
An international intercomparison exercise on passive samplers (DGT) for monitoring metals in marine waters under a regulatory context

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Abstract :

In order to move forward in the acceptance of a novel contaminant monitoring technique (Diffusive Gradients in Thin-films: DGT) for assessment of marine water bodies, sensu the WFD, an Inter-Laboratories Comparison (ILC) exercise (nine Europeans laboratories) was organized in the framework of the Interreg Atlantic Area MONITOOL project, which focused on the use of the DGT technique for the measurement of WFD priority metals (Cd, Ni and Pb).

Reproducible results were obtained for each metal by several laboratories, supporting the assertion that DGT analysis can be performed satisfactorily by laboratories experienced in measuring metals at trace levels in marine environments, even if they have limited practice in DGT analysis.

According to the Z-score analysis, among the 9 participating laboratories, 3 had 100 % of satisfactory results for Cd, Ni, and Pb, 3 had >80 % satisfactory results and 2 had about 60 % satisfactory results.

This work highlights the need to clearly describe the DGT method in order to control sources of contamination during analytical steps, in particular the resin gel retrieval and the elution steps.

Such international intercomparison exercise is an important step to develop the laboratory network involved in DGT analysis and contributes to the improvement of data quality.

Graphical abstract

Participating laboratories Z-Scores for Cd, Ni and Pb (X-axis: participating laboratories anonymously represented by a number)



Highlights

► ILC European exercise focused on the use of DGT technique in the WFD framework. ► Participation of nine expert laboratories of the Interreg MONITOOL consortium ► All performance steps during processing and analysis of DGT samples were compared. ► Cd, Ni and Pb reproducible concentrations were obtained by most laboratories. ► DGT analysis can be performed acceptably by laboratories with relevant experience.

Keywords : Participating laboratories Z-Scores for Cd, Ni and Pb (X-axis: participating laboratories anonymously represented by a number)

57

58 **1. Introduction**

59

60 The European Water Framework Directive (WFD; 2000/60/EC) aims to achieve a good
61 ecological and chemical status for all European Union water bodies, including
62 transitional/estuarine and coastal waters. The assessment of the chemical status of a water
63 body is usually based on the collection of spot water samples and the comparison of the
64 concentrations of a list of priority substances, defined at European level, to the existing
65 Environmental Quality Standards (EQS; Directive 2013/39/EU). Regarding metals, annual
66 average and maximum allowable concentration EQS (AA-EQS and MAC-EQS) are expressed
67 as the mean or maximum dissolved (*i.e.*, 0.45 µm filtered water) concentration, respectively,
68 measured in 12-monthly spot water samples. This approach presents several shortcomings,
69 such as (i) the risk of contamination during the handling and pre-treatment (*i.e.*, filtration,
70 preconcentration, extraction) of water samples before analysis, notably when working at trace
71 levels, such as in marine waters, and (ii) the lack of representativeness of "one-off" samples,
72 especially in highly dynamic systems like transitional and coastal waters (Vrana *et al.*, 2005),
73 leading to the potential under/overestimation of real concentrations (Twiss and Moffett, 2002;
74 Dunn *et al.*, 2003; Vrana *et al.*, 2005; Allan *et al.*, 2006a,b).

75

76 Passive sampling technique has been proposed as a good solution to address these problems
77 and to obtain reliable time-integrated concentrations for the chemical assessment of water
78 bodies (Vrana *et al.*, 2005). This technique consists of the deployment of devices containing a
79 resin/polymer that presents a high affinity towards the compounds of interest. Passive
80 samplers (PS), while in the kinetic phase, accumulate contaminants continuously during the
81 deployment time, and enable the measurement of time weight averaged concentrations (TWA)
82 of contaminants. This technique enables the *in situ* measurement of solutes and reduces the
83 potential contamination of the samples, while lowering the limit of quantification (LOQ).
84 Moreover, the PS technique is based on the diffusion of contaminants and the accumulation

85 of the most labile species or forms, which is considered a better proxy of the potential
86 bioavailable concentration. Among PS, Diffusive Gradients in Thin-films (DGT; Davison and
87 Zhang, 1994) is the commonly used PS for the measurement of metals and has been applied
88 in a wide variety of aqueous environments (Zhang and Davison, 1995; Davison *et al.*, 2000;
89 Twiss and Moffett, 2002; Dunn *et al.*, 2003; Forsberg *et al.*, 2006; Lafabrie *et al.*, 2007; Schintu
90 *et al.*, 2008; 2010; Gonzalez *et al.*, 2013; 2015a, b; Montero *et al.*, 2012; Marras *et al.*, 2020;
91 Rodrigo Sanz *et al.*, 2021).

92 Trace metal concentrations in the marine environment have been monitored for years, often
93 determined on grab samples after filtration at 0.45µm (Kremling *et al.*, 1988; Fileman *et al.*,
94 1991; Cotté-Krief *et al.*, 2002; Boutier *et al.*, 2000; Lagerström *et al.*, 2013; Gao *et al.*, 2019;
95 Bersuder *et al.*, 2021; Caetano *et al.*, 2022). In this sense, the directive establishes that the
96 analytical methods used for compliance should present a maximum uncertainty of
97 measurement of 50% at the level of relevant EQS and a LOQ equal or below a value of 30%
98 of the relevant EQS. However, at low concentrations (i.e., at EQS level), any error introduced
99 during the sampling and processing of water samples (e.g., filtration, preconcentration),
100 especially when working at trace levels such as in marine waters, will represent a significant
101 proportion of the chemical originally present, introducing a high uncertainty in the process. This
102 is also true for DGTs, but the use of laboratory and field blanks, enables to reduce the
103 uncertainty associated to the potential contamination of the samples. In this sense, measured
104 DGT concentrations can be safely used when the DGT blanks account for less than 10% of
105 the concentration found in deployed DGTs (e.g., Buzier *et al.* 2014; Marras *et al.* 2020;
106 Rodríguez *et al.* 2021). At higher blank concentrations, subtraction could be considered if the
107 contamination among samples is reproducible (Dabrin *et al.* 2016).

