

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

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9
10 Abstract

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

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

26

27 *Keywords:* Sediment; DGT; Metals mobilization; sequential extraction

28

29 1. Introduction

30

31 Sediments in aquatic ecosystems are often metal-contaminated as a result of natural
32 background or anthropogenic activities. A large quantity of sediments can be trapped in dams
33 and reservoirs and their adequate management requires an accurate prediction of the fate and
34 effects of metals in the aquatic environment (Álvarez-Ayuso et al., 2008; Mariani et al.,
35 2008). The partition of metals between the solid phase and solution, usually described by a
36 distribution coefficient (K_d), does not account for the kinetics of the metal exchange between
37 the solid phase and the porewaters. The DGT technique (diffusive gradients in thin films),
38 made of a diffusive layer backed by a Chelex resin, was initially developed to measure labile
39 metals in surface waters (Davison and Zhang, 1994; Zhang and Davison, 1995). In soils and
40 sediments, the rapid binding of metals to the resin induces a lowering of the concentrations of
41 metals in the porewaters and a subsequent possible resupply of metals from the particles
42 (Zhang et al., 1995). DGT provides information on the characteristics of the metal exchange
43 (Harper et al., 1998; Zhang et al., 2004; Rachou et al., 2007; Roulier et al., 2008). Some
44 researches have focused on the characteristics of the metal species (free ion and labile
45 complexes) measured by DGT in natural waters (Zhang and Davison, 2000; Tusseau-
46 Vuillemin et al., 2003). In sediments, the fraction of particulate metals involved in the
47 resupply of porewaters is not well documented.

48 The challenge is to assess which sediment phase(s) mainly control the potential lability of the
49 sediment-bound metals to the porewaters and finally towards the DGT. In order to assess
50 metals association with specific geochemical phases, scientists have proposed various
51 methodologies, including chemical extractions of sediment with single extractants or
52 sequential extractions (Tessier et al., 1979; Buyks et al., 2000; Silveira et al., 2006; Rao et al.,
53 2008).

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

60 2. Material and methods

62 2.1. Sampling methods and sediments characterization

64 Freshwater sediments were sampled from a small reservoir supplying drinking water located
65 in the southeast region of France. The uppermost 10 cm of sediments were collected, using a
66 Van Veen grab (Hydrobios, GmbH), at 5 sites located along a transect and at a depth of 5.5,
67 9.5, 14, 18 and 28 m. Surface water was collected too. All the samples were kept at about 4°C
68 and transported back to the laboratory.

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

73 organic carbon (DOC) analysis in porewaters was performed using a TOC analyser (1010, O.I
74 analytical). An aliquot of the sediments was dried at 60°C for 24 h and finely ground before
75 analysis of carbonates and loss on ignition (LOI) to estimate the content of total organic
76 matter. Total extractable metal concentrations in sediments were determined after
77 mineralization with *aqua regia* (HCl/HNO₃ -3/1) in a microwave oven.

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

81 F1: exchangeable (magnesium chloride; pH 7)

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

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

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

85 F5: residual (digestion with *aqua regia*)

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

91 Duplicate samples were run throughout the procedure.

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

97 $\mu\text{g L}^{-1}$ for Cd and $0.10 \mu\text{g L}^{-1}$ for Co and Pb in solutions. In sediments, LOQ are 0.16 mg kg^{-1}
98 for Cd and 0.33 mg kg^{-1} for Co and Pb.

99

100 2.2. DGT preparation

101

102 The DGT probe consists of a plastic piston loaded with a diffusive gel layer backed by an ion-
103 exchange resin gel (Chelex 100) and a plastic cap with a 2 cm diameter window. A protective
104 $0.45 \mu\text{m}$ cellulose nitrate filter (0.13 mm thickness, Millipore) separates the diffusive gel from
105 the sediment. Diffusive gels (0.78 mm thickness) and resin gels were purchased from DGT
106 Research Ltd (Lancaster, UK). The DGT probes were deoxygenated under nitrogen during
107 one day prior to their deployment into the sediments. Three probes were kept for DGT blank
108 determination.

