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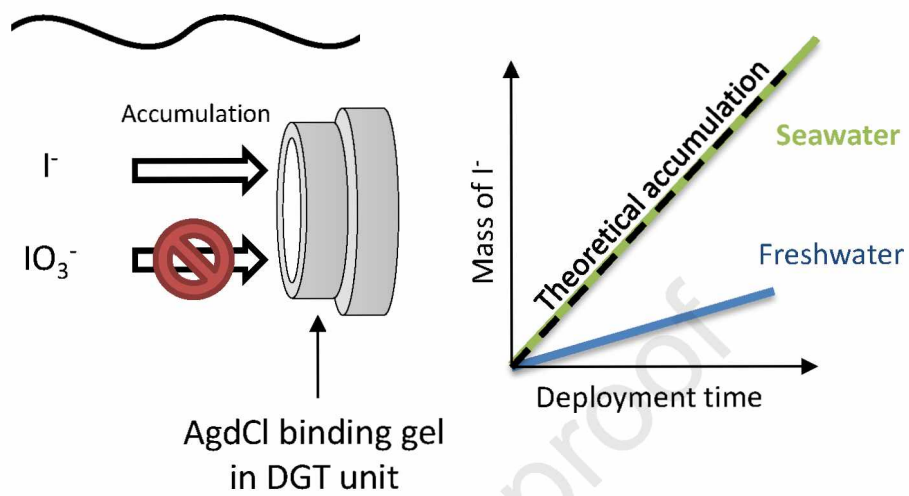
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Graphical abstract:



1 **Dissolved iodide in marine waters determined with Diffusive**
2 **Gradients in Thin-films technique.**

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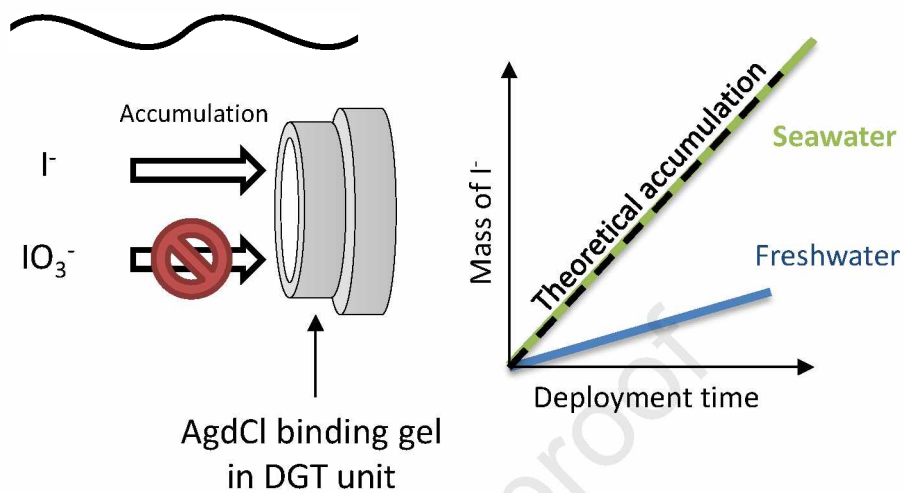
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12 **Graphical abstract:**

13

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15 Keywords:

16 Iodine; Redox speciation; Diffusive Gradients in Thin-films; Time-series experiment; Laboratory
17 validation; Iodide; Marine waters.

18 Highlights:

- 19 - A new DGT binding gel is proposed for selective iodide sampling.
- 20 - The diffusion coefficient of I species through agarose diffusive gel is reported.
- 21 - A DGT equation is developed to simultaneously consider DBL and kinetic effects.
- 22 - The method was successfully applied to measure iodide concentrations in seawater.

23 Abstract

24 For the first time, Diffusive Gradient in Thin-films (DGT) focuses on the inorganic iodine species
25 iodate (IO_3^-) and iodide (I^-). A silver-doped Cl resin (AgdCl), which is known to selectively
26 accumulate I^- , was used to make a binding gel. Laboratory investigations were designed to verify
27 the suitability of the AgdCl -DGT method to measure the total I^- concentration in environmental
28 waters. Total recovery of I^- was obtained using an elution solution containing 100 mmol L^{-1}
29 KCN . DGT validation experiments in 10 mmol L^{-1} NaCl showed linear accumulation of I^- over
30 time, contrary to IO_3^- , thus confirming the selectivity of AgdCl -binding gel. The AgdCl -DGT
31 measurement of total I^- concentration was independent of pH (4.5 – 8.8) and was not impacted by
32 the presence of bicarbonate ($1\text{-}5 \text{ mmol L}^{-1}$). Finally, the performance of AgdCl -DGT samplers
33 were tested in two continental waters and a synthetic seawater. The AgdCl -DGT samplers
34 measured 27-33 % of the total I^- concentration in the two continental waters up to 24 h of
35 deployment time, whereas the AgdCl -DGT response retrieved the total I^- concentration in
36 seawater up to 72 h ($106 \pm 7 \%$). The difference in DGT response was attributed to the low ionic
37 strength of the two continental waters, limiting the application of AgdCl -DGT method to media
38 with higher ionic strength.

39 1. Introduction

40 Natural iodine (I) is composed of the stable isotope ^{127}I and the long-lived beta-emitting
41 radioisotope ^{129}I ($t_{1/2} = 15.7 \times 10^6$ years), which is mainly produced by nuclear activities (uranium
42 and released plutonium fission in the environment especially by fuel reprocessing plants) [1].
43 Indeed, the $^{129}\text{I}/^{127}\text{I}$ ratio can reach 10^{-8} - 10^{-6} in marine waters at the vicinity (<50 km) of
44 European fuel reprocessing plants, values significantly higher in comparison of the representative
45 ratio commonly considered in the hydrosphere (1.5×10^{-12}) [2]. The behaviour and the transfer
46 between compartments of ^{129}I highly depends on its speciation, which thus must be taken into
47 account to assess short- and long-term consequences of ^{129}I releases.

