Coupling geochemical and biological approaches to assess the availability of cadmium in freshwater sediment

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Coupling geochemical and biological approaches to assess the availability of cadmium in freshwater sediment

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Abstract

Sediments are considered as a sink for metals, and the assessment of metal bioavailability for benthic organisms represents a great challenge. Diffusive Gradient in Thin films (DGT), developed to measure labile metals in aquatic media, have more recently been applied to sediment. Nevertheless, few studies have determined the relation between measurements from DGT and bioaccumulation in different benthic organisms. The aim of our work was to determine if labile metal measured by DGT in sediment is representative of bioavailable metal for benthic organisms. We focused our work on Cd and chose to use the diversity of ecological traits from different organisms to better understand the measurement given by DGT. We exposed simultaneously DGT and 3 macroinvertebrates species (the chironomid, *C. riparius*; the amphipod, *G. fossarum*; the mudsnail, *P. antipodarum*) to a natural sediment Cd-spiked at environmental relevant concentrations. The nature of sediment-bound Cd was also determined by means of sequential extractions in order to better interpret DGT measurements. Cadmium concentrations were determined in DGT and in the 3 organisms after one week of exposure. Results provided by DGT indicated that Cd was poorly released from particulate phase to pore water, suggesting that Cd measured by DGT was representative of the pore waters labile fraction. Sequential extractions showed that the percentage of Cd bound to carbonate fraction increased simultaneously with Cd-spiking level; hence, this Cd fraction was poorly reactive to supply DGT demand. Cadmium accumulation rates were similar between DGT measurements and *P. antipodarum*, suggesting that labile Cd in pore waters was representative of bioavailable Cd for this species. Cadmium accumulation rates in *C. riparius* were higher than in DGT, demonstrating that *C. riparius* can mobilize Cd bound to carbonate phase. *G. fossarum* showed the lowest Cd accumulation rates, suggesting that they were mainly exposed to Cd from overlaying waters.

Keywords: spiked-sediment, cadmium, DGT, sequential extractions, bioaccumulation, macroinvertebrates, ecological traits

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1. Introduction

Sediment is generally considered as an important compartment to be investigated for evaluating the ecological integrity of an aquatic ecosystem. It provides a habitat for a large diversity of communities, but also serves as a reservoir for many pollutants. Sediment contamination primarily occurs via hydrodynamic processes during witch many pollutants present in water are readily adsorbed on colloids that can aggregate with each other and settle to the bottom of aquatic systems (Buffle et al., 1998; Vignati et al., 2005). Once in sediment, the evaluation of pollutants mobility and bioavailability remains difficult because of the complex interactions between their own intrinsic properties, the geochemical/climatic factors and the biodiversity on-place (Munkittrick and McCarty, 1995; Chapman et al., 2003). In particular, the lability and the bioavailability of trace metals in sediments are function of the targeted metal, its colloidal, dissolved and particulate partition, its speciation, sediment physico-chemical characteristics (i.e., porosity, grain size, organic matter content), redox and pH conditions, and the physiological and ecological characteristics of the exposed organisms. Traditionally, the assessment of metal availability in sediments using a geochemical approach includes measurements of metals in dissolved and particulate phases and chemical extractions of available fractions (Tessier et al., 1979; Buykx et al., 2000). However, the total metal concentration in sediments is generally not a good proxy to predict bioaccumulation or biological effects (Di Toro et al., 1992). It was demonstrated in several case studies that pore waters metal concentration was a better tool to assess metal bioavailability in sediment (Di Toro et al., 1992; Ankley et al., 1993a; Berry et al., 1996); nonetheless, pore waters metal concentration did not reflect the supply of metals from the particulate phase when particles are ingested by organisms, such as chironomids larvaes (Bervoets et al., 1997; Warren et al., 1998). Another parameter which strongly controls metal mobility in sediments is the acid-volatile sulphides (AVS). Acid-volatile sulphides are known to bind trace metals (i.e., Cd, Cu, Ni, Pb and Zn) in marine or freshwater sediments, resulting in insoluble sulphides complexes which reduce metal mobility and toxicity (Di Toro et al., 1992; Ankley et al., 1993b; Ankley et al., 1996; Burton et al., 2005). However, the AVS model did not support the prediction of metals bioaccumulation in benthic organisms for heavily contaminated freshwater sediments (Ankley, 1996; Warren et al., 1998; Lee et al., 2000; De Jonge et al., 2009). More recently, the Diffusive Gradient in Thin films (DGT), initially developed in the 1990's to measure labile metals in surface waters (Zhang and Davison, 1995), has been applied to soil and sediment (Harper et al., 2000; Zhang and Davison, 2000; Zhang et al., 2004; Rachou et al.,

2007). When a DGT is introduced into sediments, trace metals of the pore waters are rapidly bound by the resin of the device; this results in a decrease of pore waters trace metals concentrations, inducing a variable resupply from the particulate phase (Zhang et al., 1995). Metal accumulation in DGT and in terrestrial plants has been successfully compared because it operates similarly to active transport across a cell membrane (Zhang et al., 2001; Almås et al., 2006). The comparison is more difficult with benthic organisms, since metal transfer pathways are more complex, involving dissolved, colloidal and also particulate forms when sediment is ingested.

The aim of our study was to determine if the measurement of the labile Cd fraction in freshwater sediment using the DGT device is representative of the metallic bioavailable fraction for benthic organisms. We chose to use the diversity of ecological traits and habitats from different organisms to better understand the measurement given by the DGT tool in term of bioavailability. *Chironomus riparius* (insect larvae) are a relevant indicator of metal bioaccumulation because they live within the sediment during their larvae development and a large part of the metals they accumulate comes from the particulate phase due to particles ingestion (Bervoets et al., 1997; Warren et al., 1998). *Gammarus fossarum* (amphipod) and *Potamopyrgus antipodarum* (mudsnail) have been used in ecotoxicological test, especially for the evaluation of metals exposure from the water column (Geffard et al., 2010; Gust et al., 2011), and they have also been recently used to assess sediment toxicity (Mazurová et al., 2008; Mazurová et al., 2010; Schmitt et al., 2010). *G. fossarum* are epibenthic organisms living at the sediment-water interface; hence, they are mostly influenced by metals from the overlying waters. In contrast, *P. antipodarum* are known to live at the sediment-water interface and as well within the first millimeters depth of the sediment (Michaut, 1968); so they are also exposed to metals from pore waters. The nature of sediment-bound Cd was determined by means of sequential extractions in order to better interpret DGT measurements. Therefore, we performed the following laboratory tests under controlled conditions: parallel experiments were conducted by coupling DGT measurements with bioaccumulation measurements on *C. riparius, G. fossarum* and *P. antipodarum*. Since several physico-chemical parameters (AVS concentration, organic matter concentration, carbonates…) could induce a variability of geochemical and ecotoxicological results, we decided to use a unique low contaminated natural sediment, Cd-spiked at environmentally relevant concentrations.