108 However, apart from the importance of reducing the uncertainty associated to the potential
109 contamination of the samples, the application of PS techniques in a regulatory context, for the
110 assessment of the chemical status of water bodies (in the case of DGTs, assessing the most
111 labile forms of trace metals), is conditional on obtaining valid and internationally comparable
112 analytical results that provide relevant information to policy makers. It is therefore essential to

113 ensure the reliability of measurements carried out by the different laboratories involved in the
114 implementation of the WFD. Keeping this objective in mind, in 2011, an international standard
115 guidance on passive sampling in surface waters (ISO 5667-23: 2011, reviewed in 2016) was
116 released, specifying procedures for the determination of the concentration of metals and
117 organic compounds. However, this standard procedure provided little information on the
118 analytical criteria (handling, methodology) for the DGT technique. Thus, Inter-Laboratory
119 Comparison (ILC) exercises are essential to assess laboratories' capability in processing and
120 analysing DGT passive samplers. Accordingly, metallic compounds were measured, using
121 both DGT and Chemcatcher type PSs, in an intercomparison exercise in 2010; the only
122 European level ILC to evaluate both PS types (Miege *et al.*, 2012; Dabrin *et al.*, 2016). In that
123 ILC exercise, participants deployed their own passive sampling devices at two sites
124 (continental and coastal) and used their own methodology (*i.e.*, DGT conditioning, field
125 deployment and retrieval), analytical process (analyte extraction and analysis) and TWA
126 concentration calculation. Data were interpreted in the frame of the technical validation of the
127 method (NF T90-120). However, it was beyond the scope of that ILC (intending Dabrin *et al.*
128 (2016) ILC) to investigate which steps within the handling and analytical procedures introduced
129 these biases.

130

131 Therefore, in order to move forward in the acceptance of the DGT technique for the chemical
132 status assessment of marine water bodies, *sensu* the WFD, this ILC exercise was organized
133 in the framework of the Interreg Atlantic Area MONITOOL project (EAPA_565/2016). DGTs,
134 due to their integrative capacity, could be used for compliance checking with AA-EQS, but are
135 less suitable for comparison with MAC-EQS, because peak concentrations will be integrated
136 as accumulated mass in the sampler, but the timing and magnitude of the peak cannot be
137 specified (Smedes *et al.* 2010). Currently, among the four metals classified as priority
138 substances, only Cd, Ni and Pb have an AA-EQS which could be compared to the data
139 obtained by DGTs (*i.e.*, for Hg only MAC-EQS and Biota-EQS are available), and thus, this
140 ILC exercise will focus on these metals.

141

142 Nine expert laboratories of the MONITOOL consortium participated in this ILC exercise, which
143 aimed to identify the critical handling (resin gel retrieval and elution) and analytical steps when
144 working with DGT samplers, to establish recommendations to prevent misleading results. The
145 ILC experimental design consisted of the deployment by Ifremer of DGT samplers (all from the
146 same manufacturing batch and acquired from DGT® Research Ltd, Lancaster, UK) at a marine
147 site (Lazaret Bay, France) and the subsequent delivery to participants of these DGTs and DGT
148 components at various stages of handling and analysis, to enable a “step-by-step”
149 investigation of where biases are introduced. Specifically, the following were sent to
150 participants of: (i) exposed and fully intact DGT samplers (not opened), (ii) binding resin gels
151 of exposed DGTs samplers, already peeled off and placed in a dry elution tube, (iii) binding
152 resin gels of exposed DGT samplers, already peeled off and placed in an elution tube with acid
153 and (iv) laboratory blank DGT samplers (not opened) from the same batch as the exposed
154 DGT samplers.

155 The specific objectives were: i) to test the performance of laboratories when analysing DGTs
156 for trace metals; ii) to investigate the influence of the analytical steps in the results uncertainty
157 and ultimately; iii) to propose standardized practices to improve the reliability of the results.
158 This work also provides recommendations on the critical steps in the treatment process of DGT
159 samplers.

160

161 **2. Strategy of the intercomparison exercise and material analysed**

162

163 2.1. DGT principle and description

164

165 DGT passive samplers (DGT Research Ltd., UK) were firstly described by Davison and Zhang
166 (1994) for the measurement of trace metals in natural waters, and nowadays, their use has
167 been extended to sediments and soils. Detailed description of the DGT principles and use can

168 be found elsewhere (www.dgtresearch.com; Zhang and Davison, 2001). Briefly, the DGT
169 devices (for cationic metals) used in this study are composed of a ABS (Acrylonitrile Butadiene
170 Styrene) plastic holder presenting a 2 cm exposition window, and inside, hermetically closed,
171 there are three layers: a polyethersulphone filter membrane (0.45 μm pore-size), a
172 polyacrylamide hydrogel diffusive layer (0.76 mm-thick) and a Chelex-100 binding resin gel
173 layer (0.40 mm-thick). The passive samplers used were from DGT® Research Ltd (Lancaster,
174 UK), with the reference LSNM-NP open-pore Loaded DGT device for metals (A) in solution.
175 All DGTs used were from the same production batch to minimize differences related to
176 manufacturing. This technique is based on the diffusion of metals through a diffusive layer and
177 the accumulation of the most labile forms (*i.e.*, hydrated metal ions, inorganic complexes,
178 "small" organic complexes) in the binding resin, showing a high affinity towards the compounds
179 of interest.

