate studies (PCA and cluster analysis), as well as international 'background assessment concentrations' criteria.

1. Introduction

Governmental monitoring programs based on '*Mussel Watch*' (Goldberg, 1986) have been applied to monitor the environmental situation of different coastal regions (Cantillo,1998; Kimbrough et al., 2008). Studies focused mainly on coastal areas because the response of the ecosystem to pollution control measures can be best assessed there, close to discharge and emission sources.

For the marine monitoring studies many animal and vegetal species have been proposed as 'surveillance species' (Green et al., 2000; O'Connor, 1998; Thébault et al., 2008). Bivalve molluscs, in particular mussels, constitute one of the best biological indicators of coastal pollution because they exhibit several unsurpassed advantageous characteristics: a sedentary nature; a wide geographical distribution; in general there are enough individuals at the sampling sites; they can be sampled easily; and finally, they accumulate pollutants (i.e., contaminant levels in their tissue respond to changes in environmental levels and pollutants accumulate with little metabolic transformation) (Chase et al., 2001; O'Connor, 1996; Widdows et al., 1995). Thus, their use has been strongly recommended by international organizations/conventions, such as the 'OSPAR Commission' (Convention for the Protection of the Marine Environment of the North East Atlantic) and the 'Barcelona Convention' (Convention for the Protection of the Mediterranean Sea against Pollution), among others.

Metals occur naturally in the environment although anthropogenic sources (e.g., fossil fuel and waste burning, mining and ore processing, chemical production) are responsible for most of the concentrations observed in coastal waters. Nevertheless, it has long been recognised that natural processes, such as run-off from mineralised areas, or upwelling of deep oceanic water, may also increase the natural concentrations of some metals in coastal shellfish (OSPAR, 2008).

Metals do not degrade in general; therefore, they accumulate throughout the trophic chain. Accumulation in living organisms leads to concentrations several orders of magnitude higher than those of the surrounding water (Casas et al., 2008). Despite this the relationship between the concentration of a metal in the aqueous phase and in an organism is far from straightforward as

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0278-4343/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.csr.2010.04.011

the accumulation ratio depends on many factors; some of them have an environmental origin (temperature, pH, salinity, etc.), whereas others are related to biological factors (age, sex, sexual maturity stage, etc.) (Mubiana et al., 2006; Saavedra et al., 2004).

Some countries established quality criteria to both evaluate the environmental situation of their coastal water and serve as risk-assessment criteria for several well-known hazardous metals, as Hg, Cd, Pb, Cu and Zn (when measured in wild mussels). Although the control levels derived from these criteria have been developed for the assessment of the environmental situation in some particular countries, they may be useful for comparing and monitoring the Spanish coast.

The Norwegian Pollution Control Authority developed an environmental classification system of contaminants in blue mussel to assess the different degrees of pollution (Molvaer et al., 1997; Green et al., 2008). Table 1 shows five quality levels from Class I, 'insignificantly polluted', to Class V 'extremely polluted'. Other criteria can be found at the National Status and Trends 'Mussel Watch' Program (US National Oceanic and Atmospheric Administration, NOAA). After two decades of pollution monitoring in the US Coastal Zone studying coastal contamination levels over the past 20 years, three levels were assigned to different concentration ranges of contaminants: high, medium and low—see Table 1 (Kimbrough et al., 2008). An important issue to keep in mind here is that not all studies considered the same species of mussels. In some works it was clearly specified that blue mussel corresponds to *Mytilus edulis* but nothing was stated in others. Some studies considered indistinctly *Mytilus edulis* and *Mytilus galloprovinciallis* and they all were considered as 'moules'. It also has to be stressed that in Spain wild mussels are not allowed to be captured and only cultivated mussels can be sold for human consumption. It turns out that risks associated to their intake should not be of general public concern and they were not reviewed here; more information on this topic can be found elsewhere (e.g. Storelli, 2008; Gutierrez et al., 2007).

Background concentrations (BCs) can be defined as 'the concentration of a contaminant at a 'pristine' or 'remote' site based on contemporary or historical data' (Moffat et al., 2004). For naturally occurring substances such as polycyclic aromatic hydrocarbons (PAHs) and trace metals BCs represent, typically, concentrations measured in uncontaminated locations within the OSPAR maritime area (North-East Atlantic). Specifically, in order to facilitate precautionary assessments of data collected under the OSPAR-CEMP Program (OSPAR Co-ordinated Environmental Monitoring Program), several Background Assessment Concentrations (BACs) were defined. By agreement, observed concentrations are said to be 'near background' if the mean concentration is statistically significantly below the corresponding BAC. BACs have been recently recommended for use throughout the OSPAR maritime area; BACs values in wild mussels are 0.090 mg/kg d.w. (dry weight) for Hg; 0.96 mg/kg d.w. for Cd and 1.3 mg/kg d.w. for Pb (OSPAR, 2008).

The aim of this paper is to study the spatial patterns of five heavy metals (Hg, Cd, Pb, Cu and Zn) in wild mussels sampled at 41 stations all over the Spanish North-Atlantic Coast; 24 sites at the Galician coast—Atlantic region and 17 sites at the Northern one—which includes several regions: Asturias, Cantabria and the Basque Country. In Spain, the overall North coast is also generally known as the 'Cantabrian area'. Mussel watch sites were selected to represent large coastal areas that can be used to develop a Spanish North Atlantic assessment monitoring program. Besides, the present paper presents a very first set of comparisons amongst the Spanish North-Atlantic coast and international environmental classification systems of contaminants. This is of interest because it is generally recognised that natural processes such as geological variability or upwelling of oceanic waters near the coast may lead to significant variations in background concentrations of contaminants, for example trace metals.

2. Materials and methods

2.1. Sampling and sample preparation

The sampling collection, sample preparation and analyses were carried out by the 'Centro Oceanográfico de Vigo' of the Spanish Institute of Oceanography within the *Spanish Maritime Monitoring Program* framework. Forty-one sampling sites (Fig. 1) located at the Spanish Atlantic–Galician and Northern areas (including Asturias, Cantabria and the Basque Country) were selected after a detailed study of their particular characteristics. Among them: anthropogenic inputs, availability of wild mussels, punctual pollution sources (presence of industrial areas, large cities, etc.), upwelling, location within the 'rías', farming activities, urban discharges, etc. The studied area extends for more than 2300 km, from N Portugal to SW France and the seaborne-related activities there hold main economical relevance, which justifies the continuous monitoring of the pollution of the coastal water.

Table 1
Pollution levels in wild mussels found in this study compared to international criteria (values in mg/kg dry weight). The values in parenthesis indicate the number of sampling sites included within each class.

	Norway (upper limit for Class I–IV)				
Contaminant	**Insignificant (I)**	**Moderate (II)**	**Market (III)**	**Severe (IV)**	**Extreme (V)**
Mercury	0.2 (40)	0.5 (1)	1.5	4	>4
Cadmium	2 (41)	5	20	40	>40
Lead	3 (39)	15 (2)	40	100	>100
Copper	10 (41)	30	100	200	>200
Zinc	200 (41)	400	1000	2500	>2500
	NOAA				
	Low	**Medium**	**High**		
Mercury	0.00–0.17 (31)	0.18–0.35 (6)	0.36–1.28 (4)		
Cadmium	0–3 (41)	4–9	10–20		
Lead	0–3 (31)	4–6 (7)	7–13 (3)		
Copper	5–16 (41)	17–39	40–857		
Zinc	48–139	140–320 (36)	321–11500 (5)		