48 Iodine is occurring as a redox sensitive trace element in environment with concentration
49 generally lower than $100 \mu\text{g L}^{-1}$ (for the stable isotope) [3-8]. Data on its speciation are generally
50 restricted to surface seawater environment, in which the most common I species found are iodide
51 (I^-), iodate (IO_3^-) and dissolved organic iodine [9-12]. In contrast, few data are available on the
52 behavior of I species at the water-sediment interface. These ones are mainly documented in
53 marine environment, where total I concentrations are the most elevated [13-15], reflecting the
54 high level of difficulty to analyze its speciation at very low concentration in continental
55 environment. One solution to overcome these difficulties in aquatic environment is to use passive
56 samplers, which concentrate the analyte of interest. Here, we propose to use the Diffusive
57 Gradient in Thin film (DGT) technique, which is a passive sampling technique [16, 17]. The
58 DGT sampling allows the preconcentration of the target species, leading to the improvement of
59 their determination by chemical analysis. Nowadays, the development of DGT method permits to
60 partially or totally access the redox speciation of the following elements: As [18-20], Br [21], Cr

61 [22-24], Hg [25, 26], N [27-29], P [30], S [31, 32], Sb [33, 34], Se [35] and V [36]. But, to best of
62 our knowledge there is no DGT method for I species.

63 In this study, we have investigated the possibility to develop a binding gel able to accumulate
64 specifically I. The silver-doped Cl resin, developed by Triskem international
65 (<https://www.triskem-international.com/>) has been tested as an adsorbent phase. It was already
66 used to preconcentrate I in extraction chromatography, due to its strong interaction with silver
67 [37, 38]. Laboratory validation experiments were designed: (i) to find an inert filter membrane
68 and diffusive gel to make DGT samplers; (ii) to define the selectivity of the new binding gel for
69 inorganic I species in the presence of potential competing ions (Cl^- and SO_4^{2-}) from batch
70 experiments; and (iii) to evaluate its performance in DGT in synthetic and natural matrices
71 (selectivity, effect of pH, intrinsic capacity, carbonate interferences, continental and marine
72 waters).

73 2. Experimental section

74 2.1. Reagents, materials and solutions

75 All the solutions were prepared with deionized water (18.2 M Ω cm resistivity, Milli-Q water,
76 Millipore). The polypropylene plastic containers were acid-cleaned in 1.5 mol L⁻¹ HNO₃ solution
77 over 24 h, then rinsed several times with deionized water prior to DGT sampler deployment. The
78 following chemicals were used: agarose (Bio-rad), AgNO₃ (VWR), KCN (VWR, normapur), HCl
79 (Merck, Emsure 37 %), HNO₃ (VWR Chemicals, Normapur 68 %), KI (VWR, normapur), NaCl
80 (Merck, suprapur), Na₂SO₄ (Merck, suprapur), NaOH (Merck, normapur), NH₃ (Merck, utrapur
81 20 %), cellulose acetate (CA; Sartorius, 0.45 μm pore size), polycarbonate (PC; Pall, 0.45 μm
82 pore size), polyester sulfone (PES; Pall, 0.45 μm pore size) and polyvinylidene fluoride filter
83 discs (PVDF; Merck Durapore, 0.45 μm pore size). Concerning standard solutions we used IO₃⁻

84 solution (1 g L^{-1} ; conditioned in deionized water; VWR), anions chromatography solution
85 including Cl^- , Br^- , NO_3^- , NO_2^- , I^- , SO_4^{2-} and PO_4^{3-} (100 mg L^{-1} ; conditioned in deionized water;
86 VWR), acidified Te and Pt solution (1 g L^{-1} ; VWR).

87 **2.2. Gel preparation and DGT assembly**

88 Agarose (AGE) and agarose-polyacrylamide (APA) diffusive gel were made as in [39] and [40],
89 respectively. The diffusive gel was stored in $10^{-2} \text{ mol L}^{-1}$ ultrapure NaCl solution. The thickness
90 of diffusive gel was $800 \mu\text{m}$, value controlled with an optical microscope as in [39]. The binding
91 layer was constituted by an Ag^+ loaded Cl resin (AgdCl) embedded in agarose gel. The Cl resin
92 ($50 - 100 \mu\text{m}$) was provided by Triskem international. The AgdCl resin was prepared by
93 contacting 1 g of the Cl resin with 10 mL of 10 mg mL^{-1} AgNO_3 solution in an orbital shaker
94 over a period of 2 hours. During this step, the color of the Cl resin changed from white to beige.
95 Then, the AgdCl resin was rinsed with $80 - 100 \text{ mL}$ of ultrapure water in a polypropylene
96 column connected to a vacuum box (Triskem international). The interstitial water was eliminated
97 by increasing pressure to the maximum in the vacuum box. Finally, the AgdCl resin was mixed
98 with 10 mL of 1.5% (w/v) hot agarose solution. This mixture was, then, poured between two hot
99 glass plates ($50 \text{ }^\circ\text{C}$) separated by a 0.8 mm Teflon plastic spacer at room temperature for at least
100 30 minutes. Once binding gel was completely polymerized, it was removed from the glass plates,
101 rinsed three times to remove unreacted reagents (during 24 hours), and placed into ultrapure
102 water bath (2 weeks maximum). The AgdCl binding gel, the diffusive gel and the filter were then
103 assembled in a piston-type ABS DGT sampler with a sampling area of 3.14 cm^2 (DGT Research
104 Ltd).

105 **2.3. Analytical procedures**

106 Total iodine concentration was measured by Inductively Coupled Plasma –Mass Spectrometry
107 (ICP-MS; Agilent 8800). The ICP-MS was equipped with a PFA concentric nebulizer (ESI), a
108 double-pass PFA spray chamber cooled at 2°C, a PFA T-piece with an internal solution, a
109 demountable torch with a sapphire injector, and Ni cones. ICP-MS spectrometer was calibrated
110 using freshly standard solutions following a matrix-matching procedure between samples and
111 standard solutions (*i.e.*, 150 mmol L⁻¹ NH₃ for basified water samples and 10 mmol L⁻¹ KCN for
112 eluent solution). Internal standard (¹²⁵Te in 150 mmol L⁻¹ NH₃ for basified water samples [4] or
113 ¹⁹⁵Pt (element selected due to its stability in cyanide media [41]) in 10 mmol L⁻¹ KCN for eluent
114 solution) was used to correct for instrumental signal drift of ICP-MS over time; the concentration
115 of the internal standard concentrations was adjusted to obtain 50000 – 70000 cps at m/z 125 or
116 195.

117 Speciation measurement was carried out on filtered water samples by chromatographic separation
118 using a Metrohm 940 Professional IC Vario Ion Chromatography (IC) system. The
119 chromatographic system was equipped with Metrosep A Supp 10 guard column (4.6 µm particle
120 diameter, 2 mm i.d. × 5 mm) coupled with a Metrosep A Supp 10 analytical column (4.6 µm
121 particle diameter, 2 mm i.d. × 250 mm), a 20 µL PEEK injection loop, a thermostatic column
122 oven set at 35 ± 0.1°C, a mobile phase containing 50 mmol L⁻¹ NH₄NO₃ (pH 5.5 ± 0.1), a PEEK
123 capillary (15 cm) connecting the column outlet to the nebulizer of ICP-MS. The flow rate of
124 mobile phase was fixed at 250 µL min⁻¹. Standard solutions were freshly prepared in deionized
125 water. The chromatographic conditions were developed in partnership with Metrohm France (see
126 section S1-S5, Figure S1-S4, Table S1 and S2 in supplementary information).

