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Metal bioavailability in freshwater sediment samples and their influence on ecological status of river basins

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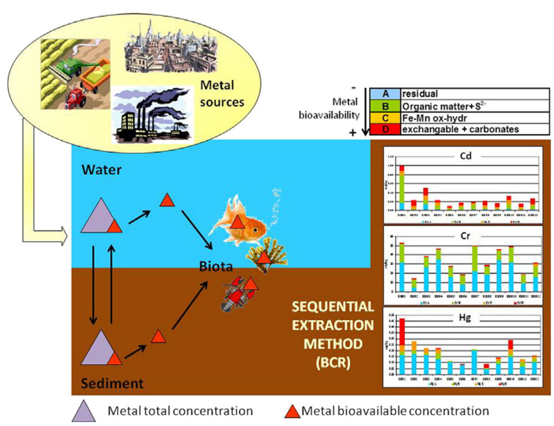
HIGHLIGHTS

- Hg, Cr, Zn, and Cu in sediments could reach values of concern although in water were undetectable.
- BCR method allows distinguish between geological and anthropic pollution of metals.
- Undetected Hg, Cd and Cr water concentrations are not guarantee of no bioaccumulation in fish.
- Diatoms presented higher sensitivity to metals compared with macroinvertebates and macrophytes.
- Pb, Zn, As, Cr and Ni seem to contribute in higher extend in the reduction of biological quality.

GRAPHICAL ABSTRACT



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ABSTRACT

The general aim of this work has been to check the ecological impact of metals on the Ebro river basin. In order to evaluate this, metal behavior considering water, sediment as well as metal bioaccumulation in fish has been studied. Total concentrations of metals, as well as the potentially bioavailable fraction of metals in sediment has also been analyzed by the application of the sequential extraction method (BCR method). In order to evaluate the influence of metal pollution on the river ecological status, according to the Water Framework Directive (WFD), diverse biological indices such as macroinvertebrates (IBMWP), diatoms (IPS) and macrophytes (IVAM), have been considered from an integrated point of view. Considering both water and sediment, metals which contributed in higher extend to the reduction of biological quality have been demonstrated to be Pb and Zn, as they presented a negative influence on macroinvertebrates, diatoms and macrophytes communities. As and Cr that seemed to have a significant influence on macroinvertebrates and diatoms too, while Ni negatively influenced only diatom communities. This study also demonstrated that monitoring programs only based on total metal determination in water are inefficient, as metals present even at undetectable concentrations in water are strongly accumulated in fish. Moreover, the

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high concentrations of Hg found in sediments indicated that this river basin may present pollution problems regarded to this metal, as demonstrated by the high Hg levels found in fish.

1. Introduction

After being released into the environment, metals can be present in soils, sediments and waters, and due to their persistence and possible bioaccumulation in biota, they can reach easily be spread along the trophyc nets (Maceda-Veiga et al., 2012). Although some metals can be considered essential elements for living organisms, even those ones can become toxic when environmental concentrations are increased (Newman, 2009). Presence of metals in the environment may have a natural or anthropogenic origin. Among the anthropogenic sources, wastewater discharges, agricultural runoff, air pollutants deposition or specific environmental accidents are the most important (Maceda-Veiga et al., 2012; Ricart et al., 2010; Suárez-Serrano et al., 2010).

Metal water analyses have been demonstrated to be inefficient at identifying metal inputs to fluvial systems because of the inherent variability of flow and contaminant concentrations. However, sediments have been considered as the largest reservoir of metals in aquatic ecosystems (Demirak et al., 2006; Maceda-Veiga et al., 2012; Ricart et al., 2010). Sediments have been found to be a reservoir of most metals released into the rivers and some elements may be recovered through biological and chemical reactions within the water column and thus including them in the aquatic trophyc nets (Nemati et al., 2011).

