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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) HNO₃ 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 km²) 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⁻¹ (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⁻¹ HNO₃ or 2 mL of 0.05 mol L⁻¹ NaOH/H₂O₂, 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 HNO₃. 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_{DGT}:**

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_{DGT}, 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; 8.9·10⁻² cm), A is the exposure area (3.14 cm²) and t is the
186 exposure time (s). The values of D at 25 °C (in cm² s⁻¹) 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) HNO₃ by dilution or spiking before the analysis by ICP-MS
194 (Agilent 7700X). The following internal standards were used: ²⁰⁹Bi, ¹¹⁸Sn, ¹¹⁵In, and ⁴⁵Sc. 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/) using the mean + 10 standard
201 deviations (SD) of the blanks (2% acidified ultrapure water). A LOQ_{DGT} 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_{DGT}), but it can be significant at specific times (19 times the
 262 LOQ_{DGT}).

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_{DGT}.
 276

	Al	Zn	Ni	Cd	Cu	Pb	Cr	As	Se	Sb
DGT contamination: Relative contamination magnitude (% , n = 100 to 102 exposures)										
Average	16	53	19	74	39	44	48	2	9	30
SD	4	41	11	64	20	29	12	1	3	7
Field repeatability: DGT duplicate relative deviation (% , n = 100 to 102 exposures)										
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).

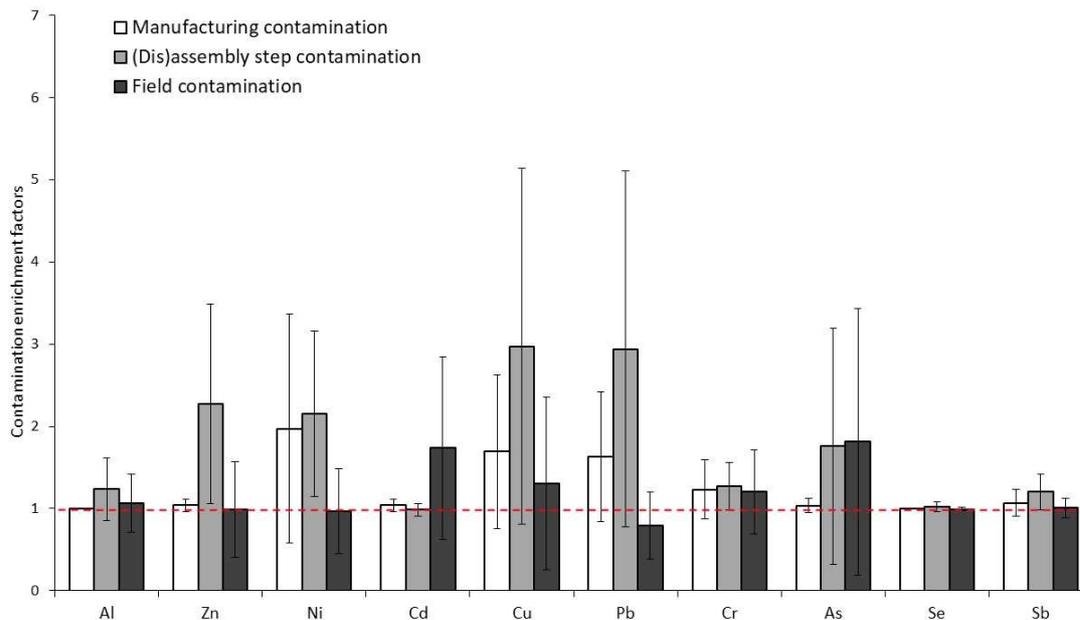


Figure 1 : Contamination enrichment factors between manufacturing, (dis)assembly and field steps for each metal/metalloid and campaign (average \pm SD; n = 6 campaigns).

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.