127 Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES; Thermo iCAPTM 7400,
128 axial view) was used to evaluate the uptake capacity of AgdCl-DGT sampler for inorganic I
129 species (section 2.5.5). Standard solutions were prepared as for ICP-MS calibration.

130 **2.4. Experiments with DGT components**

131 **2.4.1. Reactivity of filter, diffusive gel and DGT plastic holder**

132 Before performing DGT experiments, the reactivity of common diffusive gel (AGE and APA),
133 filter membrane (CA, PC, PES and PVDF) and ABS-DGT plastic holder was tested regarding
134 inorganic I species. Batch experiments were performed with each component immersed in 20 ml
135 of solution containing 25 $\mu\text{g L}^{-1}$ of IO_3^- or I^- . Experimental solution was vigorously shaken for 24
136 h using an orbital shaker. Filtered batch solutions were, then, basified with ultrapure NH_3 at 150
137 mmol L^{-1} before elemental analysis. The recovery of inorganic I species (R , %) in immersion
138 solution was calculated using the following equation (Eq. 1).

$$R = \frac{M_f}{M_i} \times 100 \quad \text{Eq. 1}$$

139 where M_i and M_f are respectively the initial and final mass (μg) of inorganic I species in
140 deployment solution.

141 **2.4.2. Reactivity of binding gel**

142 The first step was devoted to define the uptake capacities of inorganic I species by the AgdCl-
143 binding gel to confirm the possibility of using it as a new DGT binding gel. The affinity of
144 inorganic I species with AgdCl binding gels were examined by batch experiments with 20 mL of
145 solution containing 100 $\mu\text{g L}^{-1}$ of IO_3^- or I^- where one binding gel was immersed to float freely.
146 The experiments were performed at various ionic strength ($[\text{NaCl}]$ or $[\text{Na}_2\text{SO}_4] = 1 - 500 \text{ mmol}$
147 L^{-1} ; $\text{pH } 5.5 \pm 0.1$). The solution was vigorously shaken for 24 h with an orbital shaker. Filtered

148 batch solutions were, then, basified with ultrapure NH_3 at 150 mmol L^{-1} before elemental
149 analysis. The uptake factor (f_u , %, Eq. 2) was calculated from the initial mass of inorganic I
150 species in the deployment solution (M_i , μg), and the remaining mass of iodine species (M_f , μg):

$$f_u = \frac{M_i - M_f}{M_i} \times 100 \quad \text{Eq. 2}$$

151 The second step was to find a suitable eluent solution that could quantitatively recover the
152 inorganic I species from AgdCl-binding gel. As cyanides are known to form strong complexes
153 with Ag^+ [41], the AgdCl-binding gel was immersed for 24 h in 3 mL of KCN solution ($0.1 - 100$
154 mmol L^{-1}) containing $100 \mu\text{g L}^{-1}$ of inorganic I species. The recovery of inorganic I species in
155 KCN solution was calculated using Eq. 1.

156 **2.5. Laboratory evaluation of DGT performances**

157 This section focuses on the laboratory evaluation of AgdCl-DGT method in deployment
158 solutions. The general experimental setup and calculations are firstly described, followed-up by a
159 description of classical tests to specify the performances of the new DGT binding gel in terms of
160 selectivity, pH influence, uptake capacity and deployment in natural matrices.

161 **2.5.1. Experimental setup and calculations**

162 All DGT experiments were performed in polypropylene containers (30 L). After equilibration of
163 the deployment solution with the atmosphere during at least 24 hours, AgdCl-DGT samplers
164 were deployed at specific time interval. The temperature and pH were monitored. Prior to the
165 retrieval of the AgdCl-DGT, aliquots of the deployment solution were taken, filtered through
166 acetate cellulose filter ($0.45 \mu\text{m}$), then basified with ultrapur NH_3 at 150 mmol L^{-1} before
167 elemental analysis. Mean values of temperature, pH, concentration of inorganic I species are

168 included in the figures and uncertainties are expressed as the standard deviation of the variation
 169 of these parameters during the experiments.

170 The accumulated mass of inorganic I species by AgdCl-binding gel (M_{DGT} , ng) was calculated
 171 using Eq. 3.

$$M_{DGT} = \frac{C_e \times (V_{KCN} + V_{gel})}{f_e/100} \quad \text{Eq. 3}$$

172 where C_e is the eluted concentration of I in the selected elution solution (ng mL^{-1}), V_{KCN} the
 173 eluent solution volume (mL), V_{gel} the volume of the AgdCl-binding gel (mL) and f_e the eluent
 174 factor (%).

175 To determine the experimental DGT performances, the theoretical mass of inorganic I species
 176 (M_{th1} , ng) accumulated in the AgdCl-binding gel was calculated using Eq. 4, which is based on
 177 the well-established DGT equation [17].

$$M_{th1} = \frac{C_I \times A_p \times t}{\left(\frac{\delta^{mdl}}{D^{mdl}}\right)} \quad \text{Eq. 4}$$

178 where C_I is the concentration of IO_3^- or I^- in the deployment solution (ng cm^{-3}), D^{mdl} the diffusion
 179 coefficient of each inorganic I species (in the material diffusion layer) obtained by the diffusion
 180 cell method ($\text{cm}^2 \text{s}^{-1}$), A_p the geometric area of the DGT device window (3.14 cm^2), t the
 181 deployment time (s) and δ^{mdl} the thickness of the diffusive gel plus the filter membrane (0.093
 182 cm).

183 **2.5.2. Selectivity and determination of the effective diffusion coefficient**

184 The accumulation of inorganic I species was investigated by deploying five sets of triplicate
 185 AgdCl-DGT samplers in 8 L of $30 \mu\text{g L}^{-1}$ IO_3^- or I^- (prepared in $10^{-2} \text{ mol L}^{-1}$ NaCl at $\text{pH } 5.5 \pm$

186 0.1). Triplicate AgdCl-DGT samplers were removed at around 2, 4, 6, 8 and 10 h. In condition
 187 where all inorganic I species are labile, if a linear accumulation is observed over time with $R^2 >$
 188 0.95, the effective diffusion coefficient (D^{eff} , $\text{cm}^2 \text{s}^{-1}$) of considered inorganic I species value can
 189 be calculated using Eq.5.

$$D^{\text{eff}} = \frac{\alpha \times \delta^{\text{mdl}}}{C_1 \times A_p} \quad \text{Eq. 5}$$

190 where α is the slope of linear regression of the mass accumulated of considered inorganic I
 191 species over time (ng s^{-1}).

