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Juliette Rougerie, Rachel Martins de Barros, Rémy Buzier, Delphine Devillers, Patrice Fondanèche, Sophie Lissalde, Julie Leblanc, Margaux Saüt, Jean-Pierre Rebillard, Nicolas Mazzella, et al.

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# 1 Diffusive gradients in thin films (DGT): a suitable tool for metals/metalloids 2 monitoring in continental waterbodies at the large network scale

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40

41 **Abstract**

42 The contribution of Diffusive Gradients in Thin films (DGT) passive sampling to continental water  
43 quality monitoring was assessed in a real measurement network (6 sampling campaigns, 17 stations).  
44 Ten metals/metalloids (Al, Zn, Ni, Cd, Cu, Pb, Cr, As, Se and Sb) were studied using the control  
45 laboratory's working conditions with grab and DGT passive sampling. The DGT field deployments were  
46 robust, with a 3% sampler loss rate and a < 65% average relative deviation between duplicates.  
47 Compared to grab sampling, DGT showed a similar quantification frequency for half of the targeted  
48 elements but showed a higher frequency for the other half (*e.g.*, Cd quantification at 20% with grab  
49 sampling vs. 97% with DGT). Similar concentration trends were established using DGT and grab  
50 sampling at most sites throughout the year. Notably, for some elements, trends were only provided  
51 by DGT sampling. A study of several DGT blanks showed that the device contamination was occasional  
52 and originated primarily from cross-contamination during the disassembly step. Considering this  
53 contamination, the operational sensitivity by DGT was at least between 1 and 5 times greater in  
54 comparison to that by grab sampling.

55 Estimations of the economic cost revealed that measurement networks cost 2 to 3 times more when  
56 monitored by DGT compared to standard grab monitoring. However, the information obtained based  
57 on each type of sampling method is different. Grab sampling is easy to implement and can highlight  
58 high contamination peaks. The DGT concentrations are averaged over time and are relevant to chronic  
59 exposure evaluations. Considering the good performance of the DGT sampling highlighted in this study  
60 and its complementarity with grab sampling in terms of water quality assessments, a combination of  
61 these two types of sampling, which can be affordable, should improve the water quality evaluation  
62 within monitoring networks.

63 **Keywords:** water quality network; passive sampling; metals; metalloids; field sampling

64

## 65 **1. INTRODUCTION**

66 Continental waters can be contaminated with metals/metalloids from the geochemical background  
67 and/or industrial and agricultural activities (Chon et al., 2010; Udeigwe et al., 2011). To assess this  
68 contamination, and consequently organisms' exposure and toxicological risk, measurement networks  
69 are established. They are required at the European level by the Water Framework Directive (WFD  
70 2000/60/CE) to define the contamination status of watercourses, but also at the national or local level  
71 within rehabilitation action programmes to monitor the water quality for its improvement.. Currently,  
72 these water quality controls are mostly performed by grab sampling of the dissolved fraction, typically  
73 4 to 12 times per year. This sampling technique is easy to implement, is quick and can sometimes  
74 detect concentration peaks. However, it provides an instantaneous measurement of target elements  
75 concentrations, which can lead to very weak temporal representativeness of an organism's exposure  
76 within the environment (Allan et al. 2006).

77 To overcome this partial vision of the water quality, passive sampling is a promising technique. Its  
78 development is supported at the European level (Directive 2013/39/UE: 'Novel monitoring methods  
79 such as passive sampling and other tools show promise for future application, and their development  
80 should therefore be pursued'). Standard methods are developed for ten years with guidance lines  
81 given at the international level (NF EN ISO 5667-23, 2011) but also at the national level (*e.g.* French  
82 standard method NF FD T 90-012, 2020). For metals/metalloids, the use of DGT passive samplers is  
83 recommended in various documents as a monitoring tool to complement the information obtained by  
84 grab sampling (Allan et al. 2008; Hanke et al. 2009). The DGT, which has been under development since  
85 1994 (Davison and Zhang, 1994; Zhang and Davison, 2015; Menegário et al., 2017), has many  
86 recognized advantages in the literature:

- 87 1) Determination of a time-weighted average concentration, ensuring better temporal  
88 representativeness of the contamination;
- 89 2) Accumulation of the target element in the device, increasing analytical sensitivity;

90 3) In situ speciation/fractionation leading to DGT-labile fraction measurement, considered as a  
91 more biologically relevant fraction than the dissolved fraction.

92 Given the advantages of DGT sampling, several studies have addressed its contribution to  
93 metals/metalloids contamination monitoring in aquatic environments. An inter-laboratory comparison  
94 exercise (24 laboratories) was performed *in situ* in surface waters by Miège et al. (2012). They showed  
95 a RSD below 100% for the eight metals targeted (Cd, Ni, Pb, Zn, Cu, Mn, Co, Cr) which they considered  
96 as correct despite the disparity in the studied concentration levels and in the exposure and analysis  
97 procedures. Bretier et al., (2019) showed that DGT is a robust and powerful time-integrative tool for  
98 monitoring numerous trace elements in the Upper Rhône River (France). Moreover, Priadi et al. (2011)  
99 have shown that seasonal fluctuations in several trace element (Cd, Cr, Cu, Pb, Co, Mn, Ni and Zn)  
100 concentrations in the Seine river (France) can be integrated by DGT.

101 Considering the potential benefits of this tool and its recommendation by the various texts mentioned  
102 above, the study of its applicability for monitoring networks is relevant. However, current studies on  
103 the measurement of several metals/metalloids are generally limited to 2 or 3 different sites (Bretier et  
104 al., 2019) or to a single measurement campaign (Roig et al., 2011; Montero et al., 2012; Dabrin et al.,  
105 2016). Considering the sensitivity of DGT response to several environmental factors and device  
106 contamination (Buzier et al., 2014), its performance when used at a larger scale (*i.e.* monitoring  
107 networks) can be in question. Indeed, Montero et al. (2012) found 8 to 28% of 'anomalous' replicates  
108 in the 13 estuaries studied due to device contamination or to concentrations under the limits of  
109 quantification (LOQ).

110 The purposes of this work are to i) assess the DGT sampling performance when deployed in large  
111 monitoring networks (*i.e.* 10+ sites) ii) compare the contributions and cost of DGT sampling to those  
112 of traditional grab sampling and iii) discuss the merits and current limits of DGT use in the framework  
113 of monitoring networks. To address these needs, 17 stations within a continental water measurement  
114 network (SW France) were studied during 6 sampling campaigns in 2016 under routine conditions (see

115 general procedures below). The 17 stations have varying upstream watersheds in terms of size and  
116 context (natural or anthropogenic). Ten metals/metalloids (Al, Zn, Ni, Cd, Cu, Pb, Cr, As, Se and Sb)  
117 with variable environmental properties and concentrations were selected and monitored by both grab  
118 sampling and DGT passive sampling (with a Chelex or zirconium oxide binding phase).

## 119 **2. MATERIALS AND METHODS**

### 120 **2.1. GENERAL PROCEDURES**

121 The manipulations (vessels and gels preparation, DGT assembling and disassembling, gels elution,  
122 sample preparation) were performed under the standard conditions used for any analysis laboratory  
123 that performs regular quality monitoring of water bodies (*i.e.* non-expert in passive sampling). Good  
124 laboratory practices were applied to limit the risks of contamination (all reusable materials were  
125 washed using 10% (V/V) HNO<sub>3</sub> bath for 24h, handling with clean gloves, etc.), but no work was  
126 performed in a clean room. The solutions were prepared using ultrapure water (Milli Q, resistivity >  
127 18.2 MΩ.cm) and all the reagents used here were of analytical grade (purity > 95%). Nitric acid for  
128 ultra-trace (Optima® grade from Fisher scientific) was used for samples acidification and gels elution.

### 129 **2.2. TARGETED AREA AND METALS/METALLOIDS**

130 For this study, 17 monitoring network stations on the Adour-Garonne watershed (area of  
131 approximately 40,000 km<sup>2</sup>) in the south-western part of France were selected (Figure S1). They were  
132 chosen to display a wide range of rivers in terms of size, geology, or anthropogenic pressures  
133 (agricultural, industrial, and treated or untreated wastewater discharge, among others) (Table S1).  
134 Ten metals/metalloids were investigated, with 7 cations (Al, Zn, Ni, Cd, Cu, Pb, and Cr), including two  
135 trivalent elements (Al and Cr), and 3 anions (As, Se, and Sb), allowing to study a range of possible  
136 chemical behaviours and environmental concentrations. Most of these elements are commonly  
137 studied by French water agencies and include three priority substances of the WFD (Cd, Ni and Pb).

