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Assessment of sediment ecotoxicological status as a complementary tool for the evaluation of surface water quality: the Ebro river basin case study

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HIGHLIGHTS

- Whole sediment bioassays have shown more sensitivity than pore water tests.
- Ecotoxicity approach has been in agreement with the ecological status in the most polluted sites.
- A toolbox of ecotoxicity tests has shown a high potential to complement the ecological status of rivers.

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ABSTRACT

According to the European Water Framework Directive (WFD), assessment of surface water status is based on ecological and chemical status that is not always in coherence. In these situations, ecotoxicity tests could help to obtain a better characterization of the ecosystems. The general aim of this work is to design a methodology to study the ecotoxicological status of freshwater systems. This could be useful and complementary to ecological status, for a better ecological characterization of freshwater systems. For this purpose, sediments from thirteen sampling sites within the Ebro river watershed (NE Spain) were collected for ecotoxicity characterization. The ecotoxicity of pore water has been evaluated employing the test organisms *Vibrio fischeri*, *Pseudokirschneriella subcapitata* and *Daphnia magna*, while whole sediment ecotoxicity was evaluated using *Vibrio fischeri*, *Daphnia magna*, *Nitzschia palea* and *Chironomus riparius*. An analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) was performed to evaluate the sediment toxicity associated to bioavailable metals. Moreover, data about priority pollutants defined by the WFD in water, sediment and fish as well as data of surface water status of each sampling point were provided by the Monitoring and Control Program of the Ebro Water bodies. In general terms, whole sediment bioassays have shown more toxicity than pore water tests. Among the different organisms used, *P. subcapitata* and *C. riparius* were the most sensitive in pore water and whole sediment, respectively. Our evaluation of the ecotoxicological status showed high coincidences with the ecological status, established according to the WFD, especially when ecosystem disruption due to numerous stressors (presence of metals and organic pollution) was observed. These results allow us to confirm that, when chemical stressors affect the ecosystem functioning negatively, an ecotoxicological approach, provided by suitable bioassays in pore water and whole sediment, could detect these changes with accurate sensitivity.

1. Introduction

The approval of the European Water Framework Directive (WFD) meant a big step regarding aquatic ecosystem protection. It requires member states of the European Union monitoring programs to achieve a good ecological and chemical status by 2015 in all water bodies (EC 2000). Although technical implementation of the WFD purposes is a

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complex process, the use of several quality elements and establishment of typologies and reference conditions supposed a huge improvement in the water system protection (Hering et al., 2010). It represented an innovative and radical shift to measure the quality of all surface waters due to the incorporation of the study of a range of biological communities and their habitat characteristics in addition to the current chemical quality evaluation (EC 2000; Moss, 2008; Hering et al., 2010; López-Serna et al., 2012). According to this directive, assessment of ecological status is based on three quality elements: biological, physico-chemical and hydromorphological status. The evaluation of the freshwater biological status was recognized as being a much more effective integrative way to measure ecological quality (Hering et al., 2010). However, there is not a generally applicable European method for water body assessment and the methods developed differ between countries, between biological quality elements and between categories and types (Moss, 2008; Hering et al., 2010). In addition, biological status evaluation often requires more effort than the authors of the WDF intended (Hering et al., 2010). Regarding physico-chemical status evaluation the selection of physico-chemical standards regarding nutrients concentrations is already questioned due to their variability depending of geologic, geographic or environmental characteristics (Moss, 2007, 2008; Hering et al., 2010). The incorporation of the hydromorphologycal status supposed an improvement in the evaluation of water systems (Moss, 2008). The evaluation of the chemical status is capable of recording source substances and their metabolites, but it provides no data about the effect of the pollutants on organisms, and would not provide any information about synergic/antagonistic factors (Ahlf et al., 2002; Blasco and Picó, 2009). Moreover, the current analyses performed in spot water sampling provides only a 'snapshot' of the situation at the set time of sampling, and the variability of contaminant concentrations or temporal changes cannot been detected (Allan et al., 2006).