2. Material and methods

2.1 Sediment sampling and Cd spiking

The sediment used in this study (PG) was collected in October 2009 from the Ain River which is a tributary of the Rhône River in the Southeast of France (N 45°809; E 5°209). This sediment was chosen since concentrations of inorganic (Table 1) and organic contaminants were low and under Threshold Effect Concentrations (TEC; Mc Donald et al., 2000). Surface sediment (10 cm) was sampled using a Van Veen grab (Hydrobios, GmbH), then it was immediately sieved through a 2 mm mesh. It was kept at 4°C before experiments. Five environmentally relevant nominal spiking Cd concentrations (0.5, 1.3, 3.1, 7.8 and 19.5 mg kg^{-1} dry weight) were defined in order to cover a concentration range evenly spread between the Threshold Effect Concentration (TEC; 0.99 mg kg^{-1}) and the Probable Effect Concentration (PEC; 4.98 mg kg^{-1}) defined by Mc Donald et al. (2000). A Control was prepared in the same way as the spiked concentrations. Cadmium spiking ($CdCl_2$ salts) was realised by mixing wet sediment with the spiked solution using a liquid-solid ratio of 3.6. The water (FOS) used to proceed to the spiking mixing step corresponded to a spring-water adjusted to 300 µS cm^{-1} with purified water. The composition and characteristics of this water were regularly checked during experimental protocol. The pH was circa 6.9; Ca^{2+} and Mg^{2+} concentrations averaged 35 mg L^{-1} and 2.3 mg L^{-1}, respectively. Dissolved cadmium concentrations were below the limit of quantification (LQ = 0.01 µg L^{-1}). The content was mixed on a rotating wheel for 6 hours. After particles settling (48 hours), the supernatant water was removed using a vacuum pump and the sediment was homogenized with a plastic spoon prior to its introduction in test beakers. The same procedure was used for the Control sediment, but with Cd-free FOS water.

2.2 Experimental protocol

Subsamples of 100 ml of homogenized spiked sediment were distributed in 500 ml polypropylene beakers. An amount of 400 ml of FOS water was slowly added over the sediment minimising the suspension of the sediment. All beakers were placed in temperature regulated water baths at 21 ± 0.5 C, except for *G. fossarum* (12 ± 1°C), and with a 16:8 h artificial light:dark photoperiod. In order to equilibrate, systems were maintained during 10 days before introduction of DGT and organisms. Each beaker was continuously supplied with FOS water using a flow through system to obtain 4 renewals of overlaying waters per day.

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143 2.3 DGT preparation
144
145 The DGT probe consists in a plastic piston loaded with a diffusive gel layer backed by an ion-
146 exchange resin gel (Chelex 100) and a plastic cap with a 2 cm diameter window. A protective
147 0.45 μm cellulose nitrate filter (0.13 mm thickness, Millipore) separates the diffusive gel from
148 the solution. Diffuse gels (0.8 mm thickness) and resin gels were purchased from DGT
149 Research Ltd (Lancaster, UK). In order to prevent introduction of oxygen during the
150 deployment within the sediment, DGT probes were deoxygenated by immersion in a
151 suspension of 5 g L^{-1} of Chelex-100 resin (Sigma) in 0.01 M NaCl, bubbled with nitrogen
152 during 24 hours. Before their deployment into the sediment, the probes were transferred in a
153 glove box under nitrogen atmosphere, put in clean plastic jars which were immediately
154 sealed. The probes were exposed to air and oxygenated water only for a few seconds before
155 the insertion into the sediment.
156
157 2.4 Geochemical approach
158
159 Geochemical experiments were only realised for the Control and for the 3 highest
160 concentrations. DGT probes were introduced in the sediment (one DGT per beaker) by
161 pressing them carefully at the sediment-water boundary layer with a polypropylene stick. The
162 window of measurement of the DGT was positioned at a sediment depth of about 1 cm. DGT
163 devices were retrieved at 2, 4, 8, 12, 24, 48, 72 and 144 hours of deployment (except at 2 and
164 4 hours for the Control sediment). One replicate was used at each time for the Control
165 sediment and two replicates were retrieved for the Cd-spiked sediments at 4, 12, 24 and 144
166 hours. After removal, the DGT probes were thoroughly rinsed with MilliQ water and stored at
167 4°C into clean plastic bags. DGT resin gels were eluted with 2.5 ml of 1 M HNO_3 (Merck,
168 Suprapur) into acid-cleaned polypropylene tubes. At the start and at the end of the DGT
169 deployment period, pore waters were extracted from beakers by centrifugation (10 000 g,
170 30 min) and filtration (0.45 μm) under nitrogen atmosphere. Additionally, surface waters
171 were sampled and filtered (0.45 μm) in duplicate at the start of the experiment. At the end of
172 the deployment time, an aliquot of each sediment was sampled under nitrogen conditions and
173 immediately kept at 4°C for sequential extractions and at -19°C for AVS extraction.
174
175 2.5 Bioaccumulation approach
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C. riparius were obtained from the laboratory culture. *G. fossarum* and *P. antipodarum* were collected from natural populations in the Bourbre River and the Rhône River (France), respectively. The 3 test organisms were exposed to the Control sediment and to the 4 concentrations of Cd-spiked sediments in separate beakers from DGT exposure.

