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Comparison of dynamic mobilization of Co, Cd and Pb in sediments using DGT and metal mobility assessed by sequential extraction

Jean-Louis Roulier*, Sylvain Belaud, Marina Coquery

Cemagref, UR MALY, 3 bis quai Chauveau – CP220, F-69336 Lyon, France.

* Corresponding author. Tel.: +33 472 20 87 48; fax: +33 478 47 78 75.

E-mail address: jean-louis.roulier@cemagref.fr (J.L. Roulier)

Abstract

Management of metal-contaminated sediments requires an accurate knowledge of metal distribution and metal exchanges between the solid and solution phase. The DGT technique (diffusive gradients in thin films) provides information about the characteristics of metal release from the particles to the porewaters. However, the species of metals that participate in the exchange are not well documented. The aim of this paper was to explore the DGT response of Co, Cd and Pb, to a range of reservoir sediments exhibiting gradients of physico-chemical parameters. We also characterized the chemical partitioning of the 3 metals by sequential extraction to determine the nature of the sediment-bound metals species that could participate to the metal resupply to the porewaters. Results from DGT experiments and sequential extraction show that specific geochemical phases are key factors for the mobilization of individual metals towards DGT: dissolved organic matter and manganese oxides for Co, acid-volatile sulfides for Cd and particulate organic matter for Pb. Moreover,

the masses of metals trapped in DGT are mainly correlated with the concentrations of metals that are easily exchangeable, specifically sorbed or weakly bound to labile organic matter.

Keywords: Sediment; DGT; Metals mobilization; sequential extraction

1. Introduction

Sediments in aquatic ecosystems are often metal-contaminated as a result of natural background or anthropogenic activities. A large quantity of sediments can be trapped in dams and reservoirs and their adequate management requires an accurate prediction of the fate and effects of metals in the aquatic environment (Álvarez-Ayuso et al., 2008; Mariani et al., 2008). The partition of metals between the solid phase and solution, usually described by a distribution coefficient (Kd), does not account for the kinetics of the metal exchange between the solid phase and the porewaters. The DGT technique (diffusive gradients in thin films), made of a diffusive layer backed by a Chelex resin, was initially developed to measure labile metals in surface waters (Davison and Zhang, 1994; Zhang and Davison, 1995). In soils and sediments, the rapid binding of metals to the resin induces a lowering of the concentrations of metals in the porewaters and a subsequent possible resupply of metals from the particles (Zhang et al., 1995). DGT provides information on the characteristics of the metal exchange (Harper et al., 1998; Zhang et al., 2004; Rachou et al., 2007; Roulier et al., 2008). Some researches have focused on the characteristics of the metal species (free ion and labile complexes) measured by DGT in natural waters (Zhang and Davison, 2000; Tusseau-Vuillemin et al., 2003). In sediments, the fraction of particulate metals involved in the resupply of porewaters is not well documented.

The challenge is to assess which sediment phase(s) mainly control the potential lability of the sediment-bound metals to the porewaters and finally towards the DGT. In order to assess metals association with specific geochemical phases, scientists have proposed various methodologies, including chemical extractions of sediment with single extractants or sequential extractions (Tessier et al., 1979; Buyks et al., 2000; Silveira et al., 2006; Rao et al., 2008).

In this paper, we explore the DGT response, for a selection of metals (Co, Cd, Pb), to a range of sediments of various physico-chemical properties collected in a small reservoir. We investigate at the same time if we could determine the nature of the accessible sediment-bound metals to the porewaters, by comparing the DGT measurements with the results of sediment sequential extraction.

2. Material and methods

2.1. Sampling methods and sediments characterization

Freshwater sediments were sampled from a small reservoir supplying drinking water located in the southeast region of France. The uppermost 10 cm of sediments were collected, using a Van Veen grab (Hydrobios, GmbH), at 5 sites located along a transect and at a depth of 5.5, 9.5, 14, 18 and 28 m. Surface water was collected too. All the samples were kept at about 4°C and transported back to the laboratory.