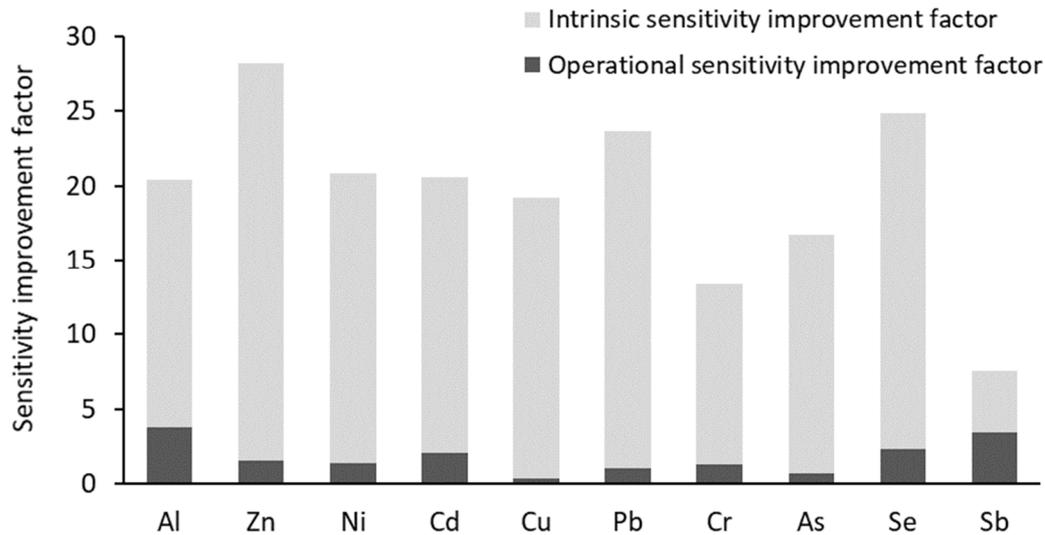


Figure 2: Intrinsic and operational sensitivity improvement factors for each metal/metalloid

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
Quantification frequency (% , n = 200 to 204 grab and DGT samplers)										
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
Site concentration trend using grab or DGT sampling (n = 17 sites)										
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%).

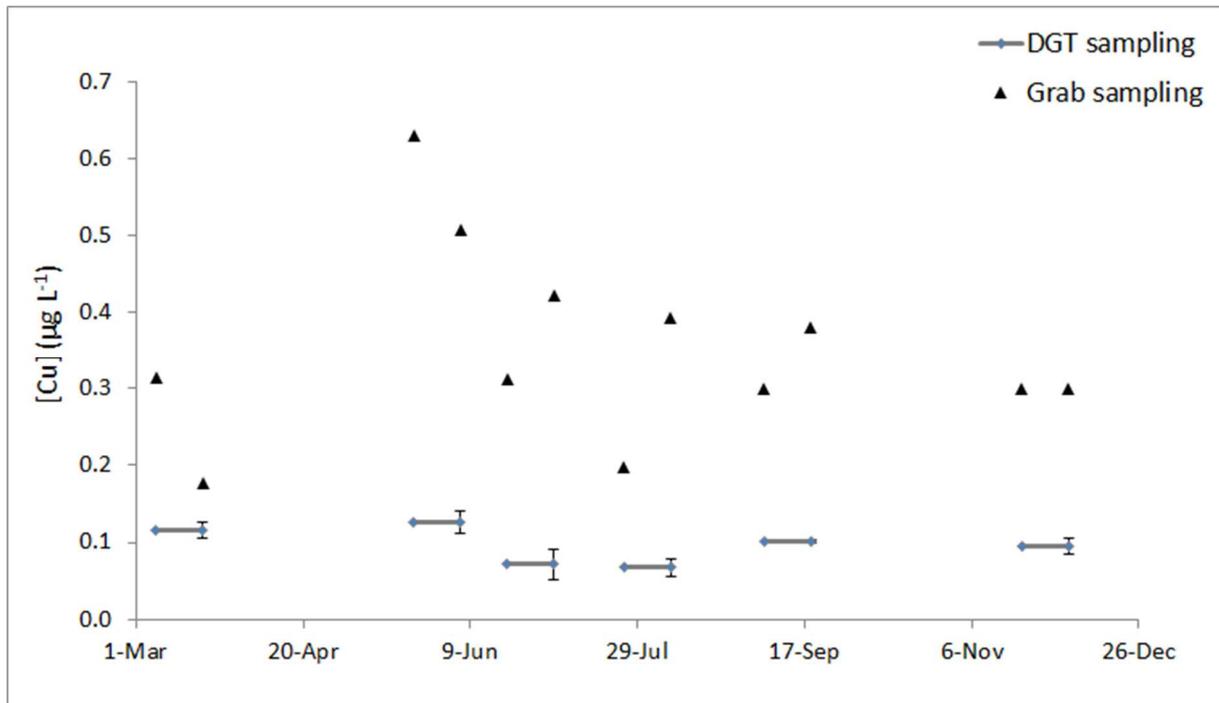
392 Lastly, for Se, the quantification frequency is low (around 20%) for both methods. The accumulating
393 capacities (operational sensitivity improvement around 2, Figure 2) for a field deployment of 14 days

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.