Cadmium bioaccumulation was measured on 3 replicate organisms pools (from 3 independent beakers) at the beginning and after 7 days (*C. riparius*, *G. fossarum*) or 10 days (*P. antipodarum*) of exposure. Depending on the mortality rates, 35 unshelled *P. antipodarum* (average of 0.033 g d.w.) , 10 *C. riparius* (average of 0.005 g d.w.) and 10 *G. fossarum* (average of 0.050 g d.w.) were retrieved for each replicate pool sample. All the organisms were thoroughly rinsed successively with FOS water, EDTA (3 mM L^{-1}, diluted in FOS water) and FOS water. The replicates were then freezed-dried (-20°C) before analysis.

2.6 Physico-chemical analyses

Sediment granulometry was determined using a Coulter LS-100. Acid-volatile sulfides (AVS) were determined on wet sediments using the procedure developed by Allen et al. (1993) and the limit of quantification was 0.12 µmol g^{-1}. Carbonates content was determined by addition of cold HCl to sediment and by measurement of liberated CO_2 volume. Loss on ignition (LOI) was realised by weighting sediment before and after heating at 500°C in order to estimate total organic matter content. In order to better assess the partitioning of Cd among the different carrier phases of the sediment, sequential extractions were realised according to Roulier et al. (2010). In order to preserve the sub-anoxic conditions in the sediment, sequential extractions procedure was realised under nitrogen atmosphere in a box glove using extractants previously deoxygenated. Duplicate samples were run throughout the procedure. To assess the percentage of recovery of the sequential extractions procedure, the bulk sediment was also mineralized with *aqua regia* (HNO_3: HCl, 3:1) using a microwave oven (MARS-5, CEM).

Organisms were mineralized with 2 mL of HNO_3 (Suprapur, 65%) using a microwave oven (MARS-5, CEM). Metal concentrations in surface waters, pore waters, DGT eluates, sediments extracts from sequential extractions and in biological samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X7 series^{II}). Blanks and certified reference materials (TM-28.3, lake water, Environment Canada; IAEA-158, marine sediment; NRCC, TORT-2, lobster hepatopancreas) were systematically used to control analytical accuracy and precision. For sediment, typical expanded uncertainties (i.e., 95%

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confidence intervals) were 5%. Relative standard deviations of Cd concentration for triplicate biological samples ranged between 6 and 38% for *G. fossarum*, between 1 and 13% for *P. antipodarum* and between 26 and 52% for *C. riparius*.

2.7 Data analysis

The flux of metals from sediment to the DGT device (F_{DGT}) provides information on the ability of the solid phase to resupply the pore waters. F_{DGT} was calculated as follows:

$$F_{DGT} = \frac{M}{A \times t} \quad (1)$$

Where M is the accumulated mass of Cd for a resin surface A (cm²), over the deployment time t (s). The time-averaged concentration at the interface of the sediment and the diffusive gel, C_{DGT} (in µg l^{-1}) was calculated as follows (Eq. 2), with D corresponding to the diffusive coefficient of the free metal ion (cm² s^{-1}) in the diffusive layer of thickness Δg (cm):

$$C_{DGT} = \frac{M \times \Delta g}{D \times t \times A} \quad (2)$$

C_{DGT} generally decreases during the deployment time because the pore waters concentration near the DGT probe progressively decreases. The R ratio, which corresponds to the ratio between C_{DGT} and the initial metal concentration in pore waters (C_{pw}) before the introduction of the DGT probes (Eq. 3), gives an indication of the depletion at the DGT interface (Harper et al., 2000):

$$R = \frac{C_{DGT}}{C_{pw}} \quad (3)$$

R can be simulated with the 2D-DIFS model (DGT-induced flux in soils) proposed by Sochaczewski et al. (2007). This model is based upon solute exchange between solid phase and pore waters, coupled to diffusion supply of metal to the interface and across the diffusion layer to the resin gel. DIFS-2D was used by fitting experimental values of R over time allowing to derive the parameters conditioning the response of the metal release from the sediment: the size of the particulate labile pool defined by the distribution coefficient K_{dl} (L kg^{-1}) and the characteristic response time (T_c) of the assumed 1st order reversible exchange process between dissolved and solid phases.

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3. Results

3.1 Geochemical approaches

Physico-chemical characteristics and particulate metal concentrations of the studied sediment are presented in Table 1. The sediment showed a relatively fine composition since 70% of particles are represented by silts and clays (< 63 µm). Acid volatil sulfides concentrations in the sediment were similar between the Control sediment and spiked sediments, with a mean concentration of 8.1 ± 0.5 µmol g^{-1}. Calcium carbonates were the main component of the sediment (54%). Particulate trace metal concentrations (Cd, Cr, Ni, Cu, Zn, As and Pb) were low and all below the TEC. Particulate Cd concentrations obtained for the 5 Cd-spiked concentrations were close to the nominal ones, respectively 0.71, 1.35, 2.97, 6.97 and 17.5 mg kg^{-1}. Dissolved Cd concentrations in overlaying waters were below the limit of quantification (0.010 µg L^{-1}) in beakers containing the Control sediment and the 2 lowest Cd-spiked concentrations. Cadmium concentrations in overlaying waters increased with Cd spiking concentrations, with 0.014, 0.020 and 0.035 µg L^{-1} for PG3.1, PG7.8 and PG19.5, respectively. Cadmium pore waters concentrations ranged between 0.02 µg L^{-1} (Control sediment) and 1.82 µg L^{-1} (PG19.5). Only for PG19.5, Cd pore waters concentrations increased at the end of the experiment (4.19 µg L^{-1}). For the other sediments, Cd pore waters concentrations were similar between the start (T0) and the end (T1: 144 hours) of the experiment. The mass of Cd accumulated by the DGT from the Control sediment was too low to be detected in the eluates (< 0.010 µg L^{-1}). In contrast, for PG3.1, PG7.8 and PG19.5 Cd-spiked sediments, the mass of Cd trapped by the DGT increased with time up to 48 hours, then remained constant (Figure 1a). Cadmium fluxes through DGT rapidly decreased to reach low and similar values for the 3 highest spiked sediments (Cd fluxes = $0.18\ 10^{-5} \pm 0.10$ ng cm^{-2} s^{-1}) after 144 hours of deployment (Figure 1b).