138 **2.3. DGT PREPARATION**

139 Two types of binding phases were used, with Chelex-100® (Na-form, 200-400 mesh, Sigma-Aldrich) for  
140 cations (Al, Zn, Ni, Cd, Cu, Pb, Cr) and zirconium oxide for anions (As, Se, Sb). The Chelex binding gels  
141 were prepared according to the procedure given by Zhang and Davison (1995) and the zirconium oxide  
142 ones according to the protocol used by Devillers et al. (2016). Polyacrylamide diffusive gels were  
143 prepared as described by Zhang et al. (1998), which had a thickness of 0.077 cm. The DGT devices were  
144 assembled using plastic holders (purchased from DGT Research Ltd.) enclosing a Chelex or a zirconium  
145 oxide binding gel, a polyacrylamide diffusive gel and a cellulose nitrate membrane (0.4 µm pore  
146 diameter, 0.012 cm thickness). In accordance with the binding gel used here, the DGTs are named DGT-  
147 Ch (Chelex binding phase) or DGT-Zr (zirconium oxide binding phase). Considering that Ernstberger et  
148 al. (2002) showed DGT-Ch selectively samples Cr(III) over Cr(VI), any further results on chromium  
149 presented here will concern Cr(III) only.

150 **2.4. FIELD STRATEGIES FOR THE TWO DIFFERENT SAMPLING METHODS**

151 The ten metals/metalloids were monitored in 2016 through 6 DGT passive sampling and 12 grab  
152 sampling (at each DGT deployment and removal day) spread over the year: March, May, June, July,  
153 September, and November 2016 (Table S2).

154 **DGT passive sampling:**

155 Duplicates of DGT-Ch and DGT-Zr were simultaneously exposed over 14 days at each sampling site for  
156 each campaign . Two sets of 204 DGTs (DGT-Ch and DGT-Zr) were deployed in rivers by two methods,  
157 depending on the water level, by hanging them on a picket (Figure S2a) or fixing them on a concrete  
158 slab that was laid at the bottom of the river (Figure S2b). To avoid any issue related to the formation  
159 of a significant diffusive boundary layer (DBL), the DGTs were deployed in rivers with a minimum water  
160 flow speed of 2 cm s<sup>-1</sup> (Gimpel et al., 2001) except one. Current was checked at each DGT deployment  
161 and removal day using a current meter (Cometec Flow-mate 2000). Temperature loggers (Tynitag)  
162 were also deployed to record the water temperature every 10 min during the 14 days of DGT exposure.

163 Moreover, chemical parameters (pH, conductivity, oxygenation, suspended matter, dissolved organic  
164 carbon) were measured at each DGT deployment and removal day (Table S1). After the exposure, the  
165 DGTs were brought back to the laboratory in an ice box and stored at 4 °C. No obvious biofilm was  
166 observed on DGT exposure windows in most cases. Within 48 h, the DGTs were dismantled for binding  
167 gel recovery. The Chelex or zirconium oxide binding gels were immediately eluted for 24 h with 2 mL  
168 of 1 mol L<sup>-1</sup> HNO<sub>3</sub> or 2 mL of 0.05 mol L<sup>-1</sup> NaOH/H<sub>2</sub>O<sub>2</sub>, respectively. The eluates were stored at 4 °C until  
169 analysis.

170

#### 171 **Grab sampling:**

172 Grab samples were taken by immersion of polyethylene bottles at each DGT deployment and removal  
173 day. To quantify the dissolved fraction of metal/metalloids, 20 mL were immediately filtered *in situ*  
174 with a syringe filter in cellulose acetate (pore diameter 0.45 μm) and then acidified with 2% (V/V)  
175 HNO<sub>3</sub>. The samples were brought back to the laboratory in an ice box and then stored at 4 °C until  
176 analysis.

## 177 **2.5. SAMPLE ANALYSIS AND LIMITS OF QUANTIFICATION**

### 178 **Calculation of C<sub>DGT</sub>:**

179 The metals/metalloids accumulated by the binding gel were determined by eluate analysis with an  
180 elution factor. The elution factors used for the Chelex and zirconium binding gels are indicated in Table  
181 S3. The time-weighted average concentration of the DGT-labile element, C<sub>DGT</sub>, was determined using  
182 equation 1 (Davison and Zhang, 1994).

$$183 \quad C_{DGT} = \frac{m \Delta g}{DA t} \quad \text{Equation 1}$$

184 where m is the mass of the metal/metalloid in the binding gel (μg), Δg is the thickness of the material  
185 diffusion layer (diffusive gel + membrane; 8.9.10<sup>-2</sup> cm), A is the exposure area (3.14 cm<sup>2</sup>) and t is the  
186 exposure time (s). The values of D at 25 °C (in cm<sup>2</sup> s<sup>-1</sup>) used in this study are listed in Table S3. They  
187 were corrected according to the average temperature of the river during the exposure time using the

188 Stokes-Einstein relationship (the water viscosity was taken from the NIST chemistry WebBook).  
189 Relative deviation of duplicates was calculated as the ratio between the absolute difference of  
190 duplicate and their mean value.

191

## 192 **Analysis by ICP-MS, quality control and limits of quantification:**

193 All the samples were adjusted to 2% (V/V) HNO<sub>3</sub> by dilution or spiking before the analysis by ICP-MS  
194 (Agilent 7700X). The following internal standards were used: <sup>209</sup>Bi, <sup>118</sup>Sn, <sup>115</sup>In, and <sup>45</sup>Sc. The SLRS-5  
195 river water standard from the National Research Council Canada was analysed at the beginning and  
196 the end of each analysis sequence to ensure accuracy. Deviations below 15% were obtained for all  
197 quantifiable elements except Pb (< 40%) and Ni (< 55%). The limits of quantification were determined  
198 at each campaign according to the IUPAC recommendations (IUPAC Compendium on Analytical  
199 Nomenclature, online version available at  
200 [https://media.iupac.org/publications/analytical\\_compendium/](https://media.iupac.org/publications/analytical_compendium/)) using the mean + 10 standard  
201 deviations (SD) of the blanks (2% acidified ultrapure water). A LOQ<sub>DGT</sub> for each element was  
202 determined from the LOQ and by using eq. 1, considering the average exposure time of the DGTs (*i.e.*,  
203 14 days) and the diffusion coefficient when corrected to the average temperature of the 6 sampling  
204 campaigns. The mean values are displayed in Table S4.

## 205 **2.6. DGT BLANKS**

206 The DGT blanks were used to control the different steps related to the use of the DGT samplers,  
207 *i.e.*, manufacturing, transport and storage, assembly/disassembly, and analysis. Different types of  
208 blanks (Figure S3) were prepared in triplicate for each type of binding gel (Chelex and zirconium oxide)  
209 and for each deployment campaign. A total of 108 DGT blanks were prepared and distributed as  
210 follows:

- 211 - Thirty-six blanks related to manufacturing: 3 Chelex and 3 zirconium oxide binding gels for the  
212 batch intended for each field campaign were taken. They were individually packaged in a 5 mL

213 polypropylene tube immediately after their production and were kept in the refrigerator until their  
214 elution and analysis with the corresponding field campaign.

215 - Thirty-six blanks (18 DGT-Ch and 18 DGT-Zr) related to the assembly/disassembly steps (including  
216 cross-contaminations): at each campaign, 3 DGT-Ch and 3 DGT-Zr that were already assembled  
217 were taken from a series intended for field deployment. They were stored separately at 4 °C  
218 according to their binding gel type during the field exposure period of the corresponding series.  
219 These blanks were then dismantled with the corresponding field campaign in a random position  
220 among the field DGTs to consider potential cross-contaminations.

221 - Thirty-six blanks (18 DGT-Ch and 18 DGT-Zr) related to transport and storage steps (called 'field  
222 blanks'): at each campaign, 3 DGT-Ch and 3 DGT-Zr conditioned for field deployment were taken  
223 on the deployment day and were exposed to the open air at one of the measurement sites but not  
224 deployed in the river. They were then brought back to the laboratory and stored in the refrigerator  
225 for the rest of the field exposure period (14 days). They were dismantled in the laboratory with all  
226 the DGTs from the campaign at a random position during the series.

227 The metal/metalloid concentrations measured in the different blanks were used to determine a  
228 contamination enrichment factor (CEF) during a specific step of the DGT use. Each one is defined as  
229 the ratio of contamination from one step to the previous step (Figure S3).

## 230 **2.7. ECONOMIC STUDY**

231 To assess the measurement costs of the ten metals/metalloids studied by grab sampling or DGT passive  
232 sampling, the following financial simulations were performed:

- 233 - A three-station measurement network requiring 50 km of travel during 1 working day;
- 234 - A ten-station measurement network (large scale) requiring 800 km of travel during 2 working  
235 days.

236 It was considered for each network one grab sampling or one 2-weeks DGT sampling (2 DGT-Ch and 2  
237 DGT-Zr per site) every two months (6 sampling campaigns). The costs were grouped into 4 categories:

- 238 - Materials: devices, sampling equipment;
- 239 - Field operations: installation/removal of equipment, travel, catering, and overnight stays;
- 240 - Analysis: treatment of DGT samples, analysis, ICP-MS depreciation;
- 241 - Data processing: quality control,  $C_{DGT}$  calculation, result analysis.