180
181 DGTs are deployed in the water column, for several days or weeks, and after retrieval, DGT
182 devices are opened in a clean-air environment and the binding phase (Chelex 100 resin gel)
183 is peeled off and eluted with ultra-pure nitric acid (1M). Accumulated metals are determined in
184 the acidic eluates (C_e , $\mu\text{g/L}$) by ICP-MS (Inductively Coupled Plasma Mass Spectrometry), or
185 similar analytical technique, and measured concentrations are used for calculating the mass
186 (M) of metals accumulated in the binding resin (Equation 1):

187
188 Eq. 1
$$M = C_e(V_{Resin} + V_{HNO_3})/f_e$$

189
190 Where, V_{Resin} (0.16 mL) and V_{HNO_3} (mL) are the volume of the resin and the nitric acid used for
191 elution, respectively, and f_e (typically 0.8) is the elution factor.

192
193 2.2. Organisation and design of the ILC experiment

194

195 The ILC exercise was organised by Ifremer and nine expert laboratories of the MONITOOL
196 consortium participated: CEFAS (UK), AZTI (Spain), IPMA (Portugal), UNICA (Italy), DCU
197 (Ireland), Ifremer (France, 3 laboratories: LBCM, LERN and LERPAC) and ITC (Spain). The
198 names of these laboratories are hereafter replaced by a code number to preserve their
199 anonymity.

200 The DGT devices used for the measurement of cationic metals came from the same batch
201 provided by DGT Research Ltd. All the DGT packaging, deployment, retrieval, processing and
202 dispatching operations were carried out by a single partner, namely Ifremer (La Seyne sur mer,
203 France), which was also in charge of the cleaning of all the materials to reduce the
204 uncertainties related to this step. All the plastic equipment used for DGT field deployments
205 (DGT supports and storage/protection boxes), sample processing and analysis (tweezers to
206 collect resins, pipette tips, elution tubes) were soaked in 10% HNO₃ suprapur® acid for several
207 days, rinsed with ultrapure water (18.2 MΩ.cm) and stored in cleaned plastic bags. In total 130
208 DGT devices were deployed.

209
210 The ILC exercise was performed in the Lazaret Bay, located in South-Eastern France
211 (Mediterranean Sea), and DGT devices were deployed for 6 days (from 19/10 to 25/10/2018)
212 to obtain a concentration of metals accumulated in the resin (Eq. 1) significantly higher than
213 the LOQs and the blank values, while reducing the potential formation of biofilms. DGT
214 Research Ltd recommends deployment times between 3 and 21 days which is sufficient for
215 coastal waters and limits the potential formation of biofilm.

216 This area is characterized by the presence of shellfish production and aquaculture sites and it
217 is located near Toulon, a port city presenting one of the most important navy bases on the
218 French Mediterranean coast. The studied area is known for its high chemical contamination,
219 as demonstrated by its inclusion within the routine environmental monitoring network of the
220 area and a large number of research projects focused on this topic (Rossi and Jamet, 2008;
221 Tessier *et al.*, 2011; Dang *et al.*, 2015; Araujo *et al.*, 2019). Previous DGT results obtained in
222 this area showed concentrations around 10 ng/L, 300 ng/L and 70 ng/L for Cd, Ni and Pb,

223 respectively (Rodríguez *et al.* 2021; Caetano *et al.* 2022). Immersion of the DGTs for 6 days
224 allowed to concentrate these metals in the eluate (Eq.1), and after dilution for ICP-MS injection
225 (depending on the laboratories), by a factor of 5 to 10.

226
227 Further details of the processing of the DGT devices after field exposure can be found in
228 Bersuder *et al.* (2021). Briefly, after collection, DGT devices were rinsed with ultrapure water
229 and immediately stored in trace-metal cleaned plastic boxes or bags and brought back to the
230 laboratory for storage (4°C) until dismantling and resin gel elution.

231 DGT devices were handled under a laminar flow hood, in accordance with the requirements
232 for avoiding contamination issues when performing trace element analysis. Diluted nitric acid
233 (1M), for the extraction of the accumulated metals was prepared using suprapur® nitric acid
234 (Merck) and ultrapure water (18.2 MΩ.cm). The processing of DGTs involved the opening of
235 the DGT holders, the removal of the binding resin gel and its placement in a trace-metal free
236 2 mL elution tube and the addition of diluted suprapur® nitric acid (1M) to perform the elution
237 (at least 24 hours at room temperature) before analysis. Taking account of potential problems
238 such as sample loss, "Reserve" DGT devices (*i.e.*, laboratory blanks and deployed DGT
239 devices) were kept in the organizing laboratory, ready to be sent to participating laboratories,
240 if needed.

241
242 The optimization and the design of ILC exercise which allowed to identify the most critical DGT
243 processing and analysis steps are summarised in table 1.