Sediments were thoroughly homogenized mechanically just prior to the onset of the experiments. The silt and clay fraction was determined as the percentage of the sediments passing through a sieve with an opening size of 50 µm. Acid volatile sulfides (AVS) were determined on wet sediments using the procedure developed by Allen et al. (1993). Dissolved

organic carbon (DOC) analysis in porewaters was performed using a TOC analyser (1010, O.I analytical). An aliquot of the sediments was dried at 60°C for 24 h and finely ground before analysis of carbonates and loss on ignition (LOI) to estimate the content of total organic matter. Total extractable metal concentrations in sediments were determined after mineralization with *aqua regia* (HCl/HNO_3 -3/1) in a microwave oven.

We determined metal speciation following a sequential extraction scheme based on the procedure of Buyks et al. (2000) for anoxic, sulphide-rich freshwater sediments. The five fractions and extractants are listed below:

F1: exchangeable (magnesium chloride; pH 7)

F2: bound to carbonates (sodium acetate/acetic acid; pH 5)

F3: bound to Fe/Mn oxides (hydroxylammonium chloride; pH 2)

F4: bound to organic material and sulfides (hydrogen peroxide; pH 2, ammonium acetate)

F5: residual (digestion with *aqua regia*)

In order to avoid evolution of the original speciation, an addition of previously deoxygenated extractants (fractions F1 to F3) to wet sediment was performed in polypropylene centrifuge tubes sealed under nitrogen atmosphere in a glove box. Between each extraction, a solid-liquid separation was performed by centrifugation (10,000 g, 30 min) and the liquid extract was filtered (cellulose acetate filter, 0.45 µm, Whatman) in the glove box before analysis. Duplicate samples were run throughout the procedure.

Metals concentrations in sediments, porewaters samples and solution extracts were determined by ICP-MS (Thermo, X7 series^{II}). Blanks and certified reference materials (CRM) (TM-23.3, lake water, Environment Canada; IAEA-433 marine sediment) were systematically used to control analytical precision and bias. The maximum deviations from certified value is about 10% for all the metals in both CRMs. Instrument quantification limits (LOQ) are 0.010

µg L^{-1} for Cd and 0.10 µg L^{-1} for Co and Pb in solutions. In sediments, LOQ are 0.16 mg kg^{-1} for Cd and 0.33 mg kg^{-1} for Co and Pb.

2.2. DGT preparation

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 sediment. Diffusive gels (0.78 mm thickness) and resin gels were purchased from DGT Research Ltd (Lancaster, UK). The DGT probes were deoxygenated under nitrogen during one day prior to their deployment into the sediments. Three probes were kept for DGT blank determination.

2.3. Experimental protocol and DGT data interpretation

For each homogenised sediment, subsamples were distributed in 12 glass beakers to obtain a 2 cm layer. Surface water from the studied site was then gently poured in the beakers to obtain a 8 cm overlying layer. All the containers were placed in a 80 L aquarium filled with water regulated at 21±0.5°C. After 6 days of equilibration with gentle aeration of the overlying water (without sediment resuspension), the DGT units were quickly inserted 1 cm deep into the sediment. The DGT devices were progressively retrieved at 7 times between 4 and 142 h. One or 2 probes were sampled at each determined time, but 3 probes were retrieved at 24 h. The porewaters were extracted by centrifugation (10,000 g, 30 min) and then filtered (cellulose acetate filter, 0.45 µm, Whatman). The resin gels were eluted with 7 mL of 1 M HNO_3 (Suprapur, Merck) for at least 24 hours at room temperature; then metals

concentrations in the eluates were determined by ICP-MS. The masses of metals trapped in the resin were calculated using these concentrations. The flux of metals from sediment to the DGT device (F_{DGT}) provides information on the ability of the solid phase to resupply the porewaters with dissolved metals. F_{DGT} was calculated as follows:

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

where M is the accumulated mass of a metal (ng) for a resin surface A (cm^2), over the deployment time t (s) (Zhang and Davison, 2000). F_{DGT} was calculated at each time with the mean value of metal masses from replicates.

