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Prediction of the bioavailability of potentially toxic elements in freshwaters. Comparison between speciation models and passive samplers

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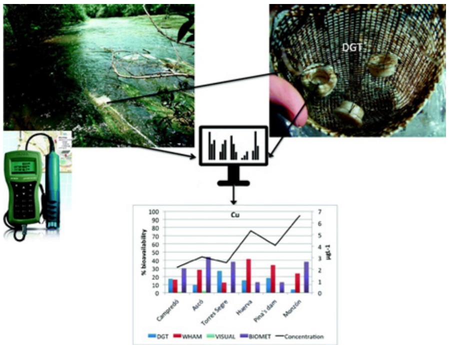
HIGHLIGHTS

- Bio-met predictions for Zn and Cu are in agreement, with DGTs results.
- WHAM 7.0 is useful when speciation is driven by dissolved organic matter (i.e. Cu).
- Both WHAM 7.0 and Visual MINTEQ bring similar predictions for Zn, Ni, Cd and Hg.
- Visual MINTEQ is useful for Cr and As speciation because considers redox reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work is to predict the bioavailability of the Potentially Toxic Elements (PTEs) Cd, Pb, Hg, Ni, Cu, Zn, As, Cr and Se in 6 sites within the Ebro River basin. *In situ* Diffusive gradient in thin-films (DGTs) and classical sampling have been used and compared. The potentially bioavailable fractions of each PTE was estimated by modelling their chemical speciation using three programs (WHAM 7.0, Visual MINTEQ 3.1 and Bio-met), following the suggestions published in recent European regulations. Results of the equilibrium-based models WHAM 7.0 and Visual MINTEQ 3.1 indicate that As, Cd, Ni, Se and Zn, predominate as free metals ions or forming inorganic soluble complexes. Copper, Pb and Hg bioavailability is conditioned by their affinity to dissolved humic substances. According to Visual MINTEQ 3.1, Cr is subjected to redox reactions, being Cr (VI) present (at low concentrations) in the studied rivers. According to Bio-met model, the bioavailability of Cu and Zn is highly influenced by soluble organic matter and water hardness, respectively. For most PTEs, the bioavailability estimated by deploying DGTs in river waters tends to be slightly lower than the estimation obtained with speciation models, since in real conditions more environmental factors take place comparing to the finite number of parameters considered in models.

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1. Introduction

The forecasted climate change will lead to a severe water scarcity in the Mediterranean region, with an expected decline of precipitation up to over 50% in summer (Gampe et al., 2016). Water scarcity may lead to lower water quality due to the increase of concentration of contaminants in rivers, which eventually affect negatively the most sensitive organisms and cause ecosystem distress. Among all the contaminants, metals are considered Potentially Toxic Elements (PTEs) responsible for the main environmental toxicological risk in Spanish basins (López-Doval et al., 2012). Current water monitoring programs in Europe, based on the Water Framework Directive (WFD) (European Community, 2000), are focused on the monitoring of total metal concentration in water. However, the total concentration of metals is not sufficient to estimate their potential toxicity and the general pollution status of freshwater systems. The European Water Framework Program (Directive 2013/39/EU) identifies metal bioavailability as a water quality issue. Consequently, the determination of bioavailable concentrations for prioritary metals has become mandatory, and the use of novel monitoring methods such as passive samplers or bioavailability models are recommended (The European Parlament and the Council of the European Union, 2013).

Chemical speciation determines the fate of PTEs in natural waters, including their bioavailability, bioaccumulation and toxicity to organisms (Omanović et al., 2015). Chemical speciation of metals in freshwater is affected by many factors, such as water pH, Eh, ionic strength, and organic and inorganic ligands and competing ions present in the water (López-Doval et al., 2012; Roig et al., 2013; Roig et al., 2015). It is generally accepted that their dissolved form is the most mobile and bioavailable, and is usually the most toxic fraction, although the uptake of metals may occur differently depending on the target organism considered (fish, algae, microorganism, *etc.*).

Computational models can estimate the bioavailable fraction and toxicity of heavy metals based on data on dissolved metals and other water chemical and physicochemical parameters (de Paiva Magalhaes et al., 2015). The most commonly used models to predict bioavailability are MINEQL+, WHAM, Visual MINTEQ, CHESS, PHREEQC and WATEQ4F, among others. These models use extensive libraries of thermodynamic data to calculate metal speciation taking into account the values of different water parameters. An interesting advance in the models has been the incorporation of the Biotic Ligand Models (BLM), which predict acute toxicity to aquatic organisms on the basis of physical and chemical factors affecting speciation, complexation, and also the competition between the metals for their interaction with a biotic ligand. The BLM is fundamentally a chemical equilibrium-based model. The biotic ligand, *i.e.* the site where the metal interacts with the organism, is one of the central components of this kind of models (Paquin et al., 2002). The main idea behind the BLM concept is that the toxic effect of a metal does not only depend on the activity of that metal in the surrounding environment and the complex interaction between physicochemical and biological factors but also on the activity of ions competing for the same biotic ligand. A good example of these type of models are HydroQual and the Bio-met Bioavailability tool (Bio-met, 2013).