244
245 The list of dispatched samples to each laboratory (identified by codes) is summarized in table
246 2. In order to enhance the comparability and the robust statistical analysis of results,
247 participating laboratories were asked to analyse a minimum of three replicates per testing
248 condition (DGT exposed, resin, eluate, DGT blank). However, a maximum number of samples
249 was not established, and laboratories were allowed to select the number of samples to be

250 analysed based on their capacities. All the DGT devices were processed and packaged under
 251 the same conditions to avoid uncertainties related to this step.
 252

Steps carried out by Ifremer laboratory (La Seyne)	Material sent to participating laboratories	Steps by participating laboratories	Possible contamination Risks
Deployment of DGTs (6 days) Retrieval of exposed DGT devices	Exposed DGT devices	Resin gel retrieval Resin gel elution (acid extraction) Trace metals analysis	Same as for "resin in elution tube" + DGT handling. Resin retrieval Tweezers "cleanliness"
Retrieval of resin gels from immersed DGTs Insertion in a "trace-metal clean" elution tube	Resin in an elution tube	Resin elution (acid extraction) Trace metals analysis	Same as for "eluate" + Elution step (reagents quality, pipette and elution tubes "cleanliness")
Resin gel retrieval Insertion in a "trace-metal clean" elution tube Resin gel elution (acid extraction)	Eluate	Trace metals analysis	"Lab Trace metals" environment No laminar flow hood Eluate handling Eluate dilution (reagents quality, pipette and dilution tubes "cleanliness")
DGT laboratory blank	DGT blank	Resin gel retrieval Resin elution (acid extraction) Trace metals analysis	Same as for exposed DGT devices

253
 254 **Table 1:** DGT handling steps for each supplied material and potential contamination sources.

255
 256 Participating laboratories did not receive any instruction or document about the processing or
 257 analysis of the received DGTs. The knowledge and equipment of the laboratories, in terms of
 258 DGT analysis, varied greatly from one laboratory to another (i.e. from no previous experience
 259 to more frequent and routine handling and analysis of DGTs), but all the laboratories are
 260 experts in marine chemistry (see Bersuder *et al.* 2021 for further details of the laboratories).
 261 With regard to the analytical capabilities, all the laboratories used ICP-MS for the analysis of
 262 metals (but depending on the models, their performance may be different), with the exception
 263 of one that used Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). One laboratory
 264 (Lab 9) encountered analytical problems and was not able to provide quantitative results.
 265

Lab code	DGT exposed unopened	Resin (DGTs exposed)	Eluates (DGT exposed)	DGT Laboratory Blank	TOTAL
1	10	4	4	7	25
2	10	6	6	4	26
3	3	3	3	3	12
4	3	3	3	3	12
5	14			6	20
6	5	5	5	5	20
7	7	3	3	6	19
8	8	5	4	6	23

266 **Table 2:** Laboratory codes (different from the order of participating laboratories listed above):
267 details of the number of DGT devices used and material sent (due to analytical problems
268 laboratory 9 could not provide results).

269

270 2.3 Applied methodology for the evaluation of the laboratory performance

271

272 The International Standard ISO 13528:2015 "Statistical methods for use in proficiency testing
273 by interlaboratory comparison" was used to analyse the obtained data and to guide the
274 interpretation in this specific proficiency testing context (Visser, 2006). Individual laboratory's
275 performance was expressed using Z scores (Eq. 2).

276

277 Eq. 2
$$z_l = \frac{(X_l - X_{ref})}{\sigma_{ref}}$$

278 Where: z_l is the Z-score value for laboratory L; X_l is the result reported by laboratory L; X_{ref} is
279 the consensus value (usually based on estimation of mean like median); σ_{ref} is the standard
280 deviation of the consensus value. Each laboratory's performance was evaluated according to
281 the generally accepted limits, fixing the performance evaluation of a laboratory as follows:
282 unsatisfactory ($Z_l > 3$), questionable ($2 < Z_l < 3$), satisfactory ($0 < Z_l < 2$).

283 Usually, reported DGT results are calculated as the mean of three replicates. Thus, each
284 laboratory sent their results for each replicate and the mean was calculated by Ifremer based
285 on the number of replicate results provided by each laboratory. When any value was below the

286 LOQ, half the value of the limit of quantification concerned was used for the calculation of
287 average values (QA/QC directive 2009/90 / EC, article 5).

288

289 **3. Results and discussion**

290

291 **3.1. Exposed DGTs**

292

293 The measured mass in exposed DGT devices, provided by each laboratory, are presented in
294 figure 1. Means and standard deviations of DGT replicates are presented for each step of the
295 analytical process (eluate, resin gel, not opened exposed DGT). The number of replicates per
296 analysis varied from 3 to 6. The number in each data marker indicates the number of replicates
297 for that data point. The LOQ of DGTs have been reported to be 0.1 µg/L for Ni, Cd and Pb
298 (Caetano *et al.*, 2022). The LOQ and LOD are calculated as the mean of at least 10 blanks
299 (MB) and the standard deviation (SD): $LOQ = MB + 10 \cdot SD$ and $LOD = MB + 3 \cdot SD$.

300

301 **Cadmium**

302 The results on eluate analysis were similar among the laboratories except for Lab 3 for which
303 a significantly higher mass of cadmium was reported. This discrepancy is an indication of
304 possible contamination that occurred during handling (operator and/or atmospheric
305 contamination), use of low-quality grade reagents, analysis measurements bias or a
306 combination of them. For all the laboratories (except Lab 3), there were few differences
307 between the cadmium results obtained for the eluates (Tab. 1) and those when the designated
308 laboratory performed the elution. However, overall, there was an increase in the mass
309 measured by most laboratories with an increase in the number of steps performed by
310 themselves. This trend was more pronounced for laboratories 1 and 7, presenting a high
311 variability among replicates, especially when they performed all the steps of the process (*i.e.*,
312 DGT opening, elution and analysis). This suggests possible contamination during the opening

313 of DGT devices and/or the binding resin retrieval step, due to atmospheric and/or handling
314 contamination.

315 The reproducibility of the DGT results for “eluates” and “resins” was good, showing that the
316 elution and analysis steps are mastered by the laboratories.

317

318 **Nickel**

319 Results for nickel show the same trend as for cadmium. The mass measured by the
320 laboratories for the “eluate” and “resins” were very similar. In contrast, the results provided by
321 Labs 1, 2, 6 and 7 showed higher mass values, and with high variability (> 40%) among
322 replicates, when these laboratories carried out all the process. This suggests a significant
323 contamination of Ni during the opening of DGT devices and/or the binding resin gel retrieval
324 step.