242 Depending on the tasks, the staff qualification was adapted for either a higher-level technician (€ 24/h)  
243 or engineer (€ 37/h). The duration of each task was estimated for the staff cost estimation. The  
244 supervision of an engineer is involved for 5% of the total time (data processing). Field operations  
245 require two agents for safety. The 2016 French administration packages are used for the travel prices  
246 (0.47€/km; 15.25€/meal; and 70€/hotel night). The DGT cost is 15€ when buying from DGT Research  
247 Ltd (Lancaster, UK). All the reagents and disposable material costs were taken from the UGAP supplier  
248 (the French organization for public purchase) catalogue prices. Reusable materials such as  
249 temperature loggers are considered according to a fixed cost per campaign (1€). More details of the  
250 costs can be found in Table S5.

## 251 **3. RESULTS**

### 252 **3.1. DGT RELIABILITY**

#### 253 **3.1.1. DGT BLANKS AND CONTAMINATION**

254 The overall contamination of the passive samplers is considered first. For this purpose, the ratio  
255 between the field blanks concentration and the  $LOQ_{DGT}$  is calculated for each campaign . These ratios  
256 show very low DGT contamination for some metals/metalloids such as Se, Sb, Cr and Al (Table S6). For  
257 these elements, only small and sporadic quantifiable contaminations (2 to 4 times the  $LOQ_{DGT}$ ) are  
258 observed for one or two campaigns. For the others, higher contamination can be observed. It is  
259 generally limited (less than 5 times the  $LOQ_{DGT}$ ), but occasional contamination peaks can appear. For  
260 example, Cu presents quantifiable contamination with high frequency (5 campaigns over 6). It is usually

261 of limited intensity (2 to 4 times the LOQ<sub>DGT</sub>), but it can be significant at specific times (19 times the  
 262 LOQ<sub>DGT</sub>).

263 In a context where an accurate element concentration in the river is needed, these contaminations  
 264 need to be considered relative to the targeted concentrations at the study sites. For this purpose, the  
 265 average contamination in the field blanks for each campaign is compared to the average amounts  
 266 accumulated in DGTs exposed in the river for each site (Table 1). The average contaminations represent  
 267 2 to 74% of a given metal/metalloid accumulated for a 14-day deployment. This magnitude of  
 268 contamination is consistent with the ones reported by Bretier et al. (2019) and Dabrin et al. (2016) for  
 269 natural systems (river and coastal lagoon). The DGT contamination is marginal for As and Se but can  
 270 be significant for the other elements. The relative contamination is the highest for Cd (74%) and Zn  
 271 (53%). An interlaboratory trial has also shown previously significant contamination issues for Zn with  
 272 DGT deployment (Dabrin et al., 2016; Miège et al., 2012). In fact, this element is usually recognized for  
 273 its ubiquity and propensity for contamination. For Cd, this high relative contamination can be explained  
 274 by the small concentrations found in the study rivers. Consequently, the slightest contamination during  
 275 DGT handling has a strong impact on the amount found in the binding layer and therefore on the C<sub>DGT</sub>.  
 276

	Al	Zn	Ni	Cd	Cu	Pb	Cr	As	Se	Sb
<b>DGT contamination: Relative contamination magnitude (% , n = 100 to 102 exposures)</b>										
Average	16	53	19	74	39	44	48	2	9	30
SD	4	41	11	64	20	29	12	1	3	7
<b>Field repeatability: DGT duplicate relative deviation (% , n = 100 to 102 exposures)</b>										
Average	65	19	18	23	23	51	41	20	3	16
Maximum	194	150	177	200	174	189	166	190	88	133

277 *Table 1: DGT performances: Relative contamination magnitude (average amounts accumulated in field blanks compared to*  
278 *the amounts accumulated in river-exposed DGTs) and field repeatability (relative deviation obtained between each DGT*  
279 *duplicate exposed to the river). Low values indicate minimal contamination and good repeatability, respectively.*

280 The analysis of the 3 different types of blanks allows us to deepen our knowledge of the contamination  
281 origin that occurred during the DGT handling. Thus, the determination of contamination enrichment  
282 factors throughout the DGT procedure (ratio between contamination types found in two successive  
283 steps) reveals the step at which a possible contamination has occurred (Figure S3). The contamination  
284 enrichment factors are displayed in Figure 1. A factor equal to 1 indicates the absence of additional  
285 contamination between the two steps used to calculate it. The manufacturing and field deployment  
286 steps do not cause contamination, except for in a few given cases (Ni, Cd, Cu, Pb, Cr and As). These  
287 contaminations may be due to uncontrolled contact between DGTs during their transportation or  
288 handling by staff. The most noticeable contamination enrichment factors are found during the  
289 (dis)assembly step, especially for Zn, Ni, Cu, Pb and As. This finding indicates contamination is coming  
290 from poorly decontaminated DGT holders or cross-contamination during binding gel handling (Figure  
291 S3). Generally, the contamination enrichment factors' standard deviations include the value of 1, which  
292 indicates that the contamination does not take place systematically but rather occasionally.  
293 Considering the random nature of the contamination among campaigns, it can be hypothesized that  
294 this contamination is primarily due to cross-contaminations occurring during DGT dismantling. Due to  
295 the development of (bio)fouling on DGT devices during field exposure, a binding phase cross-  
296 contamination from the metals/metalloids adsorbed onto the fouling can occur during the DGT  
297 disassembly. Particular attention must be paid to the cleanliness of the disassembly equipment while  
298 handling the binding phases to limit cross-contamination (*e.g.* avoid contact between the wizzle used  
299 for removing diffusive gel and binding gels). In addition, between each DGT support reuse, thorough  
300 cleaning must be performed (*e.g.* several acid bath washing if necessary).

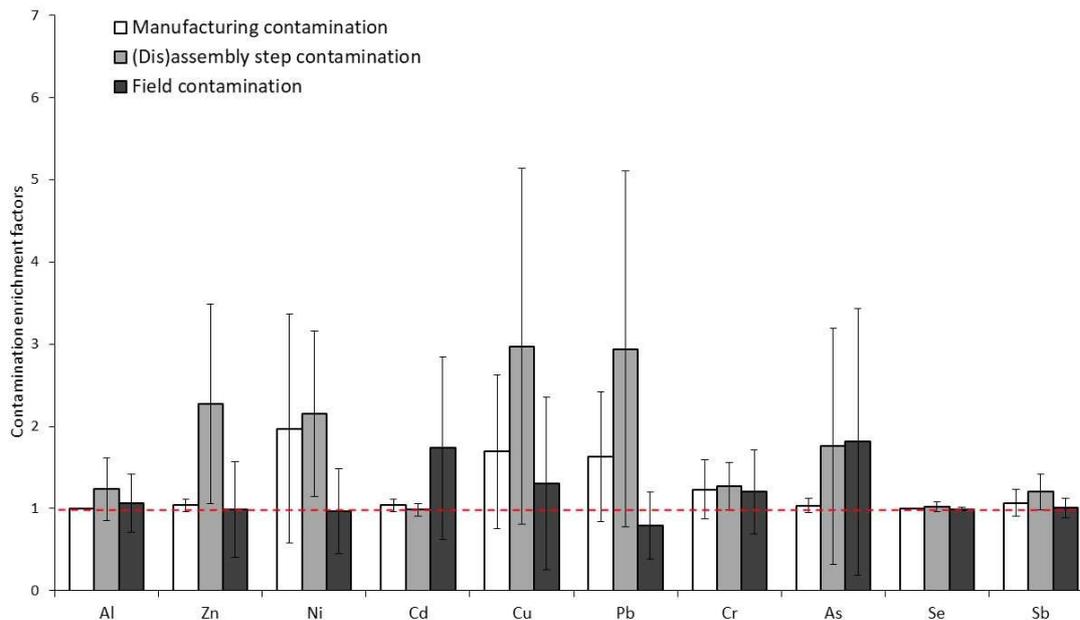


Figure 1 : Contamination enrichment factors between manufacturing, (dis)assembly and field steps for each metal/metalloid and campaign (average  $\pm$  SD; n = 6 campaigns).

301

302

### 3.1.2. METAL/METALLOID PRECONCENTRATION BY DGT

303

The preconcentration ability of DGTs allows to improve sensitivity during analysis, and it is an important advantage of non-equilibrium passive sampling techniques (Zhang and Davison, 1995).

305

However, sensitivity improvement will simultaneously be limited by any contamination during the sampling procedure. Consequently, two sensitivity improvements are discussed here: intrinsic and

307

operational improvements. An intrinsic sensitivity improvement describes the ability of DGTs to improve sensitivity in the absence of any sampler contamination and is solely related to the intrinsic

309

preconcentration ability of the DGTs. The operational sensitivity improvement describes the ability of DGTs to improve the sensitivity despite the contamination suffered during the entire sampling

311

procedure (*i.e.*, field blanks).