3. Results

Sediments are non carbonated with circumneutral pH. Pronounced gradients of granulometry and AVS concentrations are observed, while differences are smaller for DOC and LOI concentrations (Table 1). It is possible to classify the 5 studied sediments in 2 groups. Sediments 1 and 2 are relatively coarse and poor in AVS, while sediments 3, 4 and 5 have a higher silt and clay fraction, as well as elevated AVS concentration. The general Pb contamination (267±38 mg kg^{-1}) reflects the impact of former mining activities on the watershed. Significant traces of Co and Cd (10.6±1.2 and 1.6±0.2 mg kg^{-1} respectively) are measured. Metal gradients are low. Results of the sequential extraction are shown in Figure 1. Co is mostly extracted in F5 (> 50%) and F4 (> 23%). Cd and Pb are mostly extracted in fraction 4 (> 63%), showing a possible involvement of CdS and PbS in the sedimentary material, in addition to organic complexation.

3.1. DGT experiments

Metal concentrations in blank DGT devices are lower than LOQ. We studied the resupply fluxes by plotting the relation of F_{DGT} with time. The results of the experiments show that F_{DGT} depend on sediment nature but also on the metal.

Co and Cd concentrations in porewaters are low, respectively 0.59-3.63 µg L^{-1} and 0.17-0.45 µg L^{-1}. F_{DGT} is too low to be detected for Co and Cd during the first day of the experiment. After 24 h, F_{DGT} increases up to 48 or 72 h, showing a fast resupply, followed by a relative stabilization for Co and a decrease for Cd (Fig. 2). Concentrations of dissolved Pb in porewaters are high (30-127 µg L^{-1}). For Pb, F_{DGT} is detected at the beginning of the experiment, as expected, but decreases rapidly thereafter. Apart from sediment 5, an increase of F_{DGT} for this metal up to 48 or 72 h is followed by a stabilization or decrease of the intensity of the flux (Fig. 2). Sediment 5 shows a low resupply flux from particles.

Co and Pb fluxes towards DGTs are about 10 to 20 times higher than that of Cd (Fig. 2). The highest fluxes of Co are measured for fine-grained sediments 3, 4 and 5. Conversely, the highest fluxes of Cd and Pb are noted for sediments 1 and 2, which are coarser and less organic (Fig. 2).

These results are consistent with those of sequential extraction. Indeed, the percentages of the more mobile fractions (F1+F2+F3) of Co are about 20% in sediments 3, 4 and 5 and 9% in sediments 1 and 2 (Fig. 1). Concentrations of Cd and Pb extracted in F1 to F3 are higher in sediments 1 and 2 (respectively about 27 and 16%) than in sediments 3, 4 and 5 (about 15 and 10%). For each metal, linear regression models were constructed to analyse the relationship between the masses trapped by DGT (M_{metal}) at the end of the experiment and the physico-chemical parameters of the sediments (% of grain size < 50 µm, % of LOI, concentrations of AVS and DOC). The correlation coefficients are reported in Table 2. Significant linear

relationships are measured between M_{Co} and the DOC concentrations in porewaters or AVS concentrations ; but relationships between M_{Co} and organic content (LOI) or grain size are not significant. A significative negative relationship is found only between M_{Cd} and AVS concentration in the sediment; but M_{Cd} is poorly related to DOC and especially to LOI. M_{Pb} is highly but negatively related with the clay and silt fraction. A significative negative association is also found between M_{Pb} and LOI content. No significant relationships are found between M_{Pb} and AVS concentration or DOC concentration.

3.2. DGT experiments vs. sequential extraction

The correlation coefficients between the mass of metal trapped by DGT at 142 h and the metal concentration in fraction F1 or sum of fractions (F1 and F2, F1 to F3 or F1 to F4) for the 5 studied sediments are presented in Table 3.