Experimental R data, obtained from the ratio between C_{DGT} and the initial pore waters concentrations (Equation 3), were fitted from inverse 2D-DIFS modelling, which allowed to estimate the range of the partition coefficient of the particulate labile Cd pool (K_{dl}) and the response time of the sorption processes (T_c) for the 3 highest Cd-spiked sediments (Table 2). The response times of sorption processes were relatively high (34 s < Tc < 12500 s) and the labile partition coefficients (K_{dl}) very low (< 2.79). The distribution of particulate Cd concentrations obtained by sequential extractions showed that Cd was not present under exchangeable form (F1) or bound to the residual phase (F5) whatever the level of Cd spiking

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(Figure 2a). Particulate Cd concentrations in F2, F3 and F4 fractions increased with the level of Cd-spiking (Figure 2a), reaching up to 9.34, 5.77 and 1.94 mg kg^{-1} respectively, for the highest level of spiking (PG19.5). The relative contribution of each fraction (Figure 2b) showed a progressive increase of F2 fraction from 16% (Control) to 54% (PG19.5), at the expense of F3 and F4 fractions, which decreased from 54% to 34% and from 30% to 11%, respectively.

3.2 Cd bioaccumulation

Internalised Cd bioaccumulation for *C. riparius*, *G. fossarum* and *P. antipodarum* are reported in Table 3. Since exposure time was different between the tested organisms and in order to compare results, we calculated Cd bioaccumulation rates (Figure 3). Cadmium bioaccumulation rates were the highest in *C. riparius,* ranging from 0.051 ± 0.019 µg g^{-1} day^{-1} for the Control sediment to 3.68 ± 1.92 µg g^{-1} day^{-1} for PG19.5. Cadmium bioaccumulation rates ranged between 0.018 ± 0.007 µg g^{-1} day^{-1} and 0.195 ± 0.040 µg g^{-1} day^{-1} for *G. fossarum* and between 0.060 ± 0.039 µg g^{-1} day^{-1} and 0.393 ± 0.008 µg g^{-1} day^{-1} for *P. antipodarum,* depending on exposure concentration.

4. Discussion

4.1 Supply of Cd from the particulate phase

For the 3 highest Cd-spiked sediments, the mass of Cd trapped by the DGT after 144 hours of deployment was 1.3 times higher between PG3.1 and PG7.8 and 2.0 times higher between PG7.8 and PG19.5. Since total particulate Cd concentrations were about 2.5 times higher between each studied sediment, this suggests that DGT measurement did not reflect the particulate Cd concentrations. Cadmium fluxes towards DGT as a function of time (Figure 1b) showed a typical distribution, corresponding to a rapid decrease during the first hours of deployment followed by a plateau. This distribution reflects a consumption of Cd from pore waters and a poor resupply from particles. In contrast, results obtained by Roulier et al. (2010) on natural sediments, exposed in similar conditions, showed an increase of Cd fluxes between 48 and 72 h followed by a decrease. The authors proposed that the increase of Cd fluxes was linked to Mn and Fe oxides reduction at the DGT/sediment interface. They obtained Cd fluxes ranging from ~0.1 to 0.7 10^{-5} ng cm^{-2} s^{-1} between 24 and 144 h, corresponding to particulate

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Cd concentrations of 1.4 to 1.8 mg kg^{-1}. In our experiment, despite Cd particulate concentrations reaching up to 17.5 mg kg^{-1}, Cd fluxes were similar, ranging from 0.1 to 1.2 10^{-5} ng cm^{-2} s^{-1}. Moreover, the total mass of Cd was mainly trapped by DGT during the first 24 hours of deployment (38%: PG3.1; 74%: PG7.8; 71%: PG19.5). This suggests that Cd trapped by DGT mainly originated from the pore waters.

Pore waters Cd concentrations include all the metal phases (colloidal forms, inert and labile complexes, free ions), while DGT measures only free ions and labile metal. Although few data are available on Cd partition between colloidal and truly dissolved phase in sediment, Cd is known to be poorly present in colloidal complexes in surface waters (Sañudo-Wilhelmy et al., 2002). In our study, we analysed pore waters Cd concentrations at the start and at the end of the DGT deployment. Relative percent deviation (RPD) was below 10% for PG3.1 and PG7.8, showing a good reproducibility between beakers and that equilibration steady state was reached at the onset of the experiment. However, a large difference was noted for PG19.5 (RPD = 79%). This indicates an evolution of the sediment at high Cd-spiked level, probably due to a pH decrease (Hutchins et al., 2007). Indeed, metal-spiking might result in a drop of pH in relation with (i) hydrolysis of metal-spiked (ii) oxidative precipitation of Fe in pore waters and (iii) competition between protons H^+ and metal-spiked for particulate sorption sites.

Nonetheless the plot of experimental R ratio calculated for PG19.5 using initial and final pore waters concentrations showed very similar distributions (Figure 4). Moreover, the R ratio distribution for PG19.5 fitted very well with those of PG3.1 and PG7.8, calculated using means of initial and final pore waters concentrations. The distribution of the R ratio showed a fast decrease during the first 8 hours of DGT deployment, reaching a very small R ratio (< 0.16). Then, the R ratio slowly decreased and stabilized below 0.04 after 144 hours of DGT deployment. Apparently, whatever the level of Cd-spiking, Cd in pore waters was rapidly bound by the DGT in the first hours of deployment, followed by a very low resupply from the particulate phase. Ernstberger et al. (2002) exposed DGT to alluvial soil from 4 hours to 19.5 days; the R ratio was about 0.6 at the start of the experiment, then reached about 0.35 after 144 hours of deployment. In a similar study, Ernstberger et al. (2005) exposed DGT to 5 different soils with similar particulate Cd concentrations (3.24 ± 0.07 mg kg^{-1}), but with variable pH, granulometry and organic carbon content. The R ratios were higher than our results, ranging between ~0.8 and ~0.4 at the start of the experiment, and between ~0.6 and ~0.2 after 144 hours. The highest R ratios were obtained for the clayey soils with neutral pH and organic matter content from 2.6 to 5.8%. We obtained significantly lower R ratio, in spite

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of high clay (<63 μm = 70%) and high organic carbon content (LOI = 13%). This suggests that in our case, spiked Cd was probably bound to unreactive particulate phases.