Current water monitoring programs in Europe, based on the Water Framework Directive (WFD) (EC, 2000) are mainly focused on monitoring of total metal concentration in water and sediment. However, the total concentration of metals is not sufficient to estimate the real potentially toxicity and the general status of freshwater systems because of a higher number of variables such as metal bioavailability, interactions between different metals and the effects of mixtures of metals that may also play a key role in the biological effects of these elements (López-Doval et al., 2012; Roig et al., 2013). Because of this, interest in the determination of the real bioavailability of metals in aquatic systems, both in water and in sediment, has grown during the last decades (Alcorlo et al., 2006; Ankley et al., 1994; Veses et al., 2011). To this respect, the European Commission has published the Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Among the most novel requirements of this latest Directive for the State Members, one of the most important has been the mandatory determination of bioavailable concentrations of Cd, Pb, Hg and Ni in water through the adaptation and application of adequate bioavailability models (EC, 2013). Regarding to sediments, sequential extraction method has been an important and widely applied tool which has provided considerable insights over three decades into the environmental behavior of potentially toxic elements (Sutherland, 2010; Tessier et al., 1979). It is generally accepted that metal pollution in aquatic ecosystems has a negative impact on the different aquatic communities (De Jonge et al., 2008; Lainé et al., 2014; Roig et al., 2013). According to De Jonge et al. (2008), metal pollution results in the loss of metal sensitive groups of macroinvertebrates such as Ephemeroptera, Trichoptera and Plecoptera. Diatom communities are also strongly influenced by the presence of elevated metal levels (Hirst et al., 2002) and even certain species will develop teratological forms in their frustules (Triest et al., 2001). De Jonge et al. (2008), Hirst et al. (2002) and (Blanco and Bécares, 2010) agreed that diatoms reflect metal pollution mainly through variations in assemblage composition while effects on macro-invertebrates are best reflected by changes in abundance and diversity. Although the number of macrophyte indices has grown since the approval of the WFD, it is observed that most of them have been designed mainly to detect eutrophication processes, organic pollution, hydromorphological degradation or habitat destruction, but few works have been published about their relevance to detect metal pollution (Demars et al., 2012a; Haury et al., 2006). However, because they are rooted and they are able to integrate the effects of long and short term physical and chemical disturbance (Moore et al., 2012), they can be considered good indicators of river disturbances.

The general aim of this work has been to check the influence of metals on the biological quality of the Ebro river basin according to the WFD. In order to evaluate this influence, the potentially bioavailable fraction of metals in river sediment has been studied through the application of the sequential extraction method, and metal content in water and fish has been also considered. For the assessment of the biological quality, macroinvertebrates, diatoms and macrophytes indices have been evaluated along with hydromorphological, and physicochemical parameters.

2. Materials and methods

2.1. Study area

This study has been performed along the Ebro river basin, in northeastern Spain. The Ebro is the largest river in the Iberian Peninsula flowing into the Mediterranean Sea, characterized by an interannual variability with a basin draining 85 534 km^2 and about 910 km of length. Twelve sampling points of the Monitoring Network for the Priority Substances of the Confederación Hidrográfica del Ebro (CHE) (Hidrographic Ebro Confederation, organization responsible of the water management of this river) have been selected within the Ebro river watershed. The CHE designed the Monitoring Network as organization, responsible of the monitoring of the concentration of the priority and preferential substances defined by WFD in water, sediment and biota (fish) in Ebro River. The corresponding coordinates and the description of all sampling points are gathered in Table 1. Most of the sampling points have been selected according to their proximity to agricultural, urban and industrial areas. For example, EBR1 and EBR11 are located downstream important chemical industry areas based on the production of plastics and pigments, respectively. EBR9, EBR6, EBR10 and also EBR11 have been located downstream documented industrial areas that discharge or have discharged Hg into the main stream for several years (CHE, 2015).

2.2. Sediment sampling and sediment characterization

In each sampling location, composite samples of sediment were collected during summer 2013 by using a Van Veen grab (0–20 cm). Sediment samples were stored at 4 °C before and after their processing prior to characterization and metal determination analyses.

Sediment moisture was measured following UNE 77311 procedure (UNE, 2000). Porosity was measured according to DiToro (2001). Texture, organic carbon and ammonium were determined according to El Rayis (1985) and Grashoff et al. (2002) respectively. The pH was determined in pore water.

2.3. Metal determination in sediment samples

In order to calculate the metal distribution and metal bioavailability in sediments, a sequential extraction was performed, according to the Community Bureau of Reference (BCR) method (Mossop and Davidson, 2003). One gram of dried sediment was sequentially extracted by consecutively passing four reagents: acetic acid (0.11 M),