192 To check the selectivity of AgdCl-DGT samplers for both inorganic I species, complementary
 193 experiments were carried out in 8 L of $10^{-2} \text{ mol L}^{-1}$ NaCl at $\text{pH } 5.5 \pm 0.1$ containing inorganic I
 194 species with different weight ratio $[\text{I}^-] / [\text{IO}_3^-]$ (0, 0.4, 0.9, 1.7, 2.4 and 4.6; values obtained after
 195 speciation control by IC-ICP-MS). The concentration of IO_3^- was fixed at a value close to $20 \mu\text{g}$
 196 L^{-1} , whereas I^- concentrations varied. Triplicate AgdCl-DGT samplers were deployed for 10 h.

197 **2.5.3. Effect of pH**

198 The effect of pH on I^- accumulation was evaluated by deploying four AgdCl-DGT samplers in
 199 8 L of $20 \mu\text{g L}^{-1}$ I^- (prepared in $10^{-2} \text{ mol L}^{-1}$ NaCl at $\text{pH } 5.5 \pm 0.1$) for 10 h. The pH selected for
 200 these experiments were the following: 4.5, 5.5, 6.6, 7.6 and 8.8. Acidification at pH 4.5 was
 201 performed using 6 mol L^{-1} HCl solution. A pH titrator (Metler Toledo), equipped with a DGi115
 202 glass electrode (Metler Toledo) and dilute NaOH solution were used to control and adjust the pH
 203 of the deployment solutions for $\text{pH} > 6$.

204 **2.5.4. Effect of bicarbonate**

205 The effect of bicarbonate was tested by deploying five sets of triplicate AgdCl-DGT samplers in
206 8 L of 10 mmol L⁻¹ NaCl solution containing either 1 or 5 mmol L⁻¹ of NaHCO₃. The
207 concentration of I⁻ was close to 30 µg L⁻¹ in the two deployment solutions. Triplicate DGT
208 samplers were removed after 4, 6, 8, 10 and 24 h.

209 **2.5.5. Binding capacity of AgdCl-DGT samplers**

210 The intrinsic binding capacity of AgdCl-binding gel was investigated by deploying six sets of
211 triplicate AgdCl-DGT samplers in 8 L of around 20 mg L⁻¹ I⁻ (prepared in 10⁻² mol L⁻¹ NaCl at
212 pH 5.5 ± 0.1). Triplicate DGT samplers were removed after 2, 4, 6, 8, 24 and 28 h.

213 **2.5.6. Time-series experiment in natural and synthetic matrix**

214 To determine the performances of AgdCl-DGT in environmentally relevant matrices, AgdCl-
215 DGT samplers were deployed in 8 L of Vittel®, Volvic® or synthetic seawater. The Vittel® and
216 Volvic® continental waters were spiked with I⁻ at around 25 µg L⁻¹, and the synthetic seawater at
217 100 µg L⁻¹ (a higher level, due to important dilution before elemental and speciation
218 measurements). Physico-chemical characteristics of drinking waters are reported in Table 1.
219 Triplicate AgdCl-DGT samplers were removed after a defined deployment time (2 – 72 h). For
220 samplers deployed in seawater, each AgdCl-binding gel was rinsed in 5 mL of ultrapure water for
221 2 h to remove unbound salts.

222 **3. Results and discussion**

223 **3.1. Experiments with DGT components**

224 **3.1.1. Reactivity of filter, diffusive gel and DGT plastic holder**

225 The ABS DGT holder did not react with IO_3^- or I^- ($R = 101-102\%$). All filter membranes (CA,
226 PC, PES or PVDF) and diffusive gels (AGE or APA) tested did not accumulate inorganic I
227 species ($R = 98-102\%$). For more details, data are available in Figure S5 in the supplementary
228 information. To make DGT samplers for inorganic I species, there is consequently no limitation
229 using a specific combination of filter membrane and diffusive gel rather than another. This is not
230 the case when working, for example, with mercury (which adsorbs on APA diffusive gel) [42-
231 44]. For the next experiments, the CA filter membrane and AGE diffusive gel were used as
232 standard DGT components.

233 **3.1.2. Reactivity of binding gel**

234 The uptake efficiency of the AgdCl-binding gel disc is shown as a function of NaCl or Na_2SO_4
235 concentration in Figure 1 (A) and (B), respectively. Immersion time was 24 h. I^- was totally
236 accumulated by the AgdCl-binding gel without being impacted by the NaCl and Na_2SO_4
237 concentrations in the immersion solution ($f_u > 98\%$). Consequently, chloride (Cl^-) and sulfate
238 (SO_4^{2-}) ions are not a competing ion for the uptake of I^- by the AgdCl-binding gel for
239 concentration up to 500 mmol L^{-1} . The uptake factor by AgdCl-binding gel is very limited for
240 IO_3^- ($f_u < 15\%$). For these batch experiments, no speciation controls were done. The aim was
241 only to roughly determine the selectivity of AgdCl-binding gel. It might be that some redox
242 interconversion of IO_3^- to I^- could explain the low IO_3^- uptake in NaCl media. In any case, these
243 results open up the possibility to develop a DGT method selective to I^- . This hypothesis will be

244 tested through DGT experiments in the section 3.2, in which the speciation of I was checked in
245 each deployment solution.