The presence of metals in the filtered waters does not imply that these are entirely bioavailable forms. For this reason, Diffusive gradient in thin-films (DGTs) were designed by Davison and Zhang (1993) as an alternative speciation devices (Zhang et al., 2000). These are widely used passive sampling devices designed as an *in situ* speciation tool and to absorb potentially bioavailable trace elements. In this sense many works have been published showing the applicability of these devices (Zhang et al., 2000; Meylan et al., 2004; Dočekalová and Diviš, 2005; Fernández-Gómez et al., 2011; N. Roig et al., 2011; Han et al., 2013; N. Roig et al., 2013; Omanović et al., 2015; Neus Roig et al., 2015; Uher et al., 2017).

The aim of this study is to predict the bioavailability of the PTEs arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se) and zinc (Zn) in freshwaters, as it is suggested by recent regulations. For this purpose, the suitability of two novel methods, mathematic models and passive sampling devices, is assessed and compared. Water from the Ebro River basin have been sampled with the reference method (grab samples) and DGT passive samplers and chemically analysed, and the data have been modelled with Visual MINTEQ, WHAM 7.0 and Bio-met.

2. Materials and methods

2.1. Sampling site and sampling procedures

This study was performed in the Ebro River basin (North-East Spain) during July 2015. The Ebro is the largest River in the Iberian Peninsula flowing into the Mediterranean Sea, with 85,534 km^2 of basin area and about 910 km of length. From the 24 sampling points of the Monitoring Network for the Priority Substances of the Confederación Hidrográfica del Ebro (CHE), within the Ebro River watershed, 6 were selected as representative of the most impacted by agriculture, industrial or urban activities (Fig. 1).

The sampling points are located in the Ebro River and its effluents Segre River, Huerva River and Cinca River. To estimate the potential bioavailable fraction of PTEs in water, DGTs (DGT; DGT Research, Lancaster, UK) were deployed in triplicates at each location for 7 days. Point grab water samples of 500 mL were collected before and after the deployment of DGTs with new plastic bottles, previously washed with diluted HNO_3. Point grab water samples were filtered (<0.45 μm); an aliquot was acidified by adding HNO_3 at 0.1%, and an aliquot was acidified with H_2SO_4 to a pH below 2. Samples from DGTs and water were stored at 4 °C until analyses, which was performed within 48 h after sampling.

Data of pH, water temperature, electrical conductivity, turbidity, dissolved oxygen concentration and redox potential were quantified *in situ* by using a HORIBA (Kyoto, Japan) U-50 series multiparametric water quality probe. The Monitoring and Control Program of the Ebro Water bodies, coordinated by CHE, provided data about dissolved ions and alkalinity of each sampling point. Details of the methodological procedure are available in CHE web (http://www.cheebro.es).

2.2. Chemical analysis

The dissolved fraction of metals was quantified on DGTs samples and the water aliquots acidified with HNO_3 at 0.1%. The resin layer of the DGT device was placed with 1 M HNO_3 overnight before analysis, and metal concentrations were calculated as reported by Davison and Zhang (1993).

A Perkin Elmer Elan-6000 ICP-MS spectrometer was used for determining the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), selenium (Se), lead (Pb) and zinc (Zn) by inductively coupled plasma-mass spectrometry (ICP-MS). The concentrations of calcium (Ca), iron (Fe), magnesium (Mg), potassium (K) and sodium (Na) were quantified by means of a Perkin Elmer Optima 8300 simultaneous ICP-OES spectrometer. Dissolved Organic Carbon (DOC) was analysed on the aliquots of water acidified with H_2SO_4 to a pH below 2 by an AJ analyzer Multi N/C 3100 after inorganic carbon elimination.

2.3. Chemical speciation models

Three mathematical models were run simulating the environmental conditions of each sampling site. The selected models were: WHAM 7.0 (Tipping, 1994), Visual MINTEQ 3.1 (Gustafsson, 2014) and Bio-met 2.3 (Bio-met, 2013). WHAM 7.0 simulates the chemical reactions that occur