M_{Co} are positively correlated with Co concentrations in F1 ($p < 0.01$). The correlation is lower but still significant with F1+F2 concentrations. Correlations are not improved with the sum of fractions F1 to F3 and F1 to F4, in spite of the fact that F4 accounts for 51 to 82% of the total extract. The positive correlation between M_{Cd} and Cd concentrations in F1+F2 is not significant at $p < 0.05$. A Strong significant correlation is only obtained with the sum of fractions F1 to F3 . Inversely, an absence of correlation is shown with the sum of fractions F1 to F4, in spite of the fact that F4 accounts for 68 to 90% of the total extract. A significant positive correlation between M_{Pb} and Pb concentrations in F1 is shown; but a best correlation is obtained with F1+F2 concentrations. Adding F3 does not improve significantly the observed correlation. As expected, Pb extracted in F4 is not a good predictor of $M_{Pb,}$ although it accounts for 78 to 92% of the total extract.

4. Discussion

4.1. DGT experiments

The fluxes towards DGT depends on metals (Fig. 2). The estimation of the dissolved Co, Cd and Pb masses in porewaters capable to diffuse towards DGT in the first 24 h shows that Co and Cd are present in quantities that cannot be detected by DGT. The labile Pb pool in porewaters is exhausted during the first hours without resupply, resulting in a Pb flux decrease. The observed increase of metal fluxes after an initial period is unusual in measurements made by DGT using various deployment times. However, the possibility of a slow increase of fluxes during the first days was discussed recently by Letho et al. (2008). These authors re-evaluated the data published by Ernstberger et al. (2005) on Cd, Ni, Zn DGT fluxes for several soils. They reported that the time taken to reach a linear concentration gradient in the diffusive gel may be long in organic rich soils. In fact, the time to reach steady state for humic complexes can be on the order of one day as a consequence of small diffusion coefficient or accumulation in the DGT gel, and slow kinetics of metal release from the complexes. In our experiments, total deployment time largely exceeds 24 h. After the first day, the rate of mass accumulation in DGT is constant over time for the 3 metals. This corresponds to a well established gradient in the gel, being attained rapidly (steady state conditions) (Harper et al., 2000). A small percentage of the overall metal masses trapped during 142 h is detected for the 24 h deployment time: < 10-15% for Co and Cd, < 10% (sediment 1 and sediment 2) and about 20% (sediments 3-5) for Pb. Consequently, the great majority of the total metals trapped by DGT should come from sediment-bound metals. We consider that the sustained or increasing metal fluxes could be linked with Mn and Fe oxides reduction. In fact, positive significant relationships between Co or Pb mass accumulation and

Mn mass accumulation are observed for all sediments ($r > 0.959$, $p < 0.01$). This is consistent with the findings of Hamilton-Taylor et al. (1999) showing that Mn oxide dissolution was the source of Co remobilization in a water system. This suggests there may be more reducing conditions at the sediment interface where DGT is deployed. However, the cause is not clear. We propose two alternative explanations: it is possible that the sediment becomes more reducing because of the presence of DGT blocking off oxygen from above, or there could be a low supply of (reactive) organic matter at the surface of DGT, as a consequence of its introduction into the sediment surface layer.

Since Mn oxide dissolution is enhanced in reduced sediments, with higher AVS concentrations, the significant relationship between M_{Mn} and AVS ($r = 0.976$, $p < 0.01$) induces the significant relationship between M_{Co} and AVS (Table 2). The high correlation between M_{Co} and DOC could be explained by the tendency of dissolved Co to be associated with small organic colloids (Pokrovsky et al., 2002).