The 2D-DIFS model was used to model the R ratio distribution in order to determine K_{dl} and T_c parameters. An accurate determination of these two parameters was difficult due to a large number of possible combinations (K_{dl}, T_c) which can fit the experimental data (Lehto et al., 2008). Thus, several response times (T_c) and partition coefficient (K_{dl}) were proposed (Table 2). We obtained very low values for K_{dl} (< 2.79) and high T_c values (ranging between 34 and 12500 s) for the 3 highest Cd-spiked sediments. In Roulier et al. (2008), DGT were deployed in 6 polluted sediments and only one couple of K_{dl} (1) and T_c (5000) was comparable to our results. For the other sediments, K_{dl} ranged between 5 and 250, corresponding to small response times (<10 s in most cases). The highest K_{dl} values were obtained for sediments with high organic contents. Similarly, Ernstberger et al. (2005) showed that soils with poor resupply from the particulate phase were sandy and characterised by low pH and low organic matter content. Our tested sediments were fine with relatively high organic matter content (Table 1), but K_{dl} and T_c inferred from the R ratio distributions denoted a poor resupply from the particulate phase.

In our study, only total Cd concentration was modified; whatever the level of Cd-spiking, particulate Cd was strongly bound to the particles in response to the equilibrium modification induced by DGT insertion. Acid volatile sulphides are known to strongly bind Cd, reducing its mobility and its toxicity; but AVS concentrations were low in all Cd-spiked sediments (8.1 ± 0.5 μmol g^{-1}; Table 1) and could not explain the equivalent low resupply from particulate phase obtained via DGT.

In all tested sediments, Cd was not present in the more potentially mobile particulate phase nor bound to the residual fraction. Cadmium was distributed between the F2, F3 and F4 particulate fractions, corresponding to carbonates, Fe and Mn oxides, organic matter and sulfides, respectively (Figure 2). With higher Cd-spiked level, the F2 fraction increased at the expense of F3 and F4 fractions. The significant F2 fraction was due to the high carbonate contents of sediments (54%). Indeed, Cd is known to have a great affinity with carbonates. Thakur et al. (2006) showed that Cd is effectively retained on $CaCO_3$ by the mechanism of chemisorption at low Cd concentrations, while at higher concentrations, precipitation of $CdCO_3$ on $CaCO_3$ surface phase predominated. This phenomenon was also reported in several studies, which showed that Cd was not only bound to sediments by sorption but as well by precipitation of secondary minerals such as otavite ($CdCO_3$) (Papadopoulos and Rowell, 1988; Komárek and Zeman, 2004; Cubillas et al., 2005). In summary, Cd spiked to this highly

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carbonated sediment was firstly chemisorbed by carbonates surface, followed by $CdCO_3$ precipitation, inducing an exponential increase of the F2 fraction between each spiked sediment. This F2 fraction, presenting a great affinity for Cd, seems to be poorly reactive to supply the decrease of Cd in pore waters induced by the DGT demand.

4.2 Cd bioavailability

The slope of the regression between Cd accumulation in organisms, function of total particulate Cd, dissolved Cd in pore waters and in overlaying waters were more pronounced for *C. riparius* as compared to *G. fossarum* and *P. antipodarum* (Figure 3a, b, c), suggesting that *C. riparius* was exposed to a pool of Cd which, in contrast, was not available for the 2 others species. By means of in situ experiments, Warren et al. (1998) showed that prediction of Cd concentrations in most benthic animals would be more accurate if they were based on water column rather than on sedimentary Cd concentrations, except for sediment-feeding species such as Chironomids and Tubificidae, which also get Cd from sediments. Indeed, *C. riparius* live in close contact with sediments (Young and Harvey, 1991; Charbonneau et al., 1998), burrowing into sediments and creating their own microenvironment by irrigating and ingesting particles. Thus, ligands present in the gut fluid of deposit feeders, provide a complexation capacity for mobilization of sediments-bound metals (Chen et al., 2000). Roulier et al. (2008) reported a significant positive relationship between Cd concentrations in *C. riparius* and particulate Cd concentrations in freshwater contaminated sediments. Our data perfectly fit with this previous study performed under similar exposure conditions (Figure 5). Clearly, these results show that total Cd concentrations in sediments are a good predictor of Cd accumulation in *C. riparius*. Fitting our data with those of Roulier et al. (2008) indicates that particles ingestion by chironomids mobilize more Cd from the particulate phase than DGT. Since sequential extractions showed that Cd-spiked was mainly bound to the carbonate phase, we believe that chironomids are able to assimilate part of the Cd bound to carbonates. To our knowledge, this is the first time that a relationship is established between Cd bioaccumulation in chironomids and a specific Cd particulate fraction. In a similar way, Baumann and Fisher (2011) showed that bioaccumulated Cd in *Nereis Succinea* was related to exchangeable Cd and to Cd bound to the carbonate phase.

Cadmium bioaccumulated in *G. fossarum* in the Control sediment (Table 3: 0.12 mg kg^{-1}) was comparable to that obtained (0.28 mg kg^{-1}) in the study of Felten et al. (2008), for the same exposure time in a control solution (Cd < 0.30 µg L^{-1}). Cadmium concentrations in *G.*

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fossarum from the Control sediment, PG0.5 (0.204 mg kg^{-1}) and PG1.3 (0.299 mg kg^{-1}) were in the range of concentrations obtained for organisms collected on the upstream Bourbre River reference site (0.10 to 0.25 mg kg^{-1}), (Geffard et al., 2007). *G. fossarum* showed higher Cd concentration only starting from PG3.1 (0.441 mg kg^{-1}). Since *G. fossarum* are epibenthic species living at the water-sediment interface, they should mainly be influenced by Cd concentrations in overlaying waters. For PG19.5, overlaying waters Cd concentration was 0.035 µg L^{-1} and could explain Cd content in *G. fossarum* (1.37 mg kg^{-1}). In fact, on the Morcille River (Beaujolais region, France), dissolved Cd concentration was about 0.040 µg L^{-1} and Cd concentration in *G. fossarum* averaged 0.80 mg kg^{-1} (personal communication). If *G. fossarum* were exposed to Cd from pore waters (1.82 µg L^{-1}) of PG19.5 sediment, Cd concentrations in *G. fossarum* should have been higher. Indeed, for example, after one week of field exposure at 1 µg L^{-1}, Lacaze et al. (2011) obtained Cd concentrations in *G. fossarum* ranging between 4 and 12 mg kg^{-1}. Pellet et al. (2009) also reported that after one week of laboratory exposure at 1 µg L^{-1}, Cd concentration in *G. fossarum* was about 2.5 mg kg^{-1}. Clearly, all these data strongly support the conclusion that during our experiment, *G. fossarum* exposed to Cd-spiked sediment were mainly influenced by Cd present in overlying waters.