246 Then, the binding dynamics of I by AgdCl-binding gel disc was studied in 10 mmol L⁻¹ NaCl
247 and Na₂SO₄ immersion solution as shown Figure 1 (C). The mass of I bound to AgdCl-binding
248 gel disc increased steeply at the first 10-20 min, followed by a slow increase later on. The binding
249 rates at 5 min are 0.68 and 1.08 ng s⁻¹ cm⁻² for NaCl and Na₂SO₄ immersion solution,
250 respectively. These values are much greater than DGT fluxes (0.022 ng s⁻¹ cm⁻²) calculated
251 through a 0.093 cm a diffusive layer (typically used in DGT assemblies), the diffusion coefficient
252 of I in free water (Table 2), and a deployment solution containing the same concentration of I at
253 25°C. It shows that I binding to AgdCl-binding gel can be high enough to satisfy DGT uptake.
254 Furthermore, Figure 1 (C) indicates a lower uptake for the lower ionic strength (10 mmol L⁻¹ for
255 NaCl solution vs 30 mmol L⁻¹ for Na₂SO₄ solution), which was not observable in previous
256 experiments due to long immersion time (24 h). This is probably linked to the nature of AgdCl-
257 resin. One possible mechanism is hypothesized next. Once I, Cl⁻ and SO₄²⁻ enter into the AgdCl-
258 resin bead, these anions react with Ag⁺ to form precipitates. The precipitation of Ag₂SO₄ and
259 AgCl does not hinder the formation of AgI because of its lower solubility product constant value
260 (pK_{sp} = 4.8, 9.75 and 16.1 for Ag₂SO₄, AgCl and AgI precipitates [41], respectively). This was
261 also confirmed by our previous batch experiments showing total uptake of I by AgdCl-binding
262 gel disc whatever the concentration of NaCl and Na₂SO₄ in immersion solution. Nevertheless, the
263 penetration of the negatively charged I inside the AgdCl-resin bead could be restricted due to
264 residual negatively charged sites on the AgdCl-resin. The electrostatic potential difference
265 (between the resin and the solution) increases with decreasing of ionic strength [45-48], and I
266 tends to be excluded from the AgdCl-resin. So, less accumulation will follow in low ionic

267 strength. This hypothetical mechanism would explain why a faster uptake was observed in
268 Na_2SO_4 immersion solution than in the NaCl (Figure 1(C)) one with the same analyte
269 concentration, but different ionic strength. These results point out to a potential limitation of the
270 use the AgdCl-DGT method. In section 3.2, experiments will be designed to better understand how
271 to use the AgdCl-DGT method, but also to check whether this decreased accumulation at lower
272 ionic strength is negligible or not.

273 To define the eluent solution, the recovery of Γ from AgdCl-binding gel was tested using 3 mL of
274 KCN solution at different concentrations (0.1 – 100 mmol L^{-1}), as shown in Figure 2. Total
275 recovery of Γ was obtained for KCN concentration higher than 10 mmol L^{-1} ($R = 101 - 103 \%$).
276 The AgdCl-binding gel disc became white (initial color of Cl resin) when using 100 mmol L^{-1}
277 KCN, suggesting that Ag is totally removed in the eluent solution and there is no Γ left in the
278 AgdCl binding gel. Hence, this concentration was used to totally elute Γ from AgdCl binding gel.
279 To prevent signal suppression of ICP-MS linked to high potassium concentration, the eluent
280 solutions were diluted at least 10 fold with deionized water. Finally, no elution factor is needed to
281 calculate the mass of Γ accumulated by the AgdCl-binding gel ($f_e = 100 \%$ in Eq. 3).
282 Furthermore, the AgdCl-DGT blank values for Γ species were 5 ng ($n = 10$) following this
283 elution procedure. This blank value of AgdCl-DGT method is low enough to measure the low
284 concentration of Γ in environmental waters.

285 **3.2. DGT experiments**

286 **3.2.1. Speciation and lability**

287 To be sure of the stability of inorganic I species in deployment solution, speciation was checked
288 with IC-ICP-MS measurements during DGT experiment. The concentration of inorganic I species

289 was relatively stable over time in each deployment solution with RSD < 5 %, confirming that
290 there is no redox interconversion in these DGT experiments. Concerning the lability of inorganic
291 I species, speciation calculations were performed with PHREEQC version 3
292 (<https://www.usgs.gov/software/phreeqc>) with the thermodynamic database ThermoChimie
293 version 9b0 developed by Andra (<http://www.thermochimie-tdb.com/>) [49, 50]. Input data were
294 the concentrations of each component in deployment solution. Atmosphere-water equilibrium
295 with CO₂ was also assumed. pH and temperature was also introduced. Whatever the simulated
296 deployment solution, IO₃⁻ and I⁻ were mainly present as free ions (> 95 %). Hence, it was
297 considered that inorganic I species were totally available for the AgdCl-DGT samplers.

298 3.2.2. Selectivity of AgdCl-DGT method

299 Time-series experiments were used to characterize the selectivity of AgdCl-DGT samplers for
300 inorganic I species (Figure 3). AgdCl-DGT samplers were deployed up to 10 h in the presence of
301 either IO₃⁻ or I⁻ (~ 30 µg L⁻¹). The mass of IO₃⁻ stabilized at 14 ± 2 ng after 2 h of deployment
302 time, which coincides with the amount for equilibrium ([IO₃⁻]_{solution} × V_{gel} ~ 12 ng with V_{gel} = 0.42
303 ± 0.03 mL), assuming no electrostatic effect. This indicated that IO₃⁻ was not trapped over time in
304 the AgdCl binding gel. Consequently, this DGT method should not suffer from any IO₃⁻
305 interference. Selectivity control was performed using a deployment solution containing the two
306 inorganic I species, and results are discussed later on. A good linear regression was obtained
307 between the accumulated mass of I⁻ and the deployment time of DGT samplers (R² = 0.994),
308 confirming previous results on the selectivity of AgdCl-binding gel (section 3.1.2). The slope of
309 linear fitting was used to calculate D^{eff} according to Eq. 5. The D^{eff} value for I⁻ was 1.20 10⁻⁵ cm²
310 s⁻¹ (RSD = 6 %) at 25°C value. Complementarily, the diffusion cell method was used to measure
311 the diffusion coefficient of each inorganic I species in hydrogel alone (D^{gel}) and with the addition