109

110 2.3. Experimental protocol and DGT data interpretation

111

112 For each homogenised sediment, subsamples were distributed in 12 glass beakers to obtain a
113 2 cm layer. Surface water from the studied site was then gently poured in the beakers to
114 obtain a 8 cm overlying layer. All the containers were placed in a 80 L aquarium filled with
115 water regulated at $21 \pm 0.5^\circ\text{C}$. After 6 days of equilibration with gentle aeration of the
116 overlying water (without sediment resuspension), the DGT units were quickly inserted 1 cm
117 deep into the sediment. The DGT devices were progressively retrieved at 7 times between 4
118 and 142 h. One or 2 probes were sampled at each determined time, but 3 probes were
119 retrieved at 24 h. The porewaters were extracted by centrifugation (10,000 g, 30 min) and
120 then filtered (cellulose acetate filter, $0.45 \mu\text{m}$, Whatman). The resin gels were eluted with 7
121 mL of 1 M HNO_3 (Suprapur, Merck) for at least 24 hours at room temperature; then metals

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

126

$$127 \quad F_{DGT} = \frac{M}{(A \times t)} \quad (1)$$

128

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

132

133 3. Results

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

146

147 3.1. DGT experiments

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

152 Co and Cd concentrations in porewaters are low, respectively 0.59-3.63 $\mu\text{g L}^{-1}$ and 0.17-0.45
153 $\mu\text{g L}^{-1}$. F_{DGT} is too low to be detected for Co and Cd during the first day of the experiment.

154 After 24 h, F_{DGT} increases up to 48 or 72 h, showing a fast resupply, followed by a relative
155 stabilization for Co and a decrease for Cd (Fig. 2). Concentrations of dissolved Pb in
156 porewaters are high (30-127 $\mu\text{g L}^{-1}$). For Pb, F_{DGT} is detected at the beginning of the experiment,
157 as expected, but decreases rapidly thereafter. Apart from sediment 5, an increase of F_{DGT} for
158 this metal up to 48 or 72 h is followed by a stabilization or decrease of the intensity of the flux
159 (Fig. 2). Sediment 5 shows a low resupply flux from particles.

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

164 These results are consistent with those of sequential extraction. Indeed, the percentages of the
165 more mobile fractions ($F_1+F_2+F_3$) of Co are about 20% in sediments 3, 4 and 5 and 9% in
166 sediments 1 and 2 (Fig. 1). Concentrations of Cd and Pb extracted in F_1 to F_3 are higher in
167 sediments 1 and 2 (respectively about 27 and 16%) than in sediments 3, 4 and 5 (about 15 and
168 10%). For each metal, linear regression models were constructed to analyse the relationship
169 between the masses trapped by DGT (M_{metal}) at the end of the experiment and the physico-
170 chemical parameters of the sediments (% of grain size $< 50 \mu\text{m}$, % of LOI, concentrations of
171 AVS and DOC). The correlation coefficients are reported in Table 2. Significant linear

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

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180 3.2. DGT experiments vs. sequential extraction

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

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

196

197 4. Discussion

198

199 4.1. DGT experiments

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

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

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

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

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

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252 4.2. DGT experiments vs. sequential extraction

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

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

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

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

292

293 5. Conclusion

294

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

297 less equally contaminated but with gradients of physico-chemical parameters (grain size, AVS
298 and DOC concentrations). We found that the fluxes of Co, Cd and Pb measured by DGT after
299 24 h result essentially from the release of metals bound to sediment phase. These fluxes are
300 related to sediment characteristics and linked to specific metal associations with sediment
301 geochemical phases. Consequently, DGT is a sensitive tool, able to account for the
302 differences between metals behavior and sediment characteristics. The sequential chemical
303 extraction has improved our knowledge on the metallic species trapped by DGT. Our results
304 show that the concentrations of Co and Pb extracted in F1+F2 and concentration of Cd
305 extracted in F2+F3 are the best predictors of the masses of the metals trapped by DGT. These
306 results suggest that metals classified as easily exchangeable, specifically sorbed or weakly
307 bound to labile organic matter in sediments could participate to the flux of resupply to the
308 porewaters. These metal species, which we can define as “mobile pool”, are weakly bound to
309 sediment, labile and chemically available for DGT.

310

311 Acknowledgment

312

313 The authors are grateful for the financial support by the French Agence Nationale de la
314 Recherche (DIESE program “outils de Diagnostic de l’Ecotoxicité des SEDiments”, projet
315 ANR-07-ECOT-0794C0111). We would like to thank B. Motte and J. Gahou (Cemagref) for
316 technical assistance.

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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.

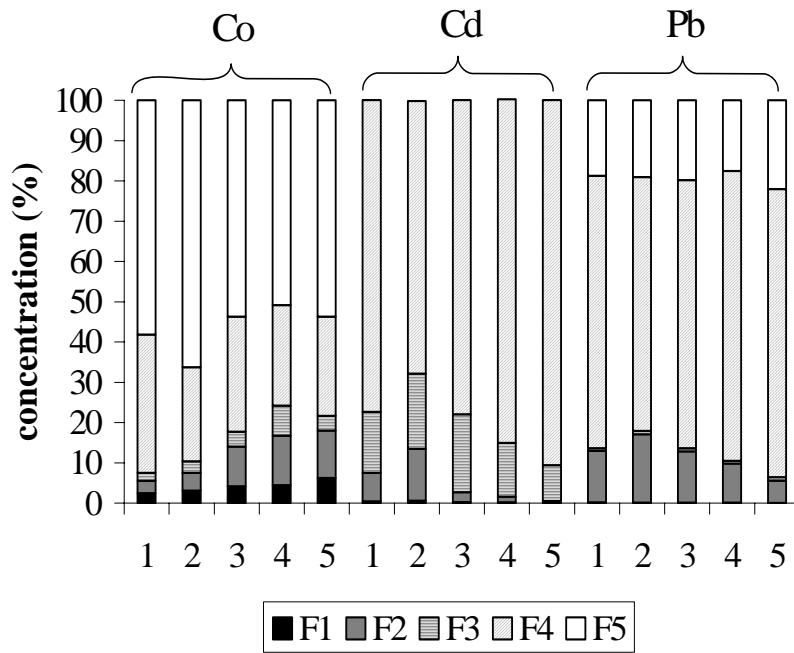
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Table 1 : Physico-chemical characteristics of the sediments and porewaters

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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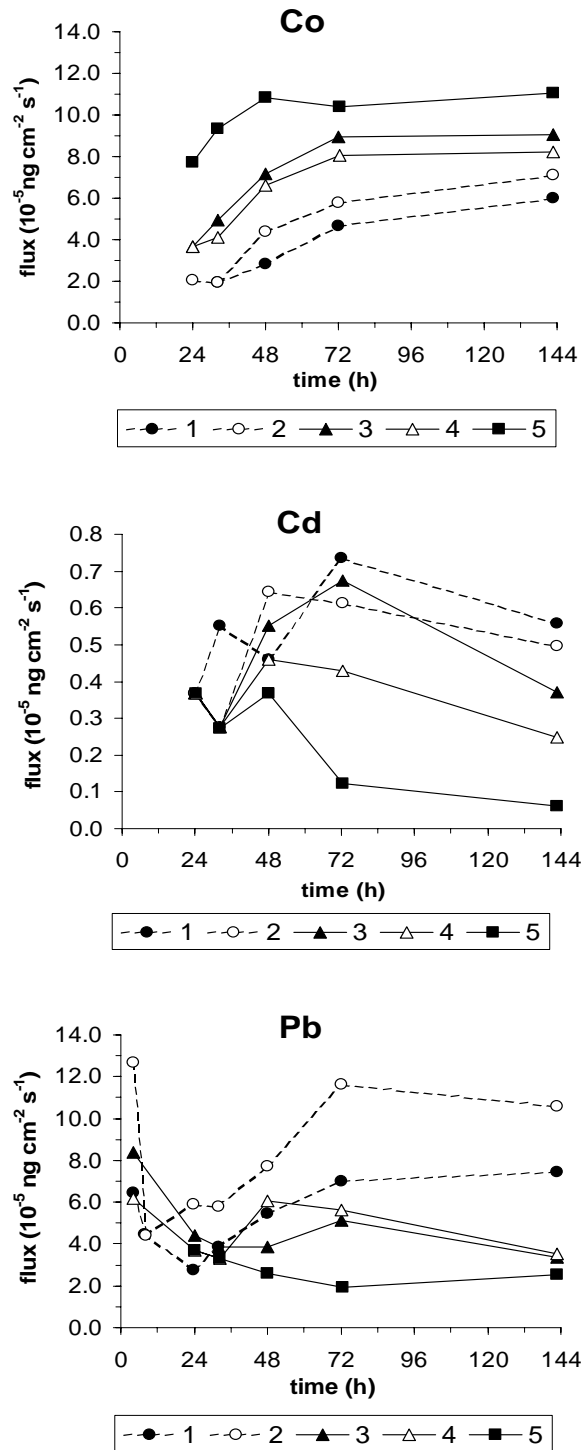


Fig. 2 : Flux of Cd, Co and Pb resupply from the solid phase (F_{DGT}) for the 5 studied sediments.

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

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sed.	depth (m)	Grain size < 50 μm (%)	CaCO ₃ (%)	LOI (%)	AVS ($\mu\text{M g}^{-1}$)	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

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

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531 Table 2 : Correlation coefficient (r) between the mass of metals trapped by DGT and the

532 percentage of grain size < 50 μm , and the concentration of DOC, LOI, AVS

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	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

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

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

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	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

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

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

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