The slope of Cd bioaccumulation in *P. antipodarum* as a function of particulate Cd concentrations was higher than the slope of Cd bioaccumulation in *G. fossarum* (Figure 3d). It looks like *P. antipodarum* were affected by a pool of Cd that was not seen by *G. fossarum*. Since *P. antipodarum* live at the sediment-water interface and within the first millimeters of the sediment (Michaut, 1968), the exposed organisms were apparently influenced by Cd from pore waters (0.46 to 4.19 µg L^{-1}). However, few data on Cd bioaccumulation in *P. antipodarum* are available to reinforce this hypothesis. Gust et al. (2011) showed on a French river with dissolved Cd concentrations of 0.6 µg L^{-1} that Cd concentrations in *P. antipodarum* were about 1.82 mg kg^{-1}. These data are comparable with Cd concentrations in *P. antipodarum* of PG3.1 (1.02 mg kg^{-1}) and PG7.8 (2.12 mg kg^{-1}), corresponding to pore waters Cd concentrations of 0.45 and 1.38 µg L^{-1}.

Cadmium accumulation rates in DGT after 144h hours as a function of total particulate concentration showed that the slope of the regression was 2 orders of magnitude lower than the slope obtained for *C. riparius* (Figure 3d). These results corroborates our hypothesis that in a highly carbonated sediment, Cd was not released from the particulate phase to the pore waters in response to the locally depleted dissolved Cd concentration at the DGT-sediment interface, whereas *C. riparius* could bioaccumulate Cd from the particulate phase. Thus, in

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highly carbonated sediment, DGT is a poor predictor for Cd bioaccumulation in chironomids. This is in accordance with results from Roulier et al. (2008), which did not show a good relationship between Cd bioaccumulated in chironomids and Cd trapped by DGT. For *G. fossarum*, the slope of the relationship was lower than the slope for DGT, corroborating the idea that *G. fossarum* exposed to Cd-spiked sediment were mainly influenced by Cd present in overlying waters, while DGT reflected labile Cd from pore waters. Thus, DGT is a poor predictor for Cd bioaccumulation in *G. fossarum* in this highly carbonated sediment.

In contrast, the slope of Cd accumulation rates as a function of particulate Cd concentrations was similar between DGT and *P. antipodarum* (Figure 3d). As previously seen, Cd trapped by DGT was represented by labile Cd from pore waters. In conclusion, among the 3 tested species, *P. antipodarum* reflected the best Cd bioavailability from sediment pore waters which was assessed by DGT in this highly carbonated sediment.

5. Conclusions

Results of our geochemical approach, coupling DGT measurements and sequential extractions, showed that in a highly carbonated sediment, Cd bound to carbonates increased simultaneously with Cd-spiking level and was poorly reactive to supply the decrease of Cd in pore waters induced by DGT demand. This suggests that, in this kind of sediment, DGT measurement correctly reflects labile Cd from pore waters.

Our coupled biological approach, which included the confrontation of Cd accumulation rates in DGT and bioaccumulation for 3 benthic organisms with different ecological life traits, showed that *C. riparius* were exposed to a larger pool of Cd because they ingest particles. Since Cd was mainly bound to the carbonate fraction, *C. riparius* were in fact able to desorb Cd from carbonates. In contrast, Cd accumulation rates in *P. antipodarum* and DGT showed the same slope, suggesting that *P. antipodarum* were exposed to pore waters only and that the Cd pore waters labile fraction measured by DGT represented the bioavailable Cd fraction for this species. Cd accumulation rates were the lowest for *G. fossarum*; hence, this species was mainly influenced by Cd from overlaying waters. Our results are consistent with the known behaviour of the 3 organisms.

Therefore, the proposed DGT technique proved its usefulness for sediment quality monitoring and bioaccumulation prediction; nevertheless, its relevance for Cd and others metals would need to be further assessed by testing DGT with a panel of sediments with contrasted characteristics. Moreover, it might be more accurate, although more complex to apply, if

DGT measurement was realised on the whole sediment-water interface, in connection with the living area of the studied species.

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679 **Table captions**

680

681 Table 1: Physico-chemical characteristics and particulate trace metal concentrations of the
682 studied sediment. Cadmium concentrations in pore waters and in overlaying waters were
683 determined during the experiment.

684

685 Table 2: Partition coefficient (Kd) and parameters (K_{dl}: labile partition coefficient; T_c:
686 characteristic response time) deduced from 2D-DIFS modelling for the Control sediment and
687 the 3 highest Cd-spiked sediment concentrations.

688

689 Table 3: Concentrations of Cd bioaccumulated in *C. riparius*, *G. fossarum* and *P.*
690 *antipodarum*.

691

692 **Figure captions**

693

694 Fig. 1: (a) Mass of Cd accumulated in the DGT resin and (b) fluxes of Cd through the DGT as
695 a function of deployment time for the 3 highest Cd-spiked sediment concentrations (PG3.1,
696 PG7.8, PG19.5).

697

698 Fig. 2: (a) Cd concentrations in F2, F3 and F4 particulate fractions (mg kg^{-1}) and (b) relative
699 contributions (%) of the 3 fractions to total particulate Cd concentrations (for the Control
700 sediment and 3 highest Cd-spiked sediments PG3.1, PG7.8 and PG19.5).

701

702 Fig. 3: Bioaccumulation Cd rates (mean ± sd, n=3) in *C. riparius*, *G. fossarum* and *P.*
703 *antipodarum* as a function of (a) total particulate Cd concentrations, (b) dissolved pore waters
704 Cd concentrations and (c) dissolved Cd concentration in overlaying waters. Accumulation Cd
705 rates in DGT after 144 hours of deployment are reported for the 3 highest Cd-spiked sediment
706 concentrations (d).