325

326 **Lead**

327 Lead presented the most pronounced increase in the measured analyte mass with increasing
328 number of steps performed by the laboratories. Moreover, for Labs 1, 6, 7 and 8, significant
329 results variation was observed at different steps. For Lab 6, a poor reproducibility was
330 observed for the eluate analysis, while this was not observed for the “resin” or “exposed DGT”.
331 Similarly, for Lab 1, poor reproducibility was observed for the “exposed DGT” but not for the
332 other steps. For Lab 8, the poor reproducibility was observed only for the “resin”, while for Lab
333 7, this was observed at both, “resin” and “exposed DGT” steps. The other Labs (2, 3, 4, 5)
334 presented similar mass values and good reproducibility.

335

336

337

338

339

340

Material sent to participating laboratories

<i>Eluate</i>	<i>Resin in an elution tube</i>	<i>Exposed DGT</i>
Steps realised by participating laboratories		
<i>Analysis</i>	<i>Elution Analysis</i>	<i>DGT opening Resin retrieval Elution Analysis</i>

Contamination Risks (see Table 1)

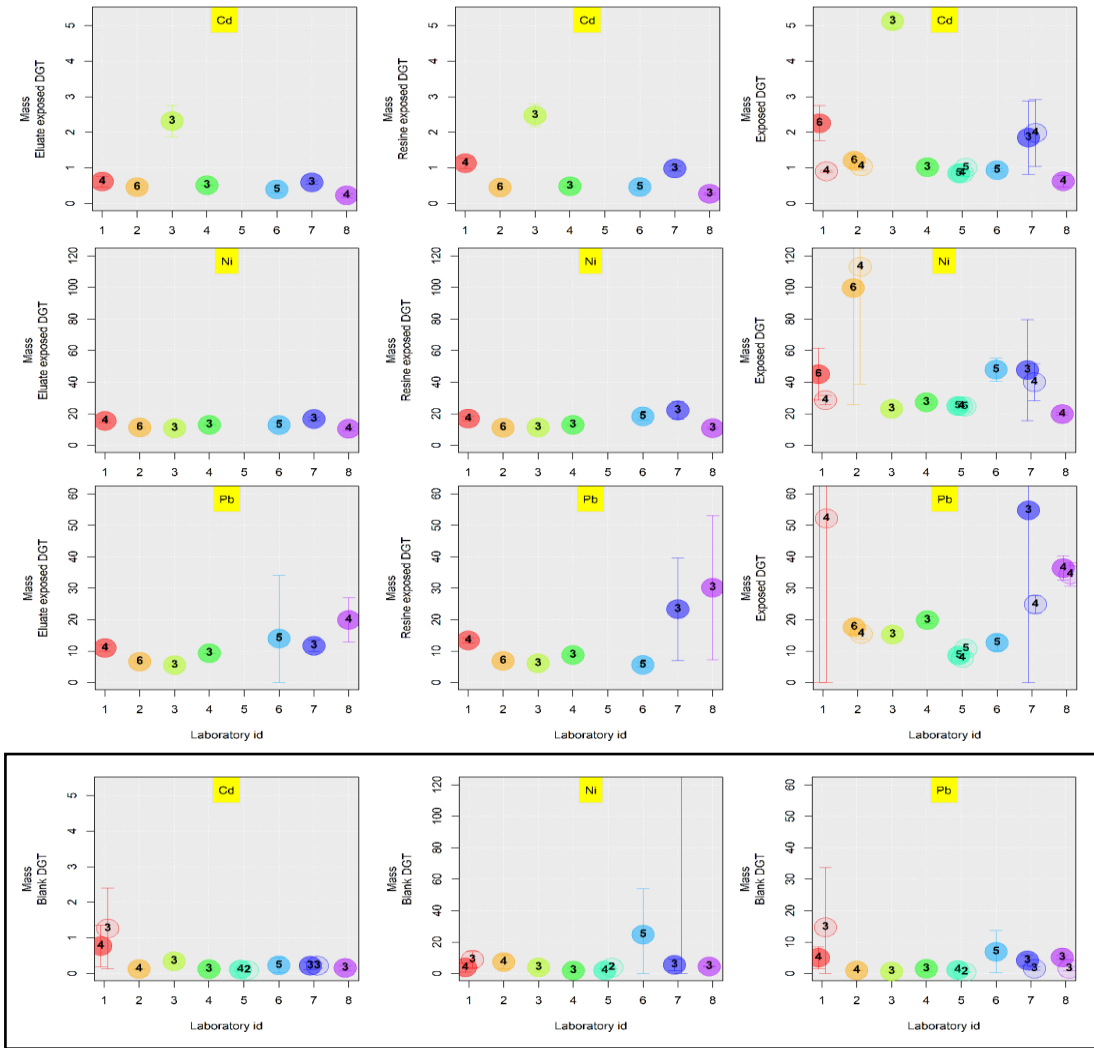


Figure 1: Results for Cd, Ni and Pb (mass in ng). X-axis: participating laboratories, anonymously represented by a number. The number shown inside the markers indicates the number of replicates used by the laboratory for analysis. Two dots for one lab indicates the use of "reserve" DGT devices (see 2.2.). The bottom figure shows mass results (in ng) measured in blank DGTs (dot outside the graph: the mean value of Ni measured by laboratory 7 in the "reserve" DGTs is 161.5 ng with a standard deviation of 140%).

366 3.2. Z-scores

367

368 In order to identify critical steps (“eluate”, “resin” or “exposed DGT”), the performance of each
369 laboratory was assessed by assessing the Z-scores (Tab. 3 and Fig. 2) obtained at each step
370 of the analytical process (“eluate”, “resin” and “exposed DGT”).