312 of a filter (D^{mdl}). Experimental details are presented in section S6, and the diffusion cell is shown
 313 in Figure S6. The concentration of IO_3^- or Γ were both constant in the source solution during each
 314 diffusion cell experiments with a RSD $< 4\%$, confirming the non-adsorption of inorganic I
 315 species by the components and the walls of diffusive cell. Linear accumulation of IO_3^- or Γ in the
 316 acceptor compartment was observed over time ($R^2 = 0.997-0.999$; Figure S7), and each slope was
 317 used to calculate the diffusion coefficient of inorganic I species according to Eq. S1. Results are
 318 displayed in Table 2. The diffusion of inorganic I species is slightly higher in hydrogel than in
 319 pure water ($D^{\text{gel}} / D^{\text{w}} \sim 110\%$). Slower diffusion of IO_3^- and Γ was observed with the addition of
 320 filter ($D^{\text{mdl}} / D^{\text{w}} \sim 80\%$), suggesting some resistance in the ensemble. These results seem to be
 321 consistent with previous experimental observations with anions [18, 51, 52]. Furthermore, there
 322 is a significant difference between D^{mdl} and D^{eff} ($D^{\text{eff}} / D^{\text{mdl}} \sim 75\%$). Consequently, M_{th1} does not
 323 match with M_{DGT} as shown with the red dashed line in Figure 3. Investigations were carried out
 324 to check whether this lower than expected M_{DGT} could be the result from a longer diffusion path.
 325 A thin diffusion-controlled layer, known as diffusive boundary layer (DBL), exists at any solid
 326 surface in aqueous environment, even in vigorously stirred solutions. The DBL is known to affect
 327 the DGT results [53, 54]. That is the reason why its thickness (δ^{dbl}) was assessed by using
 328 different thickness of diffusive gel in the AgdCl-DGT samplers. Experimental details are
 329 presented in section S7. A linear plot of the reciprocal mass of Γ versus δ^{mdl} was observed ($R^2 =$
 330 0.998 ; Figure S8). The slope and the intercept were classically used to calculate δ^{dbl} according to
 331 Eq. S2. Our δ^{dbl} is $361 \pm 40 \mu\text{m}$, indicating that the mixing of deployment solution was not
 332 optimal. Indeed, common δ^{dbl} values were close to $200 \mu\text{m}$ in well mixed solution [55]. As δ^{dbl} is
 333 not negligible, we propose now to include it in calculation of the theoretical mass accumulated of
 334 Γ (Eq. 6):

$$M_{th2} = \frac{C_I \times A_P \times t}{\left(\frac{\delta^{dbl1}}{D^w} + \frac{\delta^{mdl}}{D^{mdl}} \right)} \quad \text{Eq. 6}$$

335 Results are displayed with the orange dashed line in Figure 3. The impact of considering the DBL
 336 is a decrease of 23.5 % in theoretical accumulation when comparing M_{th1} and M_{th2} , but there is
 337 still some difference with M_{DGT} points. The reduced slope could indicate that the accumulation of
 338 Γ does not fulfil perfect sink condition *i.e.*, the concentration of Γ in the resin-diffusive gel
 339 interface is not zero and Γ penetrates into the resin domain [56]. This assumption was tested
 340 using DGT samplers equipped with a stack of two AgdCl-binding gels in two deployment
 341 solution containing 1 and 10 mmol L⁻¹ NaCl (see experiment details in section S8). Γ was present
 342 at 8.7 and 0.3 % in the back binding gel when AgdCl-DGT samplers were deployed in 1 and 10
 343 mmol L⁻¹ NaCl solution, respectively. Knowing the distribution of Γ in the stack of two AgdCl-
 344 binding gels, it is now possible to determine the penetration factor λ_M *i.e.*, the mean distance that
 345 Γ can penetrate into an AgdCl-binding gel. λ_M is calculated from Eq. S3, and the average value
 346 obtained is $312 \pm 100 \mu\text{m}$ and $140.8 \pm 8.4 \mu\text{m}$ for deployment solution composed of 1 and 10
 347 mmol L⁻¹ NaCl, respectively. The AgdCl-resin beads have a size ranging between 40 to 125 μm
 348 (Figure S9). More precisely, the diameter of AgdCl-resin beads defining 10%, 50% and 90% of
 349 the cumulative volume undersize is 55 μm , 73 μm and 97 μm , respectively. As λ_M is significantly
 350 higher than the diameter of AgdCl-resin beads, we confirm that the AgdCl-resin does not act as a
 351 perfect sink and there is a non-null concentration of Γ all along the resin disc. Consequently, for
 352 this case where there is a resulting kinetic limitation, we propose a new expression to estimate the
 353 accumulation of DGT samplers (Eq. 7):

$$M_{th3} = \frac{C_I \times A_P \times t}{\left(\frac{\delta^{dbl2}}{D^w} + \frac{\delta^{mdl}}{D^{mdl}} + \frac{\lambda_M \times \coth(\delta^r/\lambda_M)}{\Pi \times D^{gel}} \right)} \quad \text{Eq. 7}$$

354 where δ^r correspond to the thickness of AgdCl-binding gel (0.08 cm) and the term $\lambda_M \times$
 355 $\coth(\delta^r/\lambda_M)$ to the effective distance of penetration of Γ in the AgdCl-resin domain (cm). Π is
 356 the ratio between the analyte concentration inside the binding gel disc and the concentration
 357 inside the diffusive gel disc, both at the limiting interface between the two gel discs [46]. Another
 358 new equation was used to recalculate the thickness of DBL (δ^{dbl2} , cm) taking into account the
 359 penetration phenomenon and the electrostatic partitioning between the two gel discs:

$$\delta^{dbl2} = D^w \left(\frac{y}{s \times D^{mdl}} - \frac{\lambda_M \times \coth(\delta^r/\lambda_M)}{\Pi \times D^{gel}} \right) \quad \text{Eq. 8}$$

360 An electrostatic correction could be done, but it requires complementary experiments to
 361 determine Π . As a first approximation, we have taken $\Pi = 1$ in Eq.7 and Eq. 8. The δ^{dbl2} value
 362 ($326 \pm 42 \mu\text{m}$) is slightly lower than δ^{dbl1} . Results are shown with the green dashed line in Figure
 363 3. The M_{th3} curve is a better fit to simulate the uptake of Γ by AgdCl-DGT sampler (M_{DGT} / M_{th3}
 364 $= 98 \pm 8 \%$) compared to the M_{th1} and M_{th2} curves ($M_{DGT} / M_{th1} = 71 \pm 6 \%$ and $M_{DGT} / M_{th2} = 93 \pm$
 365 7%). Similar results were obtained for the DGT experiment using a stack of two AgdCl in 10
 366 mmol L^{-1} NaCl ($M_{DGT} / M_{th3} = 106 \pm 6 \%$). Eq. 7 will be used to evaluate the AgdCl-DGT
 367 performances in the following sections. Nevertheless, application of Eq. 7 (with $\Pi = 1$) does not
 368 explain the low amount of Γ found in the two AgdCl-binding gels for the DGT experiment
 369 performed in 1 mmol L^{-1} NaCl ($M_{DGT} / M_{th3} = 4.1 \pm 0.3 \%$). The low DGT response is probably
 370 linked to the partial exclusion of anions from the resin at low ionic strength, which would be
 371 quantified by the parameter Π . This exclusion from the AgdCl-resin seems more likely than
 372 exclusion from the filter and diffusive gel as previously observed in previous laboratory
 373 validation of DGT methods [43, 48]. Additional experiments will focus on the effect of ionic
 374 strength in section 3.2.6.