707

708 Fig 4: Distribution of the R ratio for sediments Cd-spiked at 3.1, 7.8 and 19.5 mg kg^{-1}.

709

710 Fig. 5: Cadmium concentrations in *C. riparius* as a function of particulate Cd concentrations
711 for (●) this study and for (○) the study of Roulier et al. (2008).

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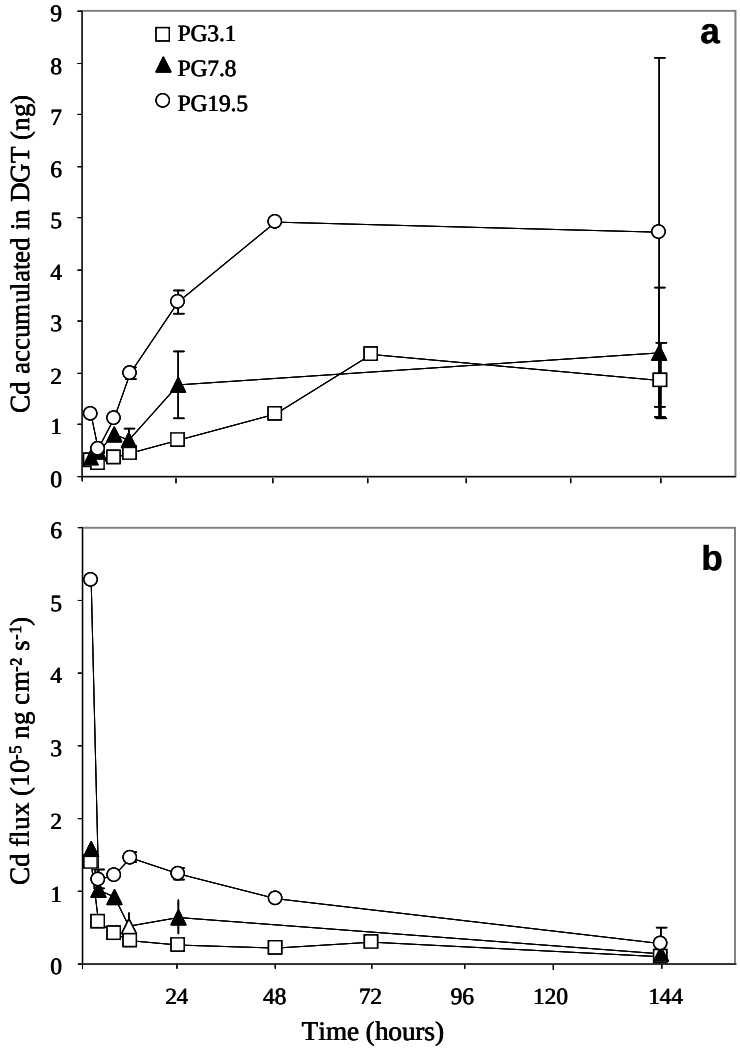

Fig. 1.

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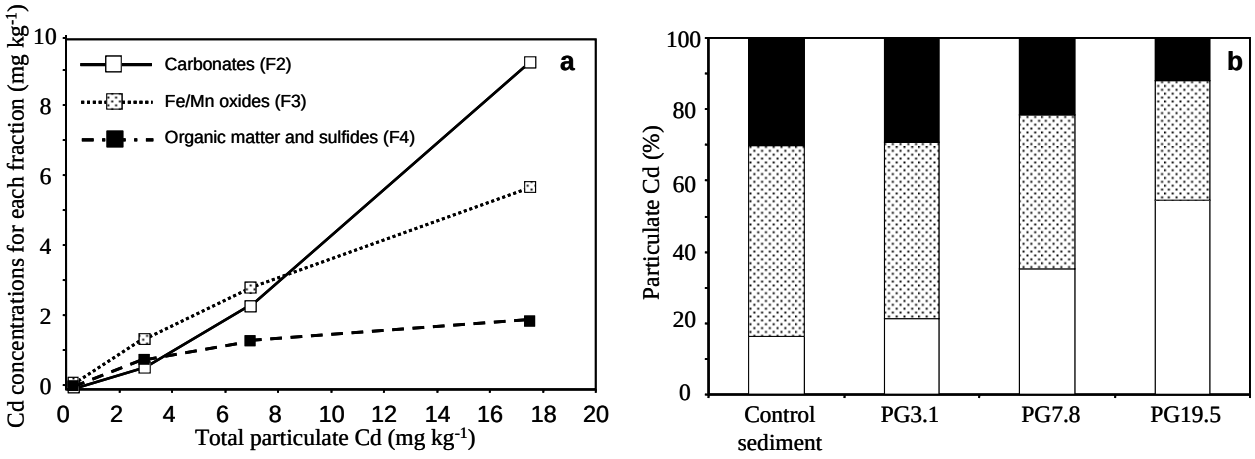

Fig. 2.