Cd resupply fluxes (F_{DGT}) are lowest in fine, more organic sediments, with higher AVS concentration. As expected, amorphous sulfides clearly lower Cd mobility towards DGT. No significant correlation is obtained between M_{Cd} and organic matter content of sediment (LOI). However, the poor gradient of LOI (13.7 to 16.6%) leads to a weak power of prediction of this parameter. Similar to our results, Rachou et al. (2007) showed that the flux of Cd to DGT from a sandy and a clayey soils decreased when organic matter was added. In contrast, Ernstberger et al. (2005) reported that the resupply of Cd to DGT from clayey soils, characterized by high pH and/or high organic matter content, was higher than that of sandy soils (low organic matter and pH). These authors suggest that Cd is less adsorbed to the humus in soils with low organic carbon and the Cd flux towards the DGT mainly comes from porewaters. So, mechanisms of resupply from soils are not easy to establish and even are more complex in sediments with AVS. As observed for Cd, the resupply fluxes of Pb in

porewaters decreased with fine sediments, richer in organic matter and AVS. Significant relationships between M_{Pb} and grain size ($p < 0.01$) and LOI ($p < 0.05$) are shown. As there is no significant relationship between M_{Pb} and AVS concentration, F_{DGT} seems to mainly depend on organic matter content, though LOI is a weak predictor of metal trapped.

4.2. DGT experiments vs. sequential extraction

In our study, the distribution of metals among the extracted fractions is different between metals and between sediments. The interpretation of experimental data must be done with caution. The characteristics and limitations of the sediment extraction techniques have been reviewed in several papers (Martin et al., 1987; Bacon and Davison, 2008; Rao et al., 2008). It was shown that the readily exchangeable metals extracted in F1 are non-specifically sorbed metals, weakly bound to organic or inorganic sites. In F2, sodium acetate acidified to pH 5 with acetic acid allows to extract trace metals from carbonates and also promotes the release of more specifically sorbed metals, i.e. bound by covalent forces. Moreover, Rao et al. (2008) reported that 0.5 M acetic acid (half the concentration used in F2) was used to extract Co sorbed onto iron oxhydroxide sites in non calcareous soils. Organic bound metals extracted in F4 are considered to be associated with stable humic substances (Rao et al., 2008). However, some metals bound to less stable organic matter could be partly liberated before this fraction (Bacon and Davison, 2008). In the same way, extraction of sulfide minerals can partly occur in F3 rather than in F4, depending on their degree of crystallization (Wallmann et al., 1993). Therefore, this relative lack of specificity will be taken into account in further interpretation of our experimental data.

Co concentration extracted in F1+F2 is a good predictor of Co trapped in DGT. These species are classified as easily exchangeable and more specifically sorbed, but some other species can

be extracted as well. Cd concentration extracted in F1+F2+ F3 is a good predictor of Cd trapped in DGT. These fractions are assumed to be representative of metals easily exchangeable, specifically sorbed and bound to Fe/Mn oxides, but probably not to AVS. In fact, it was shown in chapter 4.1 that AVS greatly decreases Cd mobility towards DGT. This is consistent with the results of a sequential extraction performed by Wallmann et al. (1993). These authors showed that extraction of CdS in F1 to F3 in Elbe sediments was rather poor. As observed for Co, Pb extracted in F1+F2 is a good predictor of Pb trapped in DGT. Since no carbonates are quantified in the studied sediments, a fraction of Pb extracted in F2 is expected to be specifically sorbed and possibly partly dissolved from organic matter.

The differences in concentrations of Co, Cd and Pb extracted in the first 3 sediment fractions, explain most of the variation in the masses trapped by DGT. In contrast, the concentration of metal extracted in F4 is a poor predictor of metals trapped by DGT. It is not easy to compare our results with those of others studies, because of the scarcity of similar approaches. In urban soils, Young et al. (2006) performed a sequential extraction, derived from Tessier scheme, and isotopic exchange experiments for Zn. They concluded that (radio)labile Zn was well correlated with extractable Zn from F1 to F3 (including exchangeable pool and adsorbed metal). Ernstberger et al. (2002) showed a good agreement between DGT and isotopic exchange measurements for Cd in a contaminated soil. Since isotopic exchange method allows to measure labile pool, including metals from exchangeable sites and chemisorbed metals, these results confirm that metals weakly bound to sediment are available for DGT.