312

#### **Intrinsic sensitivity improvement:**

313

The  $LOQ_{DGT}$  values represent the lowest quantified concentration in the absence of DGT device contamination (see section 2.5). The ratio between the  $LOQ$  and  $LOQ_{DGT}$  (Figure 2) allows us to quantify

314

315 the sensitivity increase due to the DGT preconcentration abilities. Thus, the  $LOQ_{DGT}$  values are greatly  
316 decreased compared to the LOQ, and the DGT intrinsic preconcentration factors range from 5 to 35  
317 depending on the metals/metalloids (Figure 2). These differences between the elements come directly  
318 from their different sampling rates because of their different diffusive abilities in the DGTs (as  
319 illustrated by their diffusion coefficient value, see Table S3).

320 It should be noted that, for specific purposes, sensitivity can be adapted for both grab (*e.g.* using a pre-  
321 concentration method) and DGT (*e.g.* using a longer deployment time or a thinner diffusive gel)  
322 sampling.

323

#### 324 **Operational sensitivity improvement:**

325 To discuss the operational sensitivity improvement by DGT that will be obtained after field  
326 deployments, it is necessary to consider the contamination from the sampler. Thus, a  $LOQ_{DGT\ field}$  is  
327 determined from the average field blank contamination + 10 times the standard deviations (following  
328 IUPAC recommendations). The mean values are displayed in Table S4. The sensitivity improvement  
329 including the sampler contamination is quantified using the ratio of the  $LOQ_{DGT\ field}$  to the analytical  
330 LOQ (Figure 2). The operational sensitivity improvement in DGTs is greatly decreased compared to the  
331 intrinsic sensitivity improvement because of the sampler contamination (Figure 2). The sensitivity  
332 increase is null or marginal ( $< 1.5$ ) for Cu, As, Cr, Zn, and Pb and Ni. However, for the other elements  
333 (Al, Cd, Se, and Sb), the sensitivity increase is still noticeable and falls between 2 and 5. Nevertheless,  
334 when compared to those of standard grab sampling, these factors are the minimum sensitivity  
335 improvements, because they were determined under the assumption of an absence of quantifiable  
336 contamination during the grab sampling procedure. However, grab sampling can also suffer from  
337 contamination if sampling bottles are loosely decontaminated and if consumable material (*e.g.* syringe  
338 and filters) not suitable for trace metal quantification is used. Consequently, DGT passive sampling  
339 should still be more sensitive than grab sampling for several elements.

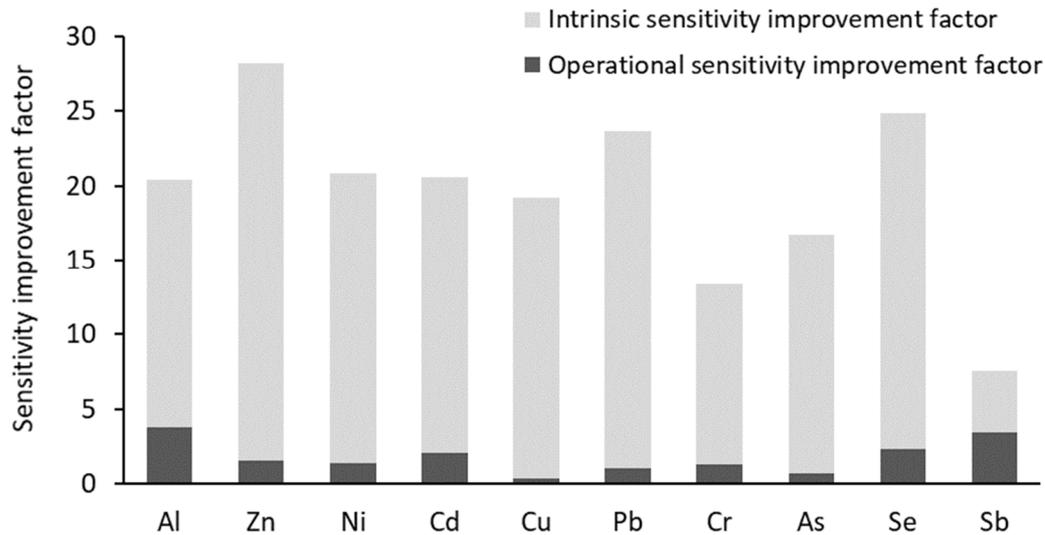


Figure 2: Intrinsic and operational sensitivity improvement factors for each metal/metalloid

### 3.1.3. FIELD LOSS RATE

Among the 408 DGTs exposed to the field, only 3 DGTs were damaged (with damaged protective membranes), and 10 were found out of the water after the 14 days of river exposure, primarily during the first field campaign, due to a large decrease in the water level linked to the end of a flood event. After their analysis, the 3 damaged DGTs were consistent with their undamaged duplicate and were consequently considered workable. On this basis, a 3% loss rate can be established (10 out of 408 DGTs).

It is noticeable that, for 6 out of the 10 DGTs recovered out of water, an exposure concentration ( $C_{DGT}$ ) can still be calculated. Thanks to the temperature data recorded every 10 minutes, their exposure time is obtained (typically one week *versus* two for the other DGTs), enabling calculation of  $C_{DGT}$ . These values, although altered, are still relevant. Therefore, the loss rate during this large-scale study is between 1 and 3% (considering or not considering the workable DGTs found out of water), which can be considered very low.

355                    3.1.4. FIELD REPEATABILITY

356    The relative deviations obtained between DGT duplicates are presented in Table 1. The average  
357    relative deviations vary from 2 to 47% depending on the metal/metalloid, and they can reach a  
358    maximum of 200%. On average, most elements (Zn, Ni, Cd, Cu, As, Se, and Sb) displayed a duplicates  
359    relative deviation < 25%. Compared to the typical 10% repeatability expected for deployments  
360    performed in laboratory, this field repeatability can be considered very satisfactory . Considering that  
361    the average repeatability was good (< 25%) for most elements and acceptable for the others ( $\leq$  65%),  
362    the use of duplicates is conceivable in a large monitoring network context in which the data are used  
363    to determine global concentrations trend. In fact, performing the DGT deployment in duplicate allows  
364    for repeatability similar to the triplicate deployments reported by Miège et al. (2012), Dabrin et al.  
365    (2016) and Bretier et al. (2019). However, high deviations (up to 200%) were sometimes observed, and  
366    only the use of triplicates should guarantee the exclusion of sporadically doubtful data.

367                    **3.2. COMPARISON BETWEEN GRAB AND DGT PASSIVE SAMPLING**

368                    3.2.1. METAL/METALLOID QUANTIFICATION FREQUENCY

369    The quantification frequencies of metals/metalloids by both DGT and grab sampling are displayed in  
370    Table 2. Using grab sampling, Cd and Se are rarely quantified ( $\leq$  20%), whereas Cu and As are quantified  
371    at a very high frequency (> 90%). The other elements are quantified with frequencies between 60 and  
372    90%. Using DGT passive sampling, all the elements are quantified at a high frequency (> 90%) except  
373    Zn (74%) and Se (20%). The generally better quantification frequency of DGT passive sampling found  
374    here is consistent with the operational sensitivity improvement found in this study (Figure 2).

375

376

377

	Al	Zn	Ni	Cd	Cu	Pb	Cr	As	Se	Sb
<b>Quantification frequency (% , n = 200 to 204 grab and DGT samplers)</b>										
Grab sampling	76	69	88	20	94	75	89	99	19	62
DGT passive sampling	93	74	99	97	99	100	100	100	20	95
<b>Site concentration trend using grab or DGT sampling (n = 17 sites)</b>										
Trends obtained with both grab and DGT sampling	13	17	17	1	17	12	15	17	2	9
Similar trends obtained with both sampling technique	10	17	15	1	16	9	11	13	2	8
Trends obtained only with DGT sampling	4	-	-	16	-	5	1	-	-	7

378 *Table 2: Comparison between grab and passive sampling: Quantification frequency and site concentration trend estimation*  
379 *according to the metals/metalloids.*

380 Nevertheless, the benefit of using DGTs in addition to grab sampling in terms of quantification  
381 frequency differs according to the metals/metalloids. For example, a strong quantification frequency  
382 increase is found in our study for Cd, which is often sought in water quality monitoring networks  
383 because of its toxicity and its mobility. This increase is linked to the respective sensitivity associated  
384 with the grab and DGT sampling methods ( $LOQ = 0.02 \mu\text{g L}^{-1}$  vs.  $LOQ_{DGT} = 0.001 \mu\text{g L}^{-1}$ ) with respect to  
385 the concentration of Cd found in the study rivers. Roig et al. (2011) showed a systematic detection of  
386 this element by DGT sampling. For other elements such as Pb, Al, Cr and Sb, sampling by DGT also  
387 shows a more frequent quantification than grab sampling, but the difference between the two  
388 methods is moderate (between 10 and 30%).

389 For other elements such as As, Cu, and Zn, quantification frequencies with the two sampling methods  
390 do not differ ( $\leq 5\%$ ) because the concentration found in the watercourses was above the quantification  
391 capacities of both sampling methods in most cases (detection at 100% except for Zn, at 70%).