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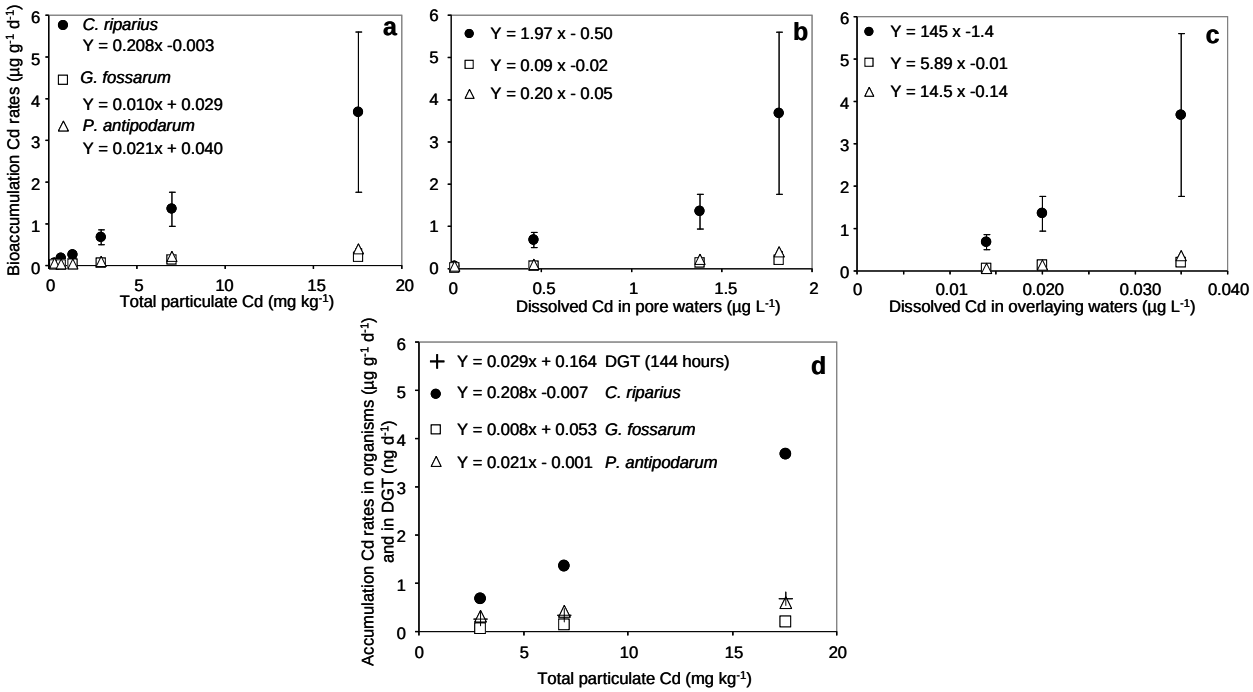

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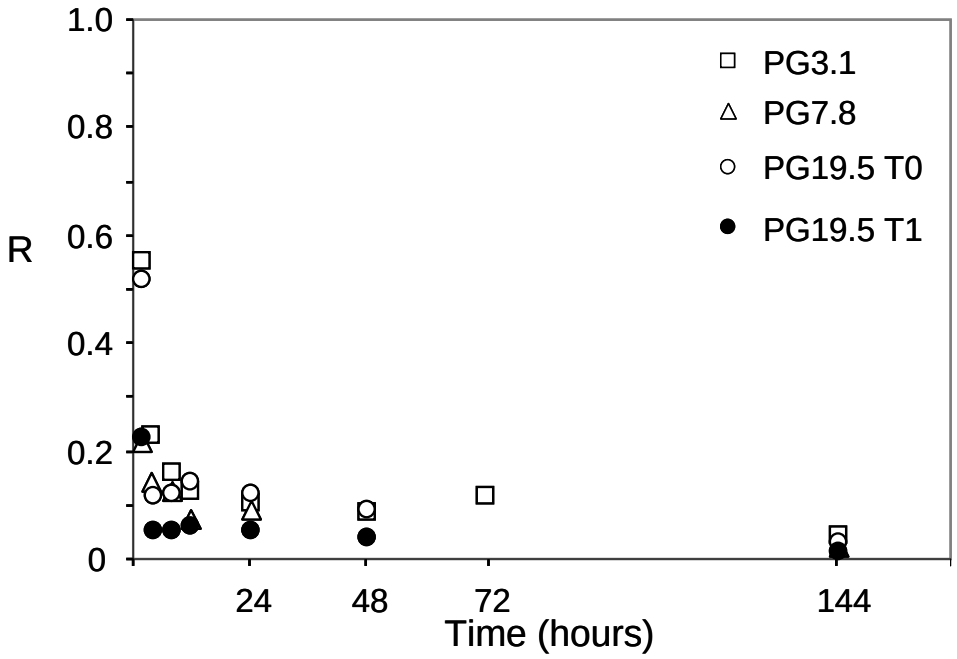

Fig 4:

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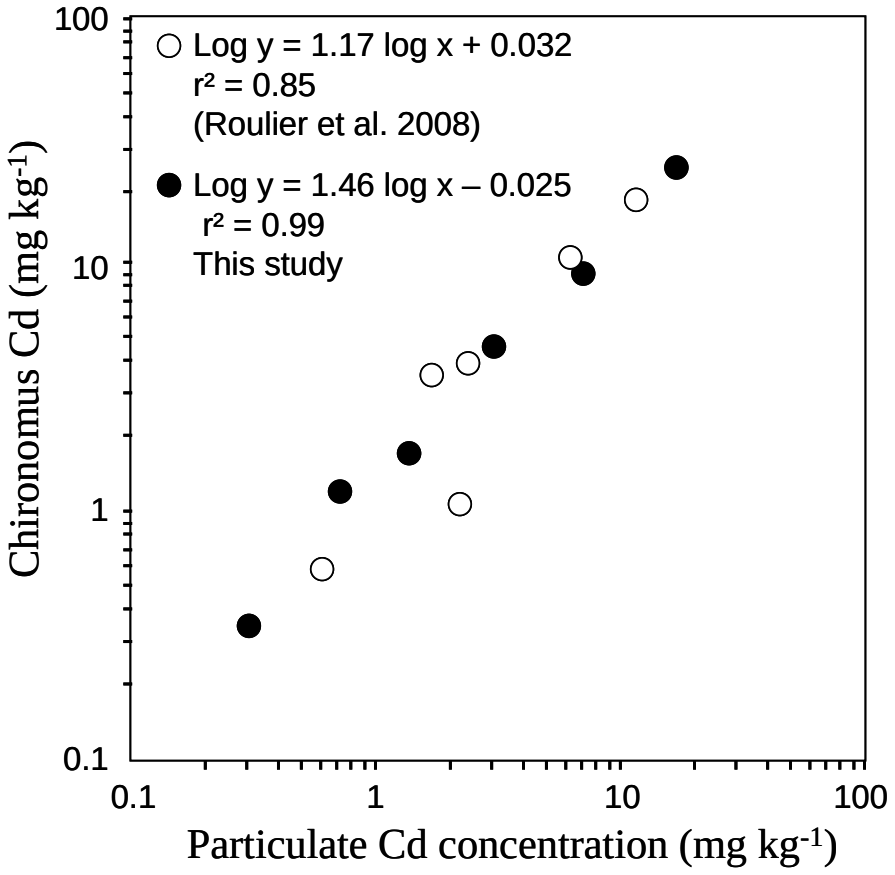

Fig. 5: