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Toxic elements and speciation in seafood samples from different contaminated sites in Europe

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ABSTRACT

The presence of cadmium (Cd), lead (Pb), mercury (THg), methylmercury (MeHg), arsenic (TAs), inorganic arsenic (iAs), cobalt (Co), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr) and iron (Fe) was investigated in seafood collected from European marine ecosystems subjected to strong anthropogenic pressure, i.e. hotspot areas. Different species (*Mytilus galloprovincialis*, $n=50$; *Chamelea gallina*, $n=50$; *Liza aurata*, $n=25$; *Platichthys flesus*, $n=25$; *Laminaria digitata*, $n=15$; and *Saccharina latissima*, $n=15$) sampled in Tagus estuary, Po delta, Ebro delta, western Scheldt, and in the vicinities of a fish farm area (Solund, Norway), between September and December 2013, were selected to assess metal contamination and potential risks to seafood consumers, as well as to determine the suitability of ecologically distinct organisms as bioindicators in environmental monitoring studies. Species exhibited different elemental profiles, likely as a result of their ecological strategies, metabolism and levels in the environment (i.e. seawater and sediments). Higher levels of Cd (0.15–0.94 mg kg^{-1}), Pb (0.37 – 0.89 mg kg^{-1}), Co (0.48–1.1 mg kg^{-1}), Cu (4.8–8.4 mg kg^{-1}), Zn (75–153 mg kg^{-1}), Cr (1.0–4.5 mg kg^{-1}) and Fe (283–930 mg kg^{-1}) were detected in bivalve species, particularly in *M. galloprovincialis* from Ebro and Po deltas, whereas the highest content of Hg was found in *P. flesus* (0.86 mg kg^{-1}). In fish species, most Hg was organic (MeHg; from 69 to 79%), whereas lower proportions of MeHg were encountered in bivalve species (between 20 and 43%). The highest levels of As were found in macroalgae species *L. digitata* and *S. latissima* (41 mg kg^{-1} and 43 mg kg^{-1}, respectively), with iAs accounting almost 50% of the total As content in *L. digitata* but not with *S. latissima* nor in the remaining seafood samples. This work highlights that the selection of the most appropriate bioindicator species is a fundamental step in environmental monitoring of each contaminant, especially in coastal areas. Furthermore, data clearly shows that the current risk assessment and legislation solely based on total As or Hg data is limiting, as elemental speciation greatly varies according to seafood species, thus playing a key role in human exposure assessment via food.

1. Introduction

Chemical pollution of aquatic ecosystems represents an ecological threat that has been receiving increased attention. Bioindicator species are organisms used to monitor the status or quality of ecosystems, providing quantitative data for the presence of pollutants. Bioindicators from different trophic levels, such as algae, bivalve molluscs or fish species, are commonly used to evaluate the chemical contamination at different stages of the food webs. In general, carnivorous fish occupy the highest ranks of aquatic food webs and tend to accumulate larger amounts of persistent contaminants in their tissues (Mansour and Sidky, 2002), while bivalve molluscs (e.g. mussels, clams and oysters) are

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sedentary and filter-feeding organisms that can concentrate contaminants from the sediment, suspended particulate material and water column (Laffon et al., 2006). Aquatic algae are also considered as important producers in marine waters, playing a key role in the whole marine ecosystem and directly reflecting the water quality (Zhou et al., 2008; Hamza-Chaffai, 2014). Brown kelp species, such as *Laminaria digitata,* have shown to have high accumulation rates and affinity for a wide range of elements, thus being interesting bioindicators of toxic metal pollution (Davis et al., 2003). Thus, given the specific characteristics of each species and depending on the target contaminant, an appropriate selection of the sentinel species is a crucial step in environmental monitoring.

Areas exposed to high environmental concentrations of contaminants from anthropogenic or natural sources are called "hotspots". Hotspots include estuaries, bays, lagoons and river mouths, which are generally associated with highly urbanized and industrialized areas (DEQ, 1998; WHO, 2012). In this sense, regular environmental monitoring of these hotspots, particularly in estuarine areas, using bioindicator species from different trophic levels, provides relevant information to understand species' biological responses towards contamination.