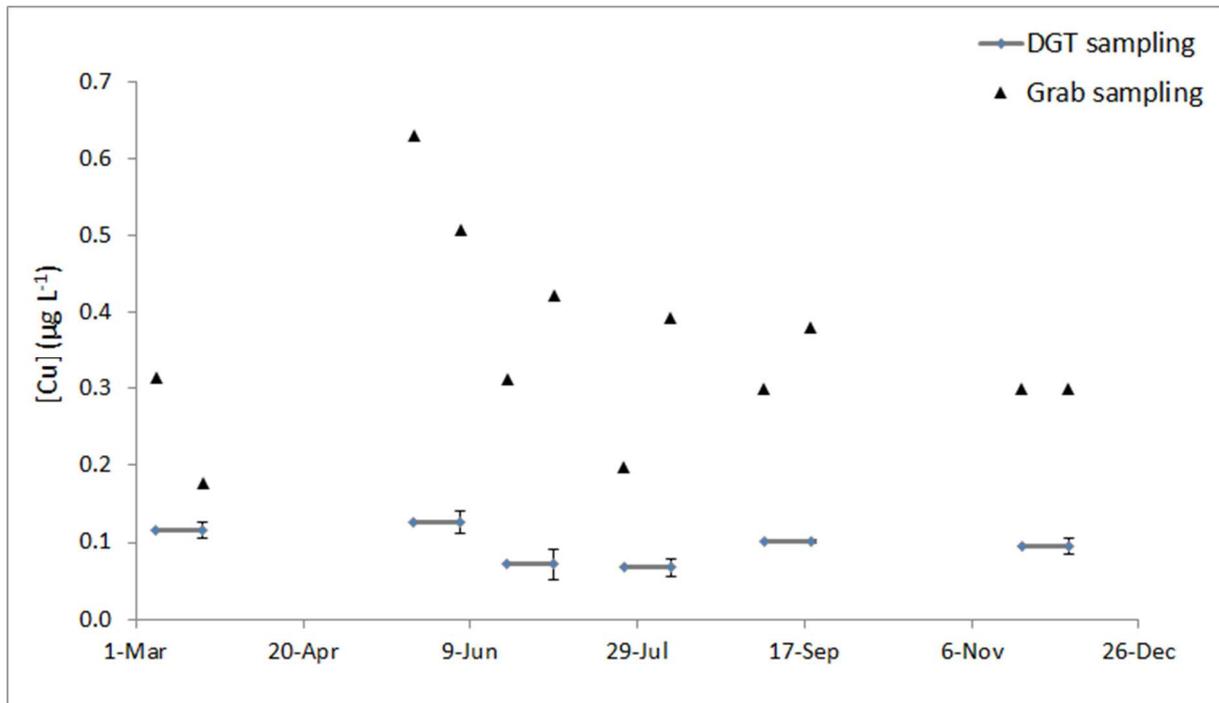
392 Lastly, for Se, the quantification frequency is low (around 20%) for both methods. The accumulating  
393 capacities (operational sensitivity improvement around 2, Figure 2) for a field deployment of 14 days

394 are not sufficient to lower the  $LOQ_{DGT}$  below the water concentration of this element. This finding can  
395 be explained by the very low concentrations of Se in the environment. The concentrations reported in  
396 the literature for unpolluted waters are in the sub- $\mu\text{g L}^{-1}$  (Fernández-Martínez and Charlet, 2009).

### 397 3.2.2. SITE CONCENTRATION TREND EVALUATION

398 The concentration evolution profiles obtained by grab and DGT sampling for each metal/metalloid at  
399 the 17 sites during the 6 campaigns are compared (Table S2). Table 2 lists the number of sites in which  
400 a concentration trend is obtained (*i.e.* quantifiable concentrations at least for 4 campaigns) with grab  
401 and/or DGT sampling. Trends obtained by the two sampling methods are considered similar for a given  
402 element in a given site when their concentrations show the same variations for at least 80% of the  
403 data. Among the 10 studied elements, similar trends are observed for Zn, Cu, Ni and As at almost all  
404 the sites. Good adequacy between concentration trends obtained with grab and DGT sampling have  
405 been already reported (Bretier et al., 2019; Cindrić et al., 2017; Cindrić et al., 2020). However, some  
406 differences are also found for these elements. The metals/metalloids concentrations of the grab  
407 samples show greater variability over time than those obtained by DGT (Figure 3).

408



410

411 *Figure 3: Example of Cu trend established in Lizonne river with the grab and DGT sampling highlighting the greater variability*  
 412 *obtained with grab sampling. DGT concentrations presented are mean of the duplicates.*

413 For the other elements, the two sampling methods are not always consistent. For the least  
 414 contaminated sites, trends cannot be obtained by grab sampling because the concentrations in the  
 415 water are too low to be quantifiable. Thus, thanks to its preconcentration capabilities, only DGT can  
 416 be used to monitor the concentration evolution for these sites. This is especially the case for Cd (16/17  
 417 sites), Sb (7/17 sites) and more occasionally for Pb, Al and Cr. However, in the case of Se, none of the  
 418 two sampling methods make it possible to quantify the concentration for 15/17 sites.

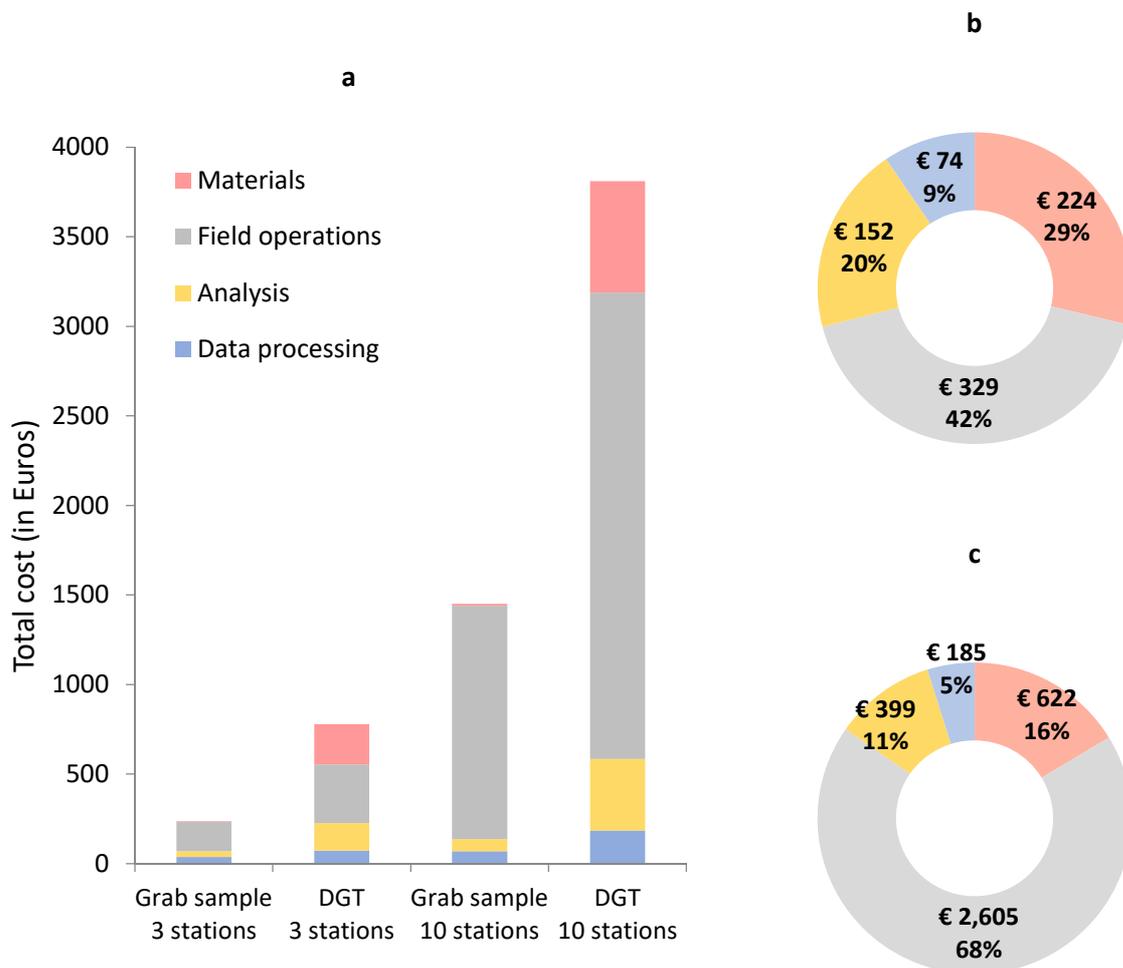
### 419 3.2.3. ECONOMIC STUDY

420 For measurement networks studied using grab sampling, the major part of the overall cost is related  
 421 to field operations (70 and 90% for 3 and 10 stations respectively), primarily because of the travel  
 422 time. Concerning the measurement networks addressed by DGT passive sampling, field operations  
 423 remain the primary expenses, but parts of the other costs increase compared to those of grab sampling  
 424 and represent between *c.a.* 2/3 (three-station networks) and *c.a.* 1/3 (ten-station network) of the total

425 expense. In fact, the purchase of DGT in duplicate for each type of metal/metalloid (cations and  
 426 oxyanions) represents an additional cost compared to the materials necessary for grab samples (vials,  
 427 filters and syringes). Moreover, the analysis time is increased due to the dismantling and elution of  
 428 DGTs, and the data processing time is considered to be double that of grab sampling.