375 Complementary, DGT experiments were done to control the possibility of using the AgdCl-
376 binding gel for redox speciation. For this experiment, IO_3^- and Γ were simultaneously present in
377 deployment solution with different weight ratio $[\Gamma] / [\text{IO}_3^-]$ up to 4.6 (Figure 4). To confirm the
378 selectivity of AgdCl-DGT method for Γ , $M_{\text{th}3}$ was calculated using the concentration of Γ
379 measured by IC-ICP-MS (Eq. 7). Acceptable DGT measurements were obtained for $M_{\text{DGT}} / M_{\text{th}3}$
380 $= 100 \pm 15 \%$ (dashed lines in Figure 4), as in other previous DGT laboratory evaluations [19, 20,
381 39]. Whatever the weight ratio $[\Gamma] / [\text{IO}_3^-]$ tested, the AgdCl-DGT estimations were good with
382 $M_{\text{DGT}} / M_{\text{th}3}$ values ranging between 89 and 107 %. As the DGT measurements were not
383 interfered by IO_3^- , it is confirmed that the AgdCl-binding gel is only selective to Γ .

384 3.2.3. Effect of pH

385 The impact of pH on the accumulation of Γ was investigated for 10 h of deployment time. Over
386 the pH range from 4.5 to 8.8, excellent agreement was observed between the predicted and
387 accumulated mass of Γ ($M_{\text{DGT}} / M_{\text{th}3} = 93 - 113 \%$; Figure S10). These results indicate that the
388 performance of the AgdCl-DGT method is independent of pH over the typical range found in
389 environmental waters (pH ~ 5-9).

390 3.2.4. AgdCl-DGT sampler binding capacity

391 To determine the AgdCl-DGT sampler binding capacity to accumulate Γ , a time-series
392 experiment was performed using a high concentration of this species ($\sim 20 \text{ mg L}^{-1}$) in deployment
393 solution with $[\text{NaCl}] = 10 \text{ mmol L}^{-1}$ and $\text{pH} = 5.5$. Linear accumulation of Γ by AgdCl-DGT
394 samplers was observed up to 6 h ($R^2 > 0.95$; Figure S11). The AgdCl-DGT response was in
395 agreement with predicted total Γ mass since the $M_{\text{DGT}} / M_{\text{th}3}$ value was $106 \pm 7 \%$ (mean \pm
396 standard deviation). After 8 h of deployment time, the M_{DGT} values decreased compared with
397 $M_{\text{th}3}$ values. The maximum mass of Γ accumulated by AgdCl-DGT samplers was $218 \pm 25 \mu\text{g}$. As

398 inorganic I species occur at trace levels in environmental waters ($< 100 \mu\text{g L}^{-1}$), this binding
399 capacity should be high enough to deploy AgdCl-DGT samplers during 24 - 96 h (typical
400 deployment times).

401 **3.2.5. Effect of bicarbonates**

402 The effect of HCO_3^- on the accumulation was investigated up to 24 h. M_{DGT} agrees with M_{th3}
403 within an error of 15 % (Figure S12; 105 ± 5 and 104 ± 7 % for 1 and 5 mmol L^{-1} HCO_3^- ,
404 respectively). In these conditions, HCO_3^- is not a competing ion for the accumulation of I^- by
405 AgdCl-DGT samplers. That is consistent with thermodynamic data. Indeed, the precipitation of
406 Ag_2CO_3 does not hinder AgI formation when comparing solubility product constant values (pK_{sp}
407 = 11.1 and 16.1 for Ag_2CO_3 and AgI, respectively [41]).

408 **3.2.6. Time-series experiment in natural and synthetic waters**

409 After carrying out numerous experiments in 10 mmol L^{-1} NaCl solutions, the performances of
410 AgdCl-DGT method were studied in Vittel® and Volvic® water spiked with I^- with a
411 concentration close to 20 $\mu\text{g L}^{-1}$. The concentration of IO_3^- was negligible in these deployment
412 solutions with values lower than 1 $\mu\text{g L}^{-1}$. The ionic strength for these two drinking waters are
413 22.6 and 3.2 mmol L^{-1} , respectively (calculations performed by using data in Table 1 and
414 PHREEQC software). The mass of I^- accumulated by AgdCl-DGT samplers was monitored over
415 time, and compared to M_{th3} (black line in Figure 5). Linear accumulation of total I mass by
416 AgdCl-DGT samplers was observed up to 24 h for Vittel® and Volvic® waters ($R^2 > 0.9$; Figure
417 5 (A) and (B)). However, the amount of I^- measured by AgdCl-DGT samplers was 33 ± 8 and 27
418 ± 5 % in Vittel® and Volvic® waters, respectively. Assuming 15 % of error on predicted total I
419 mass (dashed lines in Figure 5), the AgdCl-DGT measurements were not quantitative whatever
420 the deployment times. Although the ionic strength of these two drinking waters was significantly

421 different, similar DGT responses were obtained. It is also noted that Vittel® water had a higher
422 ionic strength than the synthetic deployment solution employed to characterize the AgdCl-DGT
423 performances, but the pH was much higher in the natural waters. Possibly, AgdCl-resin has acid-
424 base properties (data not found in the literature). If pH overcomes the pKa of the AgdCl-resin, the
425 amount of negative charge sites in the AgdCl-resin might increase remarkably. More charge
426 means more electrostatic potential, more exclusion of anions from the resin and less
427 accumulation. This speculation is not however fully consistent with the pH-impact figure (Figure
428 S10).

429 New time-series experiments were performed to verify whether the AgdCl-DGT method depends
430 on the concentration of Cl^- . Vittel® and Volvic® water were consequently spiked with ultrapure
431 NaCl salt to reach a concentration of Cl^- at 10 mmol L^{-1} (value used in previous experiments
432 using synthetic waters). The ionic strength values are 32.9 and 13 mmol L^{-1} for NaCl-doped
433 Vittel® and Volvic® water, respectively. When AgdCl-DGT samplers are deployed in the two
434 NaCl-doped drinking waters, better DGT responses were obtained compared with non-spiked
435 drinking waters (Figure 5 (C) and (D)). Indeed, the amount of total mass of Γ measured by
436 AgdCl-DGT samplers were 77 ± 4 and 72 ± 4 % in NaCl-doped Vittel® and Volvic® waters,
437 respectively. The presence of SO_4^{2-} was then tested only with Volvic® water spiked with
438 ultrapure Na_2SO_4 salt to a concentration of SO_4^{2-} at 10 mmol L^{-1} . This time, the amount of Γ
439 measured by AgdCl-DGT samplers reached 107 ± 3 % (Figure 5 (E)). This means an increase of
440 the AgdCl-DGT response with anions another than Cl^- and supports the key role of ionic strength.