371

372 Considering that some participants did not have much experience processing and analysing
373 DGT samples, metal results were highly variable, showing significant discrepancies among
374 participating laboratories (following ISO 13528 guide for the visualization of normality).
375 Consequently, the reference values (consensus value and standard deviation) were
376 determined using robust statistics, which limit the biases linked to outliers. Accordingly, the
377 Algorithm A, proposed by the ISO 13528: 2015 guide, was used, which provides robust
378 estimates of the mean (consensus value) and standard deviation of the data owing to the
379 replacement of identified outliers by successive iteration until a convergence level (here set at
380 10⁻⁴).

381

382 Regarding the analysis of eluates, it was found that 95% of the results provided by the
383 laboratories were satisfactory. This was reduced to 81% when laboratories carried out the
384 elution of the resin and to 77% when they performed the complete process, that is, the opening
385 of DGT devices, the resin retrieval and the elution (Tab. 3). Therefore, the opening of DGTs
386 and the retrieval of the resin were identified as the most critical steps in the process.
387 Accordingly, among the 14 unsatisfactory and questionable results, the major part (9 results)
388 corresponded to the unopened exposed DGTs, where the laboratories had to open the DGT
389 devices themselves for resin gel retrieval.

390

391

392

393

394

Contamination Risks (see Table 1)

395

	Eluate	Resin	Exposed DGT
Satisfactory results	6 (Cd) 7 (Ni) 7 (Pb)	6 (Cd) 6(Ni) 5 (Pb)	9 (Cd) 11 (Ni) 11 (Pb)
Questionable results		1 (Ni) 1(Pb)	1 (Cd) 2 (Pb)
Unsatisfactory results	1 (Cd)	1(Cd) 1 (Pb)	3 (Cd) 2 (Ni) 1 (Pb)
Proportion of satisfactory results among all analysis results	95 %	81 %	77 %

396

Table 3: Z-score results obtained at each step of the analytical process.

398

399 Cadmium

400 For Lab 3 (Fig. 2), Z-scores were very high regardless of the analytical step, presenting a
 401 constant offset in the results, which was most likely due to contamination during handling
 402 and/or systematic uncorrected analytical bias. Additionally, in the case of “exposed DGTs”,
 403 Labs 1 and 7 presented very high Z-scores, suggesting the contamination of the samples
 404 during the first step of DGT processing (*i.e.*, DGT opening and/or resin gel retrieval).

405

406 Nickel

407 Compared to Cd, less variability was observed in the Z-scores of the laboratories for Ni (Fig.
 408 2). However, Lab 2 obtained very high z-scores for nickel, but only in “exposed DGTs”,
 409 suggesting a contamination during the first step of the DGT processing (*i.e.*, DGT opening
 410 and/or resin gel retrieval). It was also observed that the z-score for the “Resin” analysis of Lab
 411 7 was in the warning zone, whereas values for the “Eluate” and the “Exposed DGT” were lower
 412 and within the acceptable range. These results suggest a one-off contamination event during
 413 the analysis of these samples.

414

415 **Lead**

416 Regarding lead (Fig. 2), the assessment of the obtained Z-scores suggests no particular issues
417 during the analysis of the “Eluate” for all the participating laboratories. However, several
418 laboratories (Labs 1, 7 and 8) presented high Z-score values, considered as questionable or
419 unsatisfactory results when analysing “Resin” and/or the “Exposed DGT”. This was most likely
420 due to eluting acid contamination and/or during sample handling.

421

422 3.3. DGT laboratory blanks

423

424 When performing the quality control of obtained results, two methods are commonly used to
425 account for the blank values (Lalère *et al.*, 2017). In the first approach, the blank value is
426 subtracted from the result of the sample analysis. This correction can be implemented when
427 the blank samples are handled and analysed in the same way as the samples, and thus,
428 account for the whole procedure contamination (namely “procedural blank”). Good practice is
429 to evaluate the blank reproducibility by measuring several independent blank samples
430 (equivalent to 10% of the total samples number or at least 3 blank replicates). In the second
431 approach, the blank value is not subtracted from the result of the sample analysis, because it
432 only reflects the contamination that occurred during one or more steps of the analytical
433 process, but does not represent the whole procedure. In this case, the reported value for a
434 sample cannot be less than the blank value, and the LOQ must take this into account.

435

436 Regarding the DGT data treatment, it is rarely possible to use the first approach (*i.e.*,
437 subtraction), since in most cases the minimum conditions are not fulfilled (*i.e.*, stable and
438 reproducible blank values). Therefore, it is recommended to verify that the difference between
439 the blank values and the sample results is large enough, so that not performing the blank
440 “correction” of the data would not affect significantly to the reported results (e.g., blank value
441 is < 10% of sample concentration).

442 The results of the previous DGT intercalibration exercise (Miege *et al.*, 2012; Dabrin *et al.*,
443 2016) showed rather high uncertainties in the estimation of the DGT blanks concentrations.
444 Besides, in the current study it was observed that the large variation and differences in the
445 results obtained by the laboratories could mainly be explained by the contamination that
446 occurred during DGT handling and/or analytical steps. However, it is important to discern the
447 role of DGT blanks in the observed differences; whether they represent a source of bias or a
448 negligible effect.