429

430



431 *Figure 4 : Cost per monitoring campaign for 10 metals/metalloids (As, Se, Sb, Ni, Cd, Pb, Cr, Cu, Zn, and Al) using grab or*  
 432 *passive sampling (2 DGT-Ch and 2 DGT-Zr): (a) Total cost for a network with 3 or 10 stations; (b) cost distribution for a 3-*  
 433 *station network using DGT monitoring; and c) cost distribution for a 10-station network using DGT monitoring.*

434 Compared to the cost of grab sampling (Figure 4), the cost of each campaign for a measurement  
 435 network studied with DGT passive sampling is multiplied by 3.3 and 2.6 for a 3-station or a 10-station

436 network, respectively. The cost increase between these two types of sampling is primarily due to the  
437 doubling in travel time (installation and removal of DGTs), which doubles the field operation costs. By  
438 adding the DGT purchase, these two elements account for 71% and 84% for 3- and 10-station networks,  
439 respectively, of the global cost for a network studied using passive sampling.

#### 440 **4. IMPLEMENTATION OF DGT SAMPLING IN MONITORING NETWORKS**

##### 441 **4.1. RECOMMENDATIONS FOR FIELD DEPLOYMENT**

442 Field deployment of DGT passive sampling is simple but requires precautions. Several  
443 recommendations are given in the supplementary material. The following recommendations are  
444 directly drawn from the feedback of this study:

- 445 - Place DGT devices as far as possible away from the usual passageways (limit their visibility and  
446 accessibility) to avoid vandalism. Thus, it is necessary to consider leisure activities such as  
447 fishing, bathing, canoeing, etc.
- 448 - Record the temperature using a logger to correct the diffusion coefficient for the exposure  
449 temperature and eventually determine the exposure time for the DGT devices recovered out  
450 of the water.
- 451 - Perform DGT field blanks for each sampling campaign (and for each DGT production batch) to  
452 check the contamination issues (see section 5.1.). These field blanks must be assembled and  
453 disassembled randomly among the field DGTs set to account for cross-contamination.
- 454 - Perform, if possible, deployments with triplicate DGT devices. DGT deployment in duplicate  
455 ensures a result in case of the loss of a device while obtaining correct repeatability (less than  
456 65% on average in this study). However, occasionally, poorer repeatability is obtained (up to  
457 88 to 200% depending on the metals/metalloids for this study). To limit sporadic inaccuracies  
458 due to poor repeatability and/or to possible sampler contamination, the use of triplicates  
459 should be considered if the additional costs can be financed.

#### 460 4.2. CONTRIBUTION OF DGT TO WATER QUALITY EVALUATIONS

461 Contamination, even when identified and considered during data treatment, will limit the sensitivity  
462 gains of the DGT method (Figure 2). Therefore, limiting the potential contamination of DGTs is  
463 mandatory to benefit from the preconcentration ability of DGTs. In most cases in this study, the  
464 integrative capacity of the DGTs allows for a higher quantification frequency for elements deemed to  
465 be very toxic, such as Cd (Table 2). For the least contaminated sites, the DGTs can allow for the  
466 quantification and therefore the monitoring of metal/metalloid concentrations over time in situations  
467 in which grab sampling cannot because of its excessively high LOQ.

468 It should be noted, however, that the fractions sampled by the two techniques are different. The  
469 filtered grab samples concern the dissolved fraction of metals/metalloids while the DGT samples only  
470 address part of the dissolved fraction, *i.e.*, the labile fraction. The DGT-labile fraction of  
471 metals/metalloids, which is often considered as a biologically relevant fraction by many authors (Diviš  
472 et al., 2007; Zhang and Davison, 2015; Menegário et al., 2017), has a real added value for the  
473 assessment of their impact on aquatic organisms. In fact, the concentrations of elements measured in  
474 aquatic environments by the DGTs can be compared to toxicological data in a more relevant way since  
475 it is the most active fraction of metals/metalloids for organisms. In addition, in reference to the  
476 approach used in the WFD to assess the water quality, the time integrative measurement by DGT is  
477 another advantage for the chronic toxicity evaluation of metals/metalloids. In the study case, the  
478 average concentration calculated over 6 periods of 14 days of DGT exposure is much more  
479 representative of organismal chronic exposure compared to the average concentration calculated  
480 from 6 grab samples measured at individual times (*i.e.*, 6 times 1 second). Thus, this approach could  
481 lead to a better assessment of the chronic toxicity risk in an aquatic environment. By contrast, DGT  
482 passive sampling is not suitable for assessing the acute toxicity risk since the measured data are an  
483 average concentration that 'hides' the concentration peaks responsible for the irreversible effects on  
484 aquatic organisms.

## 485 **5. CURRENT LIMITS ON DGT IMPLEMENTATION**

### 486 **5.1. CONSIDERATION OF DGT CONTAMINATION**

487 There is a risk of DGT contamination depending on the working environment (Dabrin et al. 2016, Miège  
488 et al. 2012). In this study, the contamination was found to vary over time and according to the  
489 elements. We hypothesized that the contamination came primarily from cross-contamination during  
490 DGT disassembly.

491 Although it can be hypothesized that contamination level should decrease with laboratory experience  
492 increase, a determination of the device contamination is required to assess its impact on the accuracy  
493 of the results and, if necessary, undertake corrections. The production of field blanks to assess the  
494 whole contamination is, from our point of view, mandatory in the context of large-scale deployments  
495 such as monitoring networks. For this purpose, we propose to prepare 10 DGT field blanks (ideally 10,  
496 or 3 at worst) for each campaign by the type of binding gel. These field blanks must be assembled and  
497 disassembled randomly among the field DGTs set to account for cross-contamination. When a  
498 significant (compared to the amount accumulated from the river; > 10%, Bretier et al., 2019) but  
499 repeatable contamination of the blanks is detected, a correction of the results by blank subtraction (as  
500 obtained by the average campaign's blank contamination) can be performed (Dabrin et al., 2016).  
501 However, when the dispersion of the blanks reflects randomly occurring contamination (such as what  
502 we observed in this study), correcting by blank subtraction with an average contamination will lead to  
503 the misestimation of the concentrations measured by some DGT. In this case, it is more relevant to  
504 establish a safety zone through the determination of an  $LOQ_{DGT\ field}$ , which allows for the exclusion of  
505 doubtful results (*i.e.*, lower than  $LOQ_{DGT\ field}$ ) linked to potentially significant contamination (Buzier et  
506 al. 2014).

### 507 **5.2. LIMITATIONS LINKED TO WATER COMPOSITION**

508 The oxidation state of the elements is also a parameter to consider when the different red-ox species  
509 of a single element with different behaviour in DGT (*e.g.*, binding and/or diffusive properties) can be

510 simultaneously present in an aquatic environment. Among the studied elements, As and Sb can be  
511 present in two redox species (+III) and (+V) with different diffusion coefficients (Bennett et al., 2010;  
512 Fontanella and Beone, 2016). The absence of a specific DGT device leads to the sampling of the two  
513 species. Because their relative distribution is unknown, the diffusion coefficient value to be used for  
514  $C_{DGT}$  calculation will become an issue. For example, As(III) has a diffusion coefficient *c.a.* 40% higher  
515 than that of As(V) (Bennett et al., 2010). Because it is not possible to anticipate the distribution of the  
516 two species, it is only possible to determine two  $C_{DGT}$  with the two diffusion coefficient values by  
517 considering the 100% presence of one or the other redox form. If there is no evidence that a single  
518 redox species predominates, only a range for  $C_{DGT}$  would thus be announced.

519 By contrast, some elements present under different oxidation states are selectively sampled or  
520 excluded by DGT. Among the studied elements, chromium is present as cationic Cr(III) and anionic  
521 Cr(VI). Although both species can be sampled by DGT-Zr, the robustness of chromium sampling at  
522 varying pH and ionic strength values is limited (Devillers et al., 2016). Using DGT-Ch, only Cr(III) is  
523 sampled (Ernstberger et al., 2002). Therefore, using these standard DGTs, only partial information on  
524 Cr contamination is obtained. More complete information can be obtained by adding DGTs that are  
525 able to sample Cr(VI) selectively (Pan et al., 2015), but it will significantly increase the cost of the  
526 monitoring network. Therefore, a choice between the network cost and data representativeness must  
527 be made for these elements.