5. Conclusion

It is recognised that metals mobilization from sediments is related to metal partitioning, which depends on sediment characteristics. We explored the DGT response to 5 sediments more or

less equally contaminated but with gradients of physico-chemical parameters (grain size, AVS and DOC concentrations). We found that the fluxes of Co, Cd and Pb measured by DGT after 24 h result essentially from the release of metals bound to sediment phase. These fluxes are related to sediment characteristics and linked to specific metal associations with sediment geochemical phases. Consequently, DGT is a sensitive tool, able to account for the differences between metals behavior and sediment characteristics. The sequential chemical extraction has improved our knowledge on the metallic species trapped by DGT. Our results show that the concentrations of Co and Pb extracted in F1+F2 and concentration of Cd extracted in F2+F3 are the best predictors of the masses of the metals trapped by DGT. These results suggest that metals classified as easily exchangeable, specifically sorbed or weakly bound to labile organic matter in sediments could participate to the flux of resupply to the porewaters. These metal species, which we can define as “mobile pool”, are weakly bound to sediment, labile and chemically available for DGT.

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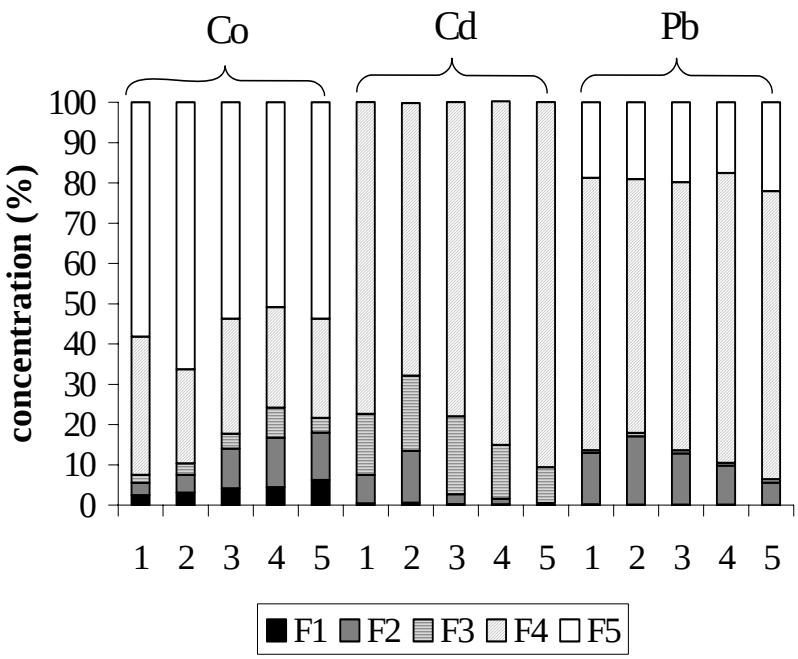
Fig. 1 : Distribution of Co, Cd, Pb concentrations in the 5 studied sediments (1 to 5) as obtained by sequential extraction: F1: exchangeable, F2: bound to carbonates, F3: bound to Fe/Mn oxides, F4: bound to organic matter and sulfides, F5: residual.

Fig. 2 : Flux of Cd, Co and Pb resupply from the solid phase (F_{DGT}) for the 5 studied sediments.

Table 1 : Physico-chemical characteristics of the sediments and porewaters

Table 2 : Correlation coefficient (r) between the mass of metals trapped by DGT and the percentage of grain size < 50 µm, and the concentration of DOC, LOI, AVS

Table 3: Correlation coefficients (r) between the mass of metal trapped by DGT and the metal concentration in fraction F1 or sum of fractions (F1 to F2, F1 to F3 or F1 to F4) from the sequential extraction.