Toxic elements such as mercury (Hg), arsenic (As), cadmium (Cd) and lead (Pb) have no known role in biological systems, being usually trace components in the aquatic environment. In addition, other trace elements essential to the adequate functioning of the human body can also play a deleterious effect to human health when reaching high concentrations. Such is the case of zinc (Zn), copper (Cu), iron (Fe) and nickel (Ni) (e.g. EFSA, 2006; USDA, 2015). However, the levels of toxic elements can increase significantly in areas subjected to industrial, agricultural and mining activities (Olmedo et al., 2013). The toxicity and environmental behavior of some elements depend on their chemical form and oxidation status, which in turn influences their bioavailability, transport, persistence and impact in the food chain (Visakh et al., 2013). Thus, assessing the chemical speciation of some elements, such as Hg and As, is highly relevant from an ecological and food safety point of view, as the different forms of these elements induce distinct toxic effects to biota and humans. Methylmercury (MeHg), is the most toxic Hg species, being highly bioaccumulated and biomagnified along the aquatic food chain (Bustamante et al., 2006; Murphy et al., 2008). In contrast, the most toxic As forms are the inorganic arsenite (As III) and arsenate (AsV), which are predominant in seawater and sediments of marine ecosystems (Francesconi and Edmonds, 1998). So far, only few studies assessed element speciation in seafood, and the human dietary exposure assessment to these species, such as MeHg or inorganic arsenic (iAs). In most cases, such assessment is based on extrapolations from the total element levels (i.e. total Hg and total As) found in food matrices (e.g. EFSA, 2009, 2012). For this reason, food safety worldwide authorities have recently adverted that further research and monitoring programs should be undertaken in order to increase the available data on the presence of MeHg and iAs in all food groups, thus enabling more accurate and reliable exposure risk assessments (FAO/WHO, 2007; EFSA, 2015). Regarding speciation of Cd and Pb, so far EFSA has no evidences of concern in food items and does not consider that further research or data collection is needed (EFSA, 2015). The toxicity of trace elements has lead food safety authorities to establish tolerable weekly intake (TWI) levels for MeHg (1.3 μg/kg bw; EFSA, 2012) and Cd (2.5 μg/kg bw; EFSA, 2009b), benchmark dose levels for iAs (0.3–8 μg/kg bw/day; EFSA, 2009a; 3 μg/kg bw/day; WHO, 2011), and tolerable upper intake levels (UL) for Zn (7–22 mg/day), Cu (1–4 mg/day), Fe (45 mg/day) and Ni (1.0 mg/day) (EFSA, 2006; USDA, 2015).

In this context, the present study aims to evaluate the bioaccumulation of toxic elements (Hg, As, Cd, Pb, Ni, Co, Cr, Zn, Cu and Fe) and speciation (MeHg and iAs) in bioindicator species from different European hotspot areas, to determine the suitability of ecologically distinct organisms as bioindicators in environmental monitoring studies, as well as to assess risks for seafood consumers.

2. Material and methods

Five hotspot areas subjected to strong anthropogenic pressures, either from domestic, industrial, or aquaculture sources, were selected in Europe (Tagus estuary, Ebro Delta, Po Delta, Western Scheldt and vicinities of a fish farm in Norway; Fig. 1). Element levels were assessed in different seafood species collected in these areas, and covering different levels of the food web, i.e. *Mytilus galloprovincialis, Chamelea gallina*, *Liza aurata, Platichthys flesus, Laminaria digitata,* and *Saccharina latissima*. Only elements (Hg, As, Cd, Pb, Ni, Co, Cr, Zn, Cu and Fe) and species (MeHg and iAs) that can potentially become toxic to biota and humans were selected in this study.

2.1. Description of the study areas

2.1.1. Tagus estuary (Portugal)

The Tagus estuary is one of the largest estuaries in Europe, occupying 320 km^2 surface area in the Lisbon region, i.e. the most populated area of Portugal (Fig. 1). Tagus River represents the second most important hydrological basin of the Iberian Peninsula with 80,000 km^2 drainage area and 400 m^3/s mean river flow with significant seasonal variation. Tagus is a mesotidal estuary with semidiurnal tides ranging from 0.4 m to 4.1 m. This estuary detains a major seaport, several commercial and fishing activities, and receives effluents from agricultural (fertilizers and pesticides), industrial (chemical, petrochemical, metallurgic, shipbuilding and cement manufacture industries), hospitals (> 20 hospitals in this area) and domestic sources from about 2.5 million inhabitants of the metropolitan area of Lisbon (Gameiro and Brotas, 2010; Duarte et al., 2014). Over the last years, a major increase and optimization in the treatment of both industrial and urban effluents has been

Fig. 1. Map showing hotspot sampling areas: (A) Tagus estuary, Portugal (mussel and mullet); (B) Ebro Delta estuary, NE Spain (mussel *Mytilus galloprovincialis* in Fangar Bay and clam *Chamelea gallina* in Alfacs Bay); (C) Sacca di Goro, Po estuary, Italy (mussel); (D) Western Scheldt estuary, The Netherlands (flounder); and (E) Solund, Norway (macroalgae *Laminaria digitata* and *Saccharina latissima*).