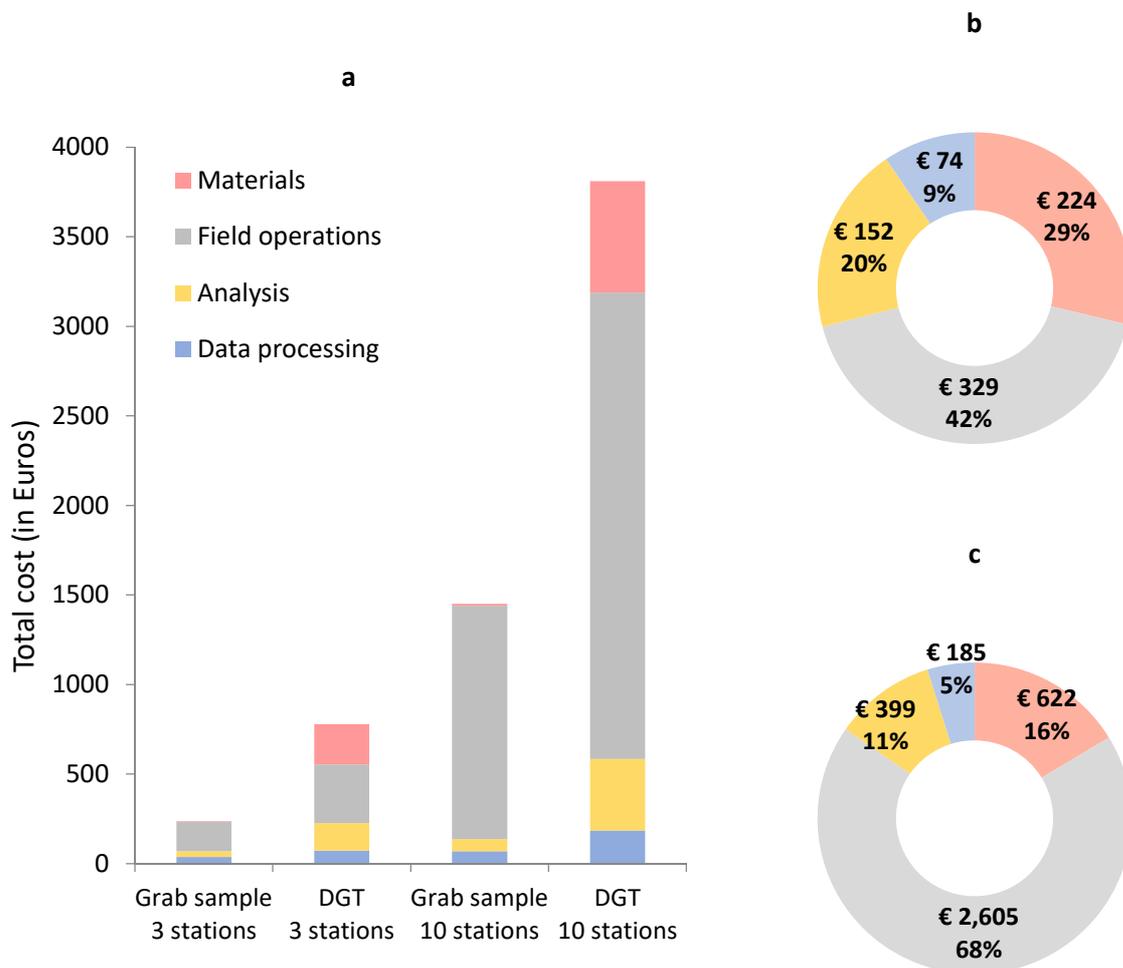
419 3.2.3. ECONOMIC STUDY

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

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