449 When considering the potential contamination of blank DGT devices, two main routes should
450 be considered. On the one hand, DGT handling (in the laboratory and the field) could be critical
451 for some elements (especially for Pb and Zn that are often present at high concentrations in
452 ambient air), requiring that the use of blanks is performed in very clean conditions in the
453 laboratory (e.g., under laminar flow hood) and taking many precautions in the field (e.g.,
454 wearing gloves, minimizing air exposure time), in the same fashion as is done for DGTs that
455 are to be immersed/retrieved from water. On the other hand, DGT devices can also be
456 randomly contaminated during manufacturing (e.g., Zn), which generates inconsistent blank
457 levels and leads to a significant variability of the results (i.e., Munksgaard *et al.*, 2003; Uher *et*
458 *al.*, 2013; Desualty *et al.*, 2015; Dabrin *et al.*, 2016). This is the reason why two types of blanks
459 are usually analysed when using DGT passive samplers; laboratory blanks (i.e., unexposed
460 DGTs) and field blanks (i.e., air-exposed at each stage of DGT handling in the field and in the
461 laboratory). However, in this ILC study only laboratory blanks were analysed and assessed, in
462 order to better evaluate the potential contamination of DGT devices during the opening stage,
463 especially when performed by each laboratory.

464

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469

Material sent to participating laboratories

<i>Eluate</i>	<i>Resin in an elution tube</i>	<i>Exposed DGT</i>
Steps realised by participating laboratories		
<i>Analysis</i>	<i>Elution Analysis</i>	<i>DGT opening Resin retrieval Elution Analysis</i>

Contamination Risks (see Table 1)

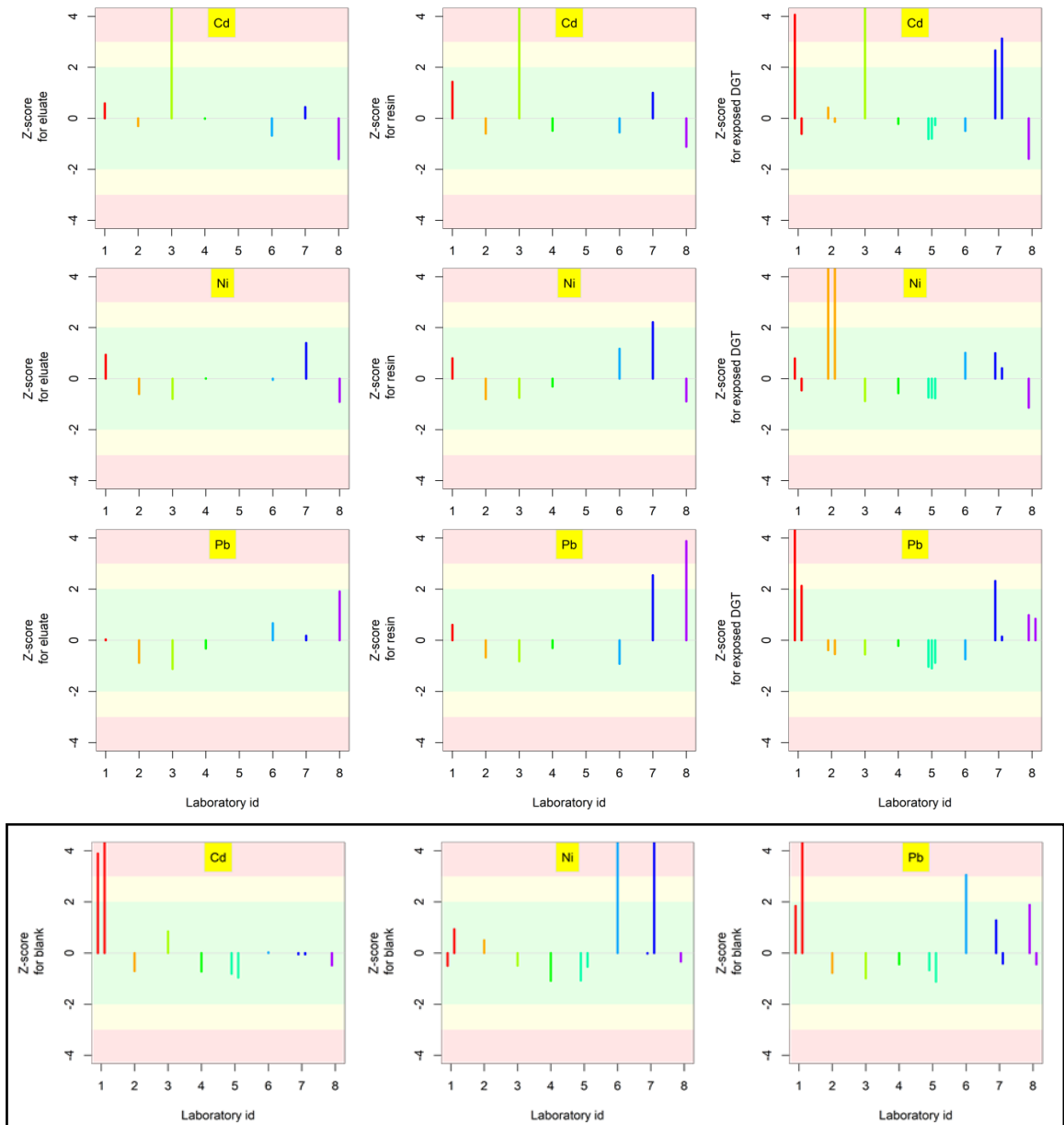


Figure 2: Participating laboratories Z-Scores for Cd, Ni and Pb (X-axis: participating laboratories anonymously represented by a number). The bottom figure shows blank DGTs Z-scores.