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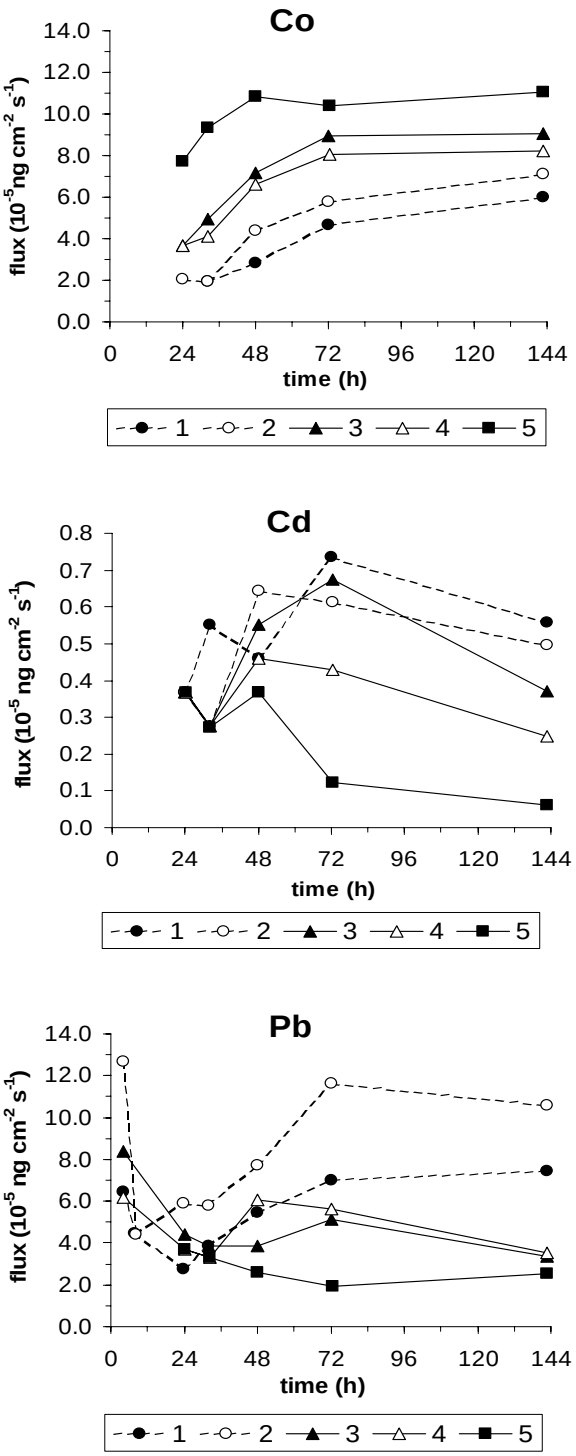

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Table 1 : Physico-chemical characteristics of the sediments and porewaters

sed.	depth (m)	Grain size < 50 µm (%)	$CaCO_3$ (%)	LOI (%)	AVS (µM g^{-1})	DOC (mg L^{-1})	Co (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})
1	-5.5	54.5	<1	13.7	1.9	16.5	9.5	1.8	240
2	-9.5	31.7	<1	13.9	2.4	22.4	9.7	1.4	298
3	-14	89.6	<1	16.6	4.4	30.7	10.8	1.6	317
4	-18	78.4	<1	16.1	4.8	26.3	10.5	1.7	240
5	-28	96.9	<1	15.8	7.6	33.7	12.5	1.5	239

LOI: loss on ignition; AVS: acid volatile sulfides; DOC: dissolved organic matter

Table 2 : Correlation coefficient (r) between the mass of metals trapped by DGT and the percentage of grain size < 50 µm, and the concentration of DOC, LOI, AVS

	Grain size (< 50 µm)	LOI	AVS	DOC
Co	0.818	0.746	0.969**	0.971**
Cd	- 0.795	- 0.695	- 0.986**	- 0.859
Pb	- 0.987**	- 0.883*	- 0.815	- 0.754

* and **: significant at 5% and 1%, respectively

Table 3: Correlation coefficients (r) between the mass of metal trapped by DGT and the metal concentration in fraction F1 or sum of fractions (F1 to F2, F1 to F3 or F1 to F4) from the sequential extraction.

	F1	F1-F2	F1-F3	F1-F4
Co	0.972**	0.879*	0.800	0.665
Cd	nd	0.877	0.983**	0.074
Pb	0.903*	0.958**	0.959**	0.590

* and **: significant at 5% and 1%, respectively

nd: not determined (value of F1 concentration < LOQ)