Since the WFD implementation, some studies have observed that biological status is not always in coherence with physicochemical status (López-Doval et al., 2012; López-Serna et al., 2012; Roig et al., 2013). This trend may be explained by adaptation mechanisms of aquatic organisms under chronic chemical exposure or regional specificities of the communities that cause high tolerance under extreme conditions (Moss, 2007; Hering et al., 2010). In this way, ecotoxicology is a good technique to integrate the biological response under the presence of different stressors in non-adapted organisms (Blanck and Wängberg, 1988). Ecotoxicity tests or bioassays are rapid and cost-effective techniques and provide a more direct measure of environmentally relevant toxicity of contaminated sites than chemical analyses alone (Keddy et al., 1995; Ahlf et al., 2002; Allan et al., 2006). Bioassays give information about the global bioavailability and toxicity of multiple chemical stressors, they can predict possibly dangerous biological effects of pollutants, and they are useful to detect community tolerance tendencies (Blanck and Wängberg, 1988; Blasco and Picó, 2009). However, extrapolation of the results obtained from single species test batteries to ecosystems may be limited, and multiple tests at different trophic levels are needed for meaningful results (Ahlf et al., 2002; Allan et al., 2006; Schmitt-Jansen et al., 2008; Blasco and Picó, 2009). Since the eighties some authors have suggested the importance of integrated approaches combining ecological, chemical and ecotoxicological tools as a challenging task in environmental risk assessment (Long and Chapman, 1985; Chapman et al., 1997; Ahlf et al., 2002; Schmitt-Jansen et al., 2008; Blasco and Picó, 2009; Roig et al., 2013). One example of these integrated evaluation tools is the sediment quality triad (SQT), that is based on combination of chemical analyses, experimental laboratory toxicity tests and field observations of sediments in marine or freshwater ecosystems (Long and Chapman, 1985; Chapman et al., 1997). Due to the fact that chemical water analyses usually give punctual information, present high variability, and acute ecotoxicity of flowing water is sometimes non-detected due to the dilution factor (Allan et al., 2006; Roig et al., 2011, 2013); this study focuses on the sediment matrix. Sediment is able to integrate stream pollution for a long time, often presents higher pollutant concentrations than water and may actually act as both sink and source of contaminants for the water column (Voutsinou-Taliadouri and Varnavas, 1995; Roig et al., 2011, 2013). For this reason, we hypothesized that sediments could be a good indicator of the global status of the freshwater system.

The general aim of this work is to design a cost-effective methodology to study the ecotoxicological status of freshwater systems that could be useful and complementary to ecological status defined by the WFD by applying a quality triad integrating chemical, physico-chemical, biological and ecotoxicological data. The specific aims of this work are: (1) to compare the effectiveness and viability of different ecotoxicity tests performed with freshwater sediments (directly and with pore water) taking as target organisms different aquatic species, and (2) to evaluate the relationship between ecological status, pollutant concentrations (paying special attention to metals), and pore water and sediment ecotoxicity.

2. Materials and methods

2.1. Study area and sampling campaign

The Ebro river basin is located in northeastern Spain. The Ebro is the largest river in the Iberian Peninsula flowing into the Mediterranean Sea, with a basin draining a total of 85,534 km^2 and about 910 km of length. It is characterized by an interannual variability associated with its intrinsic Mediterranean character.

Thirteen sampling sites within the Ebro river watershed (NE Spain) were selected for sediment sampling (Fig. 1) coinciding with the annual monitoring campaign of this river. These sites are representative of the whole basin. All sampling points except SP.21 were located near the most important agricultural, industrial and urban areas of Ebro basin. The sampling point located in headwaters of Gállego River (SP.21) was considered as a reference site because of its relatively low pressure of environmental stressors compared with the other sampling points. This is one of the main tributaries of Ebro river, fed by waters from the Pyrenees. 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 ºC before and after their processing prior to ecotoxicity analyses.

Moreover, data about some priority pollutants defined by WFD in water, sediment and fish (Tables S1, S2 and S3 of Supplementary Data) as well as data about the biological and hydromorphological status of each sampling point were provided by the Monitoring and Control Program of the Ebro Water bodies coordinated by the Confederación Hidrográfica del Ebro organization (CHE, 2013a,b,c).

2.2. Sediment characterization

Humidity was measured on basis UNE 77311 procedure (UNE. 77311, 2000), porosity according to DiToro, (2001), percentages of fines (<63 μm) and organic matter following the methodology described by Kramer et al. (1994) and organic carbon and ammonium according to El Rayis (1985) and Grashoff et al. (2002), respectively. The pH has been determined directly in pore water.

In order to distinguish the potentially cationic toxic metals associated to sulfides in sediments, an analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) was performed according to Allen et al. (1993) with some modifications. If AVS levels exceed the SEM concentration, the sediment is likely to be non-toxic. In turn, if SEM > AVS, the sediments may be toxic due to bioavailable metals.

The concentration of some potentially toxic elements (PTEs) (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn)) was analyzed in pore water of sediment, total sediment and SEM by inductively coupled plasma-