494 For most laboratories, the reported Cd, Ni and Pb mass values in resin blanks were very low
 495 (Fig. 1: Cd 0.1-1 ng; Ni 1.8-15.7 ng; Pb 0.6-5.5 ng) compared to exposed DGTs (Fig. 1: Cd
 496 0.6-5.1 ng; Ni 19.7-65.1 ng; Pb 9.1-35.4 ng). Although the majority of laboratories performed
 497 adequately even at low Cd, Ni and Pb concentrations, a great variability of the results (Fig.2)
 498 was observed for some of the metals in the case of Labs 1 (Cd and Pb), 6 (Ni and Pb) and 7
 499 (Ni). In any case, for the 3 metals under study, more than 80% of the results presented
 500 satisfactory Z-scores.

501 In order to assess the weight of blank values relative to the exposed DGT devices, the
 502 significance of DGT blanks was evaluated by R% ($R\% = \text{DGTBlank} / \text{DGTexposed} * 100$) in
 503 figure 3.

504 Regarding Cd and Pb, the R% results show (Fig. 3) that for the majority of laboratories (6 out
 505 of 8) the blanks represented around 10% or less of the accumulated amount in DGTs
 506 immersed during 6 d. It is for Ni that the weight of blanks is much more significant and
 507 problematic. There are only 3 laboratories which have R% of around 10% or lower. One of the
 508 possible explanations for these high values could be important background during the ICP-MS
 509 analysis due to skimmer cone. As a comparison, the data obtained by Dabrin *et al.* (2016)
 510 indicate R% values of 12% for Ni, 21% for Pb and 72% for Cd. This high value for Cd could be
 511 explained by a contamination already present in DGTs (contamination of the resin during its
 512 manufacturing) and/or a contamination during the elution handling steps.

513

514

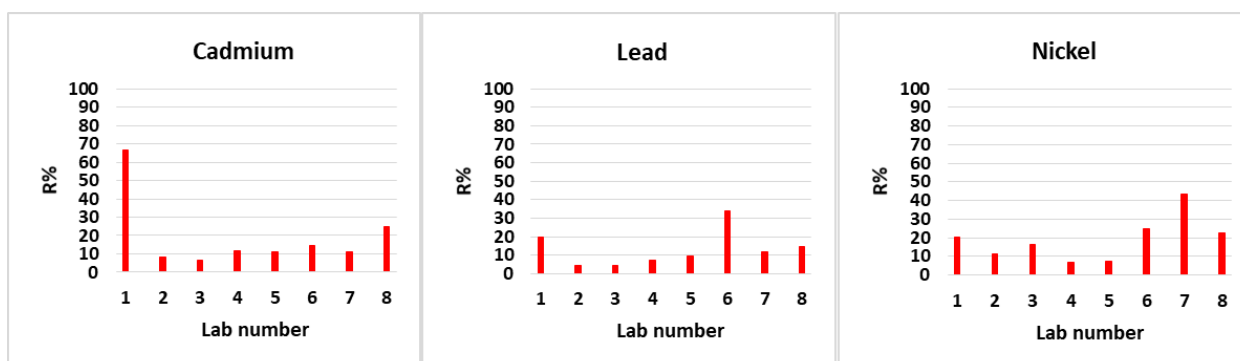
515

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519



520 **Figure 3:** DGT blanks importance given by R% (X-axis: participating laboratories anonymously
521 represented by a number). $R\% = \text{DGTBlank} / \text{DGTExposed} * 100$ (DGTExposed: steps realised
522 by participating laboratories: resin recovery; elution; analysis).

523

524 **4. Conclusions and Recommendations**

525

526 This inter-comparison exercise (ILC) aimed to assess the performance of nine participating
527 laboratories when analysing DGTs for trace metals and to identify the steps increasing the
528 biases of the obtained results, in order to propose standardized practices towards the use of
529 DGTs in a regulatory context. Most of the participating laboratories (80%) had no prior
530 experience in processing DGT devices for analysis, but they were experienced in measuring
531 traces metals in water. Therefore, this ILC exercise was the first opportunity to compare the
532 step-by-step performance of laboratories during DGT processing and analysis.

533 Regarding blanks, the majority of laboratories performed adequately even at low Cd, Ni and
534 Pb concentrations and measured values only represented a small part of the mass
535 accumulated in deployed DGTs, enabling their use for reducing the uncertainties associated
536 to potential contamination episodes. The ILC showed that blank values should be used as
537 systematic "quality controls" to be checked for the three studied metals (Cd, Ni, Pb).

538 In the case of deployed DGTs, the analysis was done satisfactorily by 8 labs out of 9, even if
539 they did not have previous experience in DGT analysis. However, according to the Z-score
540 analysis, increasing variability in the results was observed when increasing the number of
541 steps in the DGT processing. Most of the unsatisfactory or questionable results (9/14)
542 concerned the "exposed DGT", suggesting that DGT-handling and retrieval of the resin gels
543 can be important sources of contamination if not performed carefully. These critical steps must
544 be optimized to reduce contamination sources (e.g. by using Teflon coated tools for DGT
545 opening and resin gel recovery, wearing protective sleeves above lab coat cuffs, improving
546 clean bench air circulation, avoiding underflow hand positions, reducing manipulation time ...).

547 This work also highlights the need to clearly describe the DGT method to control sources of
548 contamination during the analytical steps such as the resin gel retrieval and the elution step.
549 To move in this direction and to contribute to disseminating sound practice methodology, the
550 experience gained in this ILC exercise has been incorporated in different methodological
551 protocols (Bersuder *et al.*, 2021; Millán Gabet *et al.*, 2021) and operational tutorials (accessible
552 in <https://ccem.ifremer.fr/en/News/Passive-Samplers>; www.monitoolproject.eu). Such ILC is
553 an important step to develop the laboratory network involved in DGT analysis and it contributes
554 to the improvement of data quality and further validation of the technique.

555

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609 **Declaration of competing interest**

610

611 The authors declare that they have no known competing financial interests or personal
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613

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