528 During the DGT exposure, the sampler surface may be fouled by the possible development of biofilm.  
529 This fouling is highly suspected of inducing a bias into the quantification (Pichette et al., 2007) by  
530 modifying the element accumulation by interaction with them (Uher et al. 2012, Uher et al. 2017).  
531 Devillers et al. (2017) highlight the intervention of the sorption phenomenon, which affects metal  
532 cations (Pb in particular) but not anions (As(V), Cr(VI), Sb(V) and Se(VI)). They show that fouling limits  
533 the quantity of cations accumulated by the binding phase and can induce an underestimation of the  
534  $C_{DGT}$  of 40 to 90% in the worst cases. Since the impact of DGT fouling is poorly understood, no  
535 correction of this bias is currently available. In a large-scale monitoring network context, feedback on

536 the first deployments should be very useful to adapt sampling procedure to each targeted site. If  
537 biofilm on samplers is found for a given site, it is safer to discard the data for cationic elements. Then,  
538 shorter exposures should be considered to limit its development. However, because a shorter  
539 exposure duration leads to poorer sensitivity, this strategy will probably not be relevant for poorly  
540 contaminated systems.

### 541 **5.3. NETWORK MONITORING COST INCREASE**

542 Contrary to some opinions (*e.g.*, discussions heard during conferences such as IPSW), the cost of a  
543 passive sampling network is not similar to that of a grab sampling network for metals/metalloids (see  
544 section 3.2.3). However, the additional cost should be acceptable (factor *c.a.* 3) considering the benefit  
545 of implementing DGT passive sampling in monitoring networks (see section 4.2). As suggested by  
546 Guibal et al. (2018) for neutral pesticide pollution, the practice of the two sampling techniques (grab  
547 and passive) allows for a complementary vision of the water quality with respect to the target  
548 pollutants. Beyond the necessary budgets, the type of sampling and the number of campaigns should  
549 be chosen according to the objectives of the networks.

550 To limit the network cost increase to implement two sampling types, there are two primary strategies:

551 1) Optimizing the working time during the field operations and the material purchase, which  
552 mostly underlie the additional cost. Optimizing the working time is possible by having well-trained  
553 technicians, but also by keeping the travel times to a minimum, since it is the staff cost per hour that  
554 is the primary factor influencing the field operation cost. However, care must be taken to comply with  
555 road regulations and the safety of drivers and passengers. For the material cost, the manufacture and  
556 assembly of DGTs by purchasing the components from DGT Research Ltd. instead of the complete  
557 devices can divide their cost by 2 (€7.4 vs. €15). Therefore, the cost differences between the two types  
558 of sampling drops from 3.3 to 2.9 and from 2.6 to 2.4 for three and ten-station networks, respectively.  
559 Moreover, depending on the targeted elements, the use of DGT equipped with mixed binding gels

560 (Wang et al., 2017) can be considered to use a single device instead of the two (DGT-Ch and DGT-Zr)  
561 used in this study.

562 2) Reducing the number of measurement campaigns. Depending on the targeted information,  
563 a reduced measurement frequency may be acceptable given the multiple gains in using the DGT  
564 passive sampling technique. For example, if the costs of the field operations and materials are  
565 optimized, then the cost difference is a factor of 2 between networks monitored using grab or passive  
566 sampling. Under this condition, a network of 10 measurement stations with 3 campaigns by DGT  
567 passive sampling will have a similar cost to that of the same network with 6 campaigns by grab  
568 sampling.

569 In addition, the number of replicates can be optimized in certain cases with a reasonable additional  
570 cost for better data reliability. This study shows that the deployment of duplicates is sufficient to  
571 ensure knowledge of the trends in variations in the metals/metalloids in the measurement network.  
572 However, triplicate deployments allow for the determination of more reliable average concentrations  
573 (see section 3.1.4.). For a large measurement network (*i.e.*, with 10 stations), the deployment of DGTs  
574 in triplicate instead of duplicate represents an additional cost of 7%, while for a smaller network  
575 (*i.e.*, with 3 stations), the increase is 11%.

## 576 **6. CONCLUSION**

577 This study has shown that the use of DGT passive sampling for monitoring metals/metalloids in  
578 watercourses at a network scale is feasible both financially, for an aquatic environment manager, and  
579 technically, for an analysis laboratory trained in this special technique. The passive sampling of  
580 metals/metalloids by DGT provides different but complementary information than grab sampling (*e.g.*  
581 longer time-integrated period and biologically relevant labile fraction targeted). Efforts to develop this  
582 tool within the framework of measurement networks should therefore be pursued. In fact, the recent  
583 development (May 2020) of a standard method (NF FD T 90-012, 2020) for DGT-Ch and cation  
584 measurements in water is an important step in the development of DGT sampling. Mixed monitoring

585 strategies using passive and grab sampling methods in parallel or alternately, depending on the studied  
586 sites, could be envisaged to couple their advantages. Nevertheless, feedback on DGT deployments at  
587 a larger scale must increase to continue adapting/defining their use for the monitoring of watercourses  
588 quality as well as possible and extend their advantages to other environments, such as marine or  
589 estuarine waters.

590

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594

## 595 **References**

596 AFNOR, 2011. NF EN ISO 5667-23- Water quality - Sampling - Part 23: Guidance on passive sampling  
597 in surface waters.

598 AFNOR, 2020. NF FD T 90-012 (in French) - Dosage des métaux - Méthode pour la mesure de  
599 concentration en métaux après échantillonnage passif par gradient diffusif en couche mince.

600 Allan, I., Vrana, B., Greenwood, R., Mills, G., Knutsson, J., Holmberg, A., Guigues, N., Fouillac, A.,  
601 Laschi, S., 2006. Strategic monitoring for the European Water Framework Directive. Trends  
602 Anal. Chem. 25, 704–715. <https://doi.org/10.1016/j.trac.2006.05.009>

603 Allan, I.J., Knutsson, J., Guigues, N., Mills, G.A., Fouillac, A.-M., Greenwood, R., 2008.  
604 Chemcatcher® and DGT passive sampling devices for regulatory monitoring of trace metals in  
605 surface water. J. Environ. Monit. 10, 821–829. <https://doi.org/10.1039/B802581A>

606 Bennett, W., R Teasdale, P., Panther, J., Welsh, D., Jolley, D., 2010. New Diffusive Gradients in a Thin  
607 film technique for measuring inorganic arsenic and selenium(IV) using a titanium dioxide based  
608 adsorbent. Anal. Chem. 82, 7401–7. <https://doi.org/10.1021/ac101543p>

609 Bretier, M., Dabrin, A., Bessueille-Barbier, F., Coquery, M., 2019. The impact of dam flushing event  
610 on dissolved trace elements concentrations: Coupling integrative passive sampling and discrete  
611 monitoring. *Sci. Total Environ.* 656, 433–446. <https://doi.org/10.1016/j.scitotenv.2018.11.303>

612 Buzier, R., Charriau, A., Corona, D., Lenain, J.-F., Fondanèche, P., Joussein, E., Poulhier, G., Lissalde,  
613 S., Mazzella, N., Guibaud, G., 2014. DGT-labile As, Cd, Cu and Ni monitoring in freshwater:  
614 Toward a framework for interpretation of in situ deployment. *Environ. Pollut.* 192, 52–58.  
615 <https://doi.org/10.1016/j.envpol.2014.05.017>

616 Cindrić, A.-M., Cukrov, N., Durrieu, G., Garnier, C., Pižeta, I., Omanović, D., 2017. Evaluation of  
617 discrete and passive sampling (Diffusive Gradients in Thin-films – DGT) approach for the  
618 assessment of trace metal dynamics in marine waters – a case study in a small harbor. *Croat.*  
619 *Chem. Acta* 90. <https://doi.org/10.5562/cca3163>

620 Cindrić, A.-M., Marcinek, S., Garnier, C., Salaiün, P., Cukrov, N., Oursel, B., Lenoble, V., Omanović,  
621 D., 2020. Evaluation of diffusive gradients in thin films (DGT) technique for speciation of trace  
622 metals in estuarine waters - A multimethodological approach. *Sci. Total Environ.* 721, 137784.  
623 <https://doi.org/10.1016/j.scitotenv.2020.137784>

624 Chon, H.-S., Ohandja, D.-G., Voulvoulis, N., 2010. Implementation of E.U. Water Framework  
625 Directive: source assessment of metallic substances at catchment levels. *J. Environ. Monit.* 12,  
626 36–47. <https://doi.org/10.1039/b907851g>

627 Dabrin, A., Ghestem, J.-P., Uher, E., Gonzalez, J.-L., Allan, I.J., Schintu, M., Montero, N., Balaam, J.,  
628 Peinerud, E., Miège, C., Coquery, M., 2016. Metal measurement in aquatic environments by  
629 passive sampling methods: Lessons learning from an in situ intercomparison exercise. *Environ.*  
630 *Pollut.* 208, 299–308. <https://doi.org/10.1016/j.envpol.2015.08.049>

631 Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural waters  
632 using thin-film gels. *Nature* 367, 546–548. <https://doi.org/10.1038/367546a0>

633 Devillers, D., Buzier, R., Grybos, M., Charriau, A., Guibaud, G., 2017. Key role of the sorption process  
634 in alteration of metal and metalloid quantification by fouling development on DGT passive  
635 samplers. *Environ. Pollut.* 230, 523–529. <https://doi.org/10.1016/j.envpol.2017.07.005>

636 Devillers, D., Buzier, R., Simon, S., Charriau, A., Guibaud, G., 2016. Simultaneous measurement of  
637 Cr(III) and Cr(VI) in freshwaters with a single Diffusive Gradients in Thin Films device. *Talanta*  
638 154, 533–538. <https://doi.org/10.1016/j.talanta.2016.04.009>

639 Directive 2000/60/CE of the European Parliament and of the Council of 23 October 2000 establishing a  
640 framework for Community action in the field of water policy, 2000.

