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Measurement of dynamic mobilization of trace metals in sediments using DGT and comparison with bioaccumulation in *Chironomus riparius*: First results of an experimental study

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Abstract

Sediments in aquatic ecosystems are often contaminated as a result of anthropogenic activities. Sediments and benthic organisms have been used to monitor trace metals contamination. However, due to the high variability of contaminant bioavailability, the attempt to link metal concentration in sediments and contamination of the organisms or ecotoxicological effect often lead to disappointing results. The technique of diffusive gradients in thin films (DGT) has been proposed as a relevant tool to study metal bioavailability, for example for accumulation in plants. In the present study, laboratory microcosm experiments were conducted with six contaminated sediments to compare metal accumulation in DGT and bioaccumulation in a chironomid (*Chironomus riparius)* for Cu, Cd and Pb . Metal accumulation in DGT was measured over time then modelled to determine two parameters of the dynamic response of the metals to DGT deployment: the size of the particulate labile pool and the kinetic of the solid-dissolved phase exchange. The mobility of metals was found metal and sediment dependent. A significant relationship between metal accumulated in DGT and bioaccumulated in chironomids was found for Cu and Pb. However, total metals in sediments were the best predictors of bioaccumulation. Nevertheless, the knowledge of the metals dynamic enhanced our ability to explain the different biological uptake observed in sediments of similar total metal concentrations.

Keywords: Sediment; DGT; Metals mobilization; Bioaccumulation; *Chironomus riparius*

1. Introduction

Metal-contaminated sediments can lead to ecotoxicological risk for the aquatic environment depending on the bioavailable concentration of the contaminant. Di Toro et al. (1992) stated that total metal concentration in sediment is not able to predict adequately biological effects of trace metals. The determination of metal concentration in porewaters can provide a better indication of bioavailability than the total concentration in sediment (Di Toro et al., 1992; Ankley et al., 1993), but it does not account for the supply of metals from the particles following depletion by benthic organisms uptake. In fact, sediment trace metals bioavailability and related biological effect have been shown to be dependent on two processes: a physico-chemical desorption of metals from the particles and a physiologically driven uptake process followed by the distribution and transport of contaminants to specific targets within the organism (Koster et al., 2005). Various sampling and extraction methods with chemical reagents have been proposed to assess the bioavailable fraction of metals in sediments. Nevertheless, such assessments are method dependent and their results are not necessarily comparable (Luoma, 1989). The AVS (Acid Volatile Sulfide) model was successfully used in studies dealing with metal toxicity in

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freshwater and marine sediments (Di Toro et al., 1992; Burton et al., 2005; Doig and Liber, 2006). However, Ankley (1996) and Warren et al. (1998) reported results of experiments in which the AVS model did not support the prediction of metals bioaccumulation in benthic organisms. Thus, it seems that geochemical approaches address only one part of the interaction between organisms and metals from sediment.

We decided to study the capacity of DGT measurements in sediments to improve the prediction of metals bioaccumulation in benthic invertebrate. Indeed, the technique of diffusive gradients in thin films (DGT) has been proposed as a tool allowing to determine free and labile metal species in water (Davison and Zhang, 1994; Zhang and Davison, 1995), soil and sediments (Zhang et al., 1998, 2002; Harper et al., 1998; Wegener et al., 2002; Nowack et al., 2004; Leermakers et al., 2005), as well as water and sediments in extreme environments (Larner et al., 2006). Measurements by DGT can be considered relevant to study metals bioavailability in water and sediments (Zhang et al., 1995; Zhang and Davison, 2000; Wegener et al., 2002; Nowack et al., 2004). However, Tusseau-Vuillemin et al. (2004) showed that the relevance of DGT to estimate the bioavailable fraction of Cu in waters to *Daphnia magna* depended on the type of binding organic matter. In laboratory experiments with media spiked with different dissolved organic matter, these authors demonstrated that DGTs are most powerful in estimating the bioavailable fraction of Cu in a humic acid solution, but less efficient in the case of algae exudates solution. Zhang et al. (2001) found that Cu accumulation in a terrestrial plant (*Lepidium heterophyllum*) was strongly correlated with Cu measured by DGT in various types of soils. These authors showed that the kinetically labile solid phase pool plays an important role in the metal uptake and that DGT is relevant to study bioavailability because the device operates similarly to active transport across a cell membrane. However, DGT predicted well the bioavailability of Zn and Cd in spinach and ryegrass only at non-toxic concentrations in the soil solution (Almås et al., 2006) and cannot be used to predict Cu uptake in aerial parts of a tolerant plant (maize) (Cattani et al., 2006).

In this paper, we explore how the combination of DGT measurements of metal fluxes from contaminated sediments and the inverse modelling of trace metal mobilization with DIFS (DGT-induced fluxes in soils; Harper et al., 1998) could help us to interpret the bioaccumulation of metals by a benthic invertebrate, *Chironomus riparius* (chironomid). Experiments were conducted in laboratory microcosms, coupling DGT measurements and bioaccumulation during a 7 days period.

2. Material and methods

2.1. Sampling

In order to run the experiments, freshwater sediments with variable metal contaminations were sampled from 6 reservoirs located in southwest, centre and northwest region of France. Four sediments were sampled from hydroelectric reservoirs (sites named G, S, C, R), one from a storage basin supplying cooling water for a nuclear power plant (site M) and one from a reservoir supplying drinking water (site T). At each site, 7 kg of the uppermost 10 cm of sediment was sampled using a Van Veen grab (Hydrobios, GmbH) and was immediately transferred into a plastic container, hermetically closed before transport to the laboratory. Additionally, 20 l of surface water were collected at each site. All the samples were kept at 4 °C for less than one month before the testing.

2.2. Culture of chironomids

Test organisms came from our laboratory culture (Cemagref, Lyon). Organisms were cultured by placing Fontainebleau sand substrate into a 10 l glass container filled with artificial water (conductivity: 300–320 μS cm^{-1}, total hardness: 120–180 mg l^{-1} as $CaCO_3$). The water was aerated and maintained at 23 ± 1 °C. Cultured *Chironomus riparius* were fed daily with Tetramin® suspension. Two days before the test, hatched masses previously isolated from the culture were placed in glass jars with coarse sand, artificial water and food (50 mg Tetramin® per mass). Recipients were then set at 22 ± 1 °C with 16:8 h light:dark photoperiod during 2 days.

2.3. DGT preparation and deployment

The DGT probe consists of a plastic piston loaded with a diffusive gel layer backed by an ion-exchange resin gel (Chelex 100) and a plastic cap with a 2 cm diameter window. A protective 0.45 μm cellulose nitrate filter (0.13 mm thickness, Millipore) separates the diffusive gel from the solution. Diffusive gels (0.8 mm thickness) and resin gels were purchased from DGT Research Ltd (Lancaster, UK). In order to prevent the introduction of oxygen during the deployment, DGT probes were deoxygenated by immersing them in a suspension of 5 g l^{-1} of Chelex 100 resin (Sigma) in 0.01 M NaCl bubbled with nitrogen. After 2 days, the probes were transferred in a glove box under nitrogen atmosphere, put in clean plastic jars which were immediately sealed. They were then rapidly deployed into the sediment. The probes were exposed to air and oxygenated water only for a few seconds before the insertion into the sediment.

2.4. Experimental protocol

For each of the six studied sites, a similar experimental protocol was applied. The whole sediment was gently stirred with a plastic spoon, quickly sieved through a 2 mm mesh nylon sieve and homogenised before the experiment. Subsamples of homogenised sediment were distributed in 40 glass beakers (600 ml) to obtain a 2 cm layer. Water