641 Directive 2013/39/UE of the European Parliament and of the Council of 12 August 2013 amending  
642 Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water  
643 policy.

644 Diviš, P., Dočekalová, H., Brulík, L., Pavliš, M., Hekera, P., 2007. Use of the diffusive gradients in thin  
645 films technique to evaluate (bio)available trace metal concentrations in river water. *Anal.*  
646 *Bioanal. Chem.* 387, 2239–2244. <https://doi.org/10.1007/s00216-006-0996-y>

647 Ernstberger, H., Zhang, H., Davison, W., 2002. Determination of chromium speciation in natural  
648 systems using DGT. *Anal. Bioanal. Chem.* 373, 873–879. [https://doi.org/10.1007/s00216-002-](https://doi.org/10.1007/s00216-002-1370-3)  
649 1370-3

650 Fernández-Martínez, A., Charlet, L., 2009. Selenium environmental cycling and bioavailability: a  
651 structural chemist point of view. *Rev. Environ. Sci. Biotechnol.* 8, 81–110.  
652 <https://doi.org/10.1007/s11157-009-9145-3>

653 Fontanella, M.C., Beone, G.M., 2016. Determination of Sb(III) and Sb(V) by HPLC - Online isotopic  
654 dilution - ICP MS. *MethodsX* 3, 102–109. <https://doi.org/10.1016/j.mex.2015.12.001>

655 Gimpel, J., Zhang, H., Hutchinson, W., Davison, W., 2001. Effect of solution composition, flow and  
656 deployment time on the measurement of trace metals by the diffusive gradient in thin films  
657 technique. *Anal. Chim. Acta* 448, 93–103. [https://doi.org/10.1016/S0003-2670\(01\)01323-X](https://doi.org/10.1016/S0003-2670(01)01323-X)

658 Guibal, R., Lissalde, S., Leblanc, J., Cleries, K., Charriau, A., Poulier, G., Mazzella, N., Rebillard, J.-  
659 P., Brizard, Y., Guibaud, G., 2018. Two sampling strategies for an overview of pesticide  
660 contamination in an agriculture-extensive headwater stream. *Environ. Sci. Pollut. Res.* 25,  
661 14280–14293. <https://doi.org/10.1007/s11356-017-9883-7>

662 Hanke, G., Lepom, P., Quevauviller, P., Allan, J., Batty, J., Bignert, A., Borga, K., Boutrup, S., Brown,  
663 B., Carere, M., Maagd, G.-J., Dominguez, E., Duffek, A., Glesne, O., Green, N., Greenwood,

664 R., Loos, R., Amparo, M., Andersen, J., Wollgast, J., 2009. Guidance Document No. 19  
665 Guidance on surface water chemical monitoring under the water framework directive.

666 Menegário, A.A., Yabuki, L.N.M., Luko, K.S., Williams, P.N., Blackburn, D.M., 2017. Use of diffusive  
667 gradient in thin films for in situ measurements: A review on the progress in chemical  
668 fractionation, speciation and bioavailability of metals in waters. *Anal. Chim. Acta* 983, 54–66.  
669 <https://doi.org/10.1016/j.aca.2017.06.041>

670 Miège, C., Schiavone, S., Dabrin, A., Coquery, M., Mazzella, N., Berho, C., Ghestem, J.-P., Togola, A.,  
671 Gonzalez, C., Gonzalez, J.-L., Lalere, B., Lardy-Fontan, S., Lepot, B., Munaron, D., Tixier, C.,  
672 2012. An in situ intercomparison exercise on passive samplers for monitoring metals, polycyclic  
673 aromatic hydrocarbons and pesticides in surface waters. *Trends Anal. Chem.*, Chemical  
674 monitoring activity for the implementation of the Water Framework Directive 36, 128–143.  
675 <https://doi.org/10.1016/j.trac.2012.01.009>

676 Montero, N., Belzunce-Segarra, M.J., Gonzalez, J.-L., Larreta, J., Franco, J., 2012. Evaluation of  
677 diffusive gradients in thin-films (DGTs) as a monitoring tool for the assessment of the chemical  
678 status of transitional waters within the Water Framework Directive. *Mar. Pollut. Bull.* 64, 31–  
679 39. <https://doi.org/10.1016/j.marpolbul.2011.10.028>

680 National Institute of Standards and Technology. WebBook de Chimie NIST.  
681 <https://doi.org/10.18434/T4D303>

682 Pan, Y., Guan, D.-X., Zhao, D., Luo, J., Zhang, H., Davison, W., Ma, L.Q., 2015. Novel speciation  
683 method based on Diffusive Gradients in Thin-films for in situ measurement of CrVI in aquatic  
684 systems. *Environ. Sci. Technol.* 49, 14267–14273. <https://doi.org/10.1021/acs.est.5b03742>

685 Pichette, C., Zhang, H., Davison, W., Sauve, S., 2007. Preventing biofilm development on DGT devices  
686 using metals and antibiotics. *Talanta* 72, 716–722. <https://doi.org/10.1016/j.talanta.2006.12.014>

687 Priadi, C., Bourgeault, A., Ayrault, S., Gourlay-Francé, C., Tusseau-Vuillemin, M.-H., Bonté, P.,  
688 Mouchel, J.-M., 2011. Spatio-temporal variability of solid, total dissolved and labile metal:  
689 passive vs. discrete sampling evaluation in river metal monitoring. *J. Environ. Monit.* 13, 1470–  
690 1479. <https://doi.org/10.1039/c0em00713g>

691 Roig, N., Nadal, M., Sierra, J., Ginebreda, A., Schuhmacher, M., Domingo, J.L., 2011. Novel approach  
692 for assessing heavy metal pollution and ecotoxicological status of rivers by means of passive  
693 sampling methods. *Environ. Int.* 37, 671–677. <https://doi.org/10.1016/j.envint.2011.01.007>

694 Udeigwe, T., Eze, P., Teboh, J., Stietiya, M.H., 2011. Application, chemistry, and environmental  
695 implications of contaminant-immobilization amendments on agricultural soil and water quality.  
696 *Environ. Int.* 37, 258–67. <https://doi.org/10.1016/j.envint.2010.08.008>

697 Uher, E., Compère, C., Combe, M., Mazeas, F., Gourlay-Francé, C., 2017. In situ measurement with  
698 diffusive gradients in thin films: effect of biofouling in freshwater. *Environ. Sci. Pollut. Res.*  
699 24, 13797–13807. <https://doi.org/10.1007/s11356-017-8972-y>

700 Uher, E., Zhang, H., Santos, S., Tusseau-Vuillemin, M.-H., Gourlay-Francé, C., 2012. Impact of  
701 biofouling on Diffusive Gradient in Thin film measurements in water. *Anal. Chem.* 84, 3111–  
702 3118. <https://doi.org/10.1021/ac2028535>

703 Wang, Y., Ding, S., Shi, L., Gong, M., Xu, S., Zhang, C., 2017. Simultaneous measurements of cations  
704 and anions using diffusive gradients in thin films with a ZrO-Chelex mixed binding layer. *Anal.*  
705 *Chim. Acta* 972, 1–11. <https://doi.org/10.1016/j.aca.2017.04.007>

706 Zhang, H., Davison, W., 2015. Use of diffusive gradients in thin-films for studies of chemical speciation  
707 and bioavailability. *Environ. Chem.* 12, 85-. <https://doi.org/10.1071/en14105>

708 Zhang, H., Davison, W., Knight, B., McGrath, S., 1998. In situ measurements of solution concentrations  
709 and fluxes of trace metals in soils using DGT. *Environ. Sci. Technol.* 32, 704–710.  
710 <https://doi.org/10.1021/es9704388>

711 Zhang, Hao., Davison, William., 1995. Performance characteristics of Diffusion Gradients in Thin films  
712 for the in situ measurement of trace metals in aqueous solution. *Anal. Chem.* 67, 3391–3400.  
713 <https://doi.org/10.1021/ac00115a005>

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