441 Although the direct application of AgdCl-DGT method will not be possible in continental waters,
442 the deployment of AgdCl-DGT samplers could be envisaged in seawater and brine due to high
443 concentration of Cl^- and SO_4^{2-} . To confirm the latter hypothesis, a time-series experiment was

444 performed in synthetic seawater spiked with Γ concentration close to $100 \mu\text{g L}^{-1}$. Long
445 deployment times were used to reveal possible interferences of AgdCl-binding gel. As shown in
446 Figure 5 (F), linear accumulation of Γ by AgdCl-DGT samplers was observed up to 72 h ($R^2 >$
447 0.95). The mass of Γ recovered by the AgdCl-DGT samplers reached $107 \pm 5 \%$, validating the
448 suitability of the AgdCl-DGT method for application in seawater. The AgdCl-DGT method
449 allowed to concentrate Γ by a factor 24 (C_e / C_D), which is useful to measure low Γ
450 concentrations. Furthermore, the saturation of AgdCl-binding gel was not experimentally
451 observed in this long time-series experiment. This result also confirms that there is no
452 interference with HCO_3^- (2.38 mmol L^{-1}).

453 **4. Conclusions**

454 The DGT performances of AgdCl-DGT binding gel to measure the concentration of at least one
455 inorganic I species have been tested. A rigorous experimental design involving batch and time-
456 series experiments was performed in order to gain knowledge on AgdCl-binding gel selectivity
457 and limitations as well as to establish a robust DGT deployment protocol. This works shows that
458 the AgdCl-DGT sampler is able to accumulate selectively Γ . The AgdCl-DGT response is not pH
459 dependent (4.5 -8.8). The quantification of Γ concentration is not impacted by the presence of
460 IO_3^- and HCO_3^- . Nevertheless, the current AgdCl-DGT method requires high ionic strength in
461 deployment solution limiting the application of to sea or brine waters. Further work should
462 investigate the possibility of analyzing freshwaters using an effective diffusion coefficient
463 determined at the same pH and ionic strength as the one of the natural sample.

464 This analytical development validates a first step to perform redox speciation for I using DGT
465 techniques, and other developments could be performed to find a binding gel only able to
466 accumulate IO_3^- or the two inorganic I species simultaneously. To avoid the harmful

467 manipulation of KCN eluent solution, laboratory equipped with pyrolyser could develop
468 alternative extraction strategies by trapping the gaseous iodine from AgdCl binding in alkaline
469 solution (TMAH, NaOH-NaHSO₃) [57-61]. Finally, future research should focus on the
470 application of the AgdCl-DGT method to study the biochemistry of iodide in marine or brine
471 environments, but also to better predict the ¹²⁹I behavior from spent nuclear fuel reprocessing
472 plants.

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661 **Figure caption**

662 Figure 1: Uptake factor of inorganic I species by AgdCl-binding gel as a function of: (A) NaCl
663 concentration for 24 h of immersion time; (B) Na₂SO₄ concentration for 24 h of immersion time;
664 and (C) immersion time-series in an immersion solution containing either 10 mmol L⁻¹ NaCl or
665 Na₂SO₄. Experimental conditions: 20 mL of immersion solution; [NaCl] or [Na₂SO₄] = 1-500
666 mmol L⁻¹; [IO₃⁻] or [I⁻] ~ 100 µg L⁻¹; pH = 5.5 ± 0.1.

667 Figure 2: Recovery of I⁻ species in the presence of AgdCl-binding gel as a function of KCN
668 concentration. Black dashed line corresponds to the minimum acceptable recovery of I⁻ (75 %).
669 Experimental conditions: 3 mL of eluent solution; [KCN] = 0.1-100 mmol L⁻¹; [I⁻] ~ 100 µg L⁻¹;
670 24 h of immersion.

671 Figure 3: Evolution of the mass of IO₃⁻ or I⁻ accumulated by AgdCl-DGT samplers over time.
672 Dashed lines correspond to the DGT response simulations using Eq. 4, Eq.6 and Eq. 7 for M_{th1} ,
673 M_{th2} and M_{th3} , respectively. Experimental conditions: 8 L of deployment solution; [NaCl] = 10
674 mmol L⁻¹; [IO₃⁻] or [I⁻] ~ 30 µg L⁻¹; pH = 5.5 ± 0.1; $T = 20.7 ± 1.0^{\circ}\text{C}$; up to 10 h of deployment
675 time.

676 Figure 4: Confirmation of the selectivity of AgdCl-DGT samplers for inorganic I species. Black
677 dashed lines correspond to ± 15 % acceptable error on the DGT measurement. Experimental
678 conditions: 8 L of deployment solution; [NaCl] = 10 mmol L⁻¹; weight ratio
679 [I⁻]/[IO₃⁻] = 0-4.6 obtained by IC-ICP-MS; [IO₃⁻] ~ 20 µg L⁻¹; pH = 5.5 ± 0.1; 10 h of deployment
680 time.

681 Figure 5: Results of time-series experiments performed with (A) Vittel® water ([I⁻] = 31.6 ± 0.6
682 µg L⁻¹; $T = 20.5 ± 1.1$; pH = 8.3 ± 0.2), (B) Volvic® water ([I⁻] = 24.0 ± 0.4 µg L⁻¹; $T = 20.5 ±$

683 1.1; pH = 8.0 ± 0.2), (C) Vittel® water with 10 mmol L⁻¹ NaCl salt addition ([I] = 24.7 ± 1.1 µg
684 L⁻¹; T = 20.5 ± 1.1 °C; pH = 8.3 ± 0.2); (D) Volvic® water with 10 mmol L⁻¹ NaCl salt addition
685 ([I] = 26.3 ± 1.2 ; pH = 8.1 ± 0.2 ; T = 20.5 ± 1.1 °C); (E) Volvic® water with 10 mmol L⁻¹
686 Na₂SO₄ salt addition ([I] = 16.7 ± 0.9 ; pH = 8.0 ± 0.2 ; T = 20.4 ± 0.4 °C); and (F) synthetic
687 seawater ([I] = 103.8 ± 1.2 ; T = 20.9 ± 0.3 °C; pH = 8.2 ± 0.1). The concentration of IO₃⁻ was
688 still lower than 1 µg L⁻¹ in each deployment solution. Lines for theoretical prediction as in Figure
689 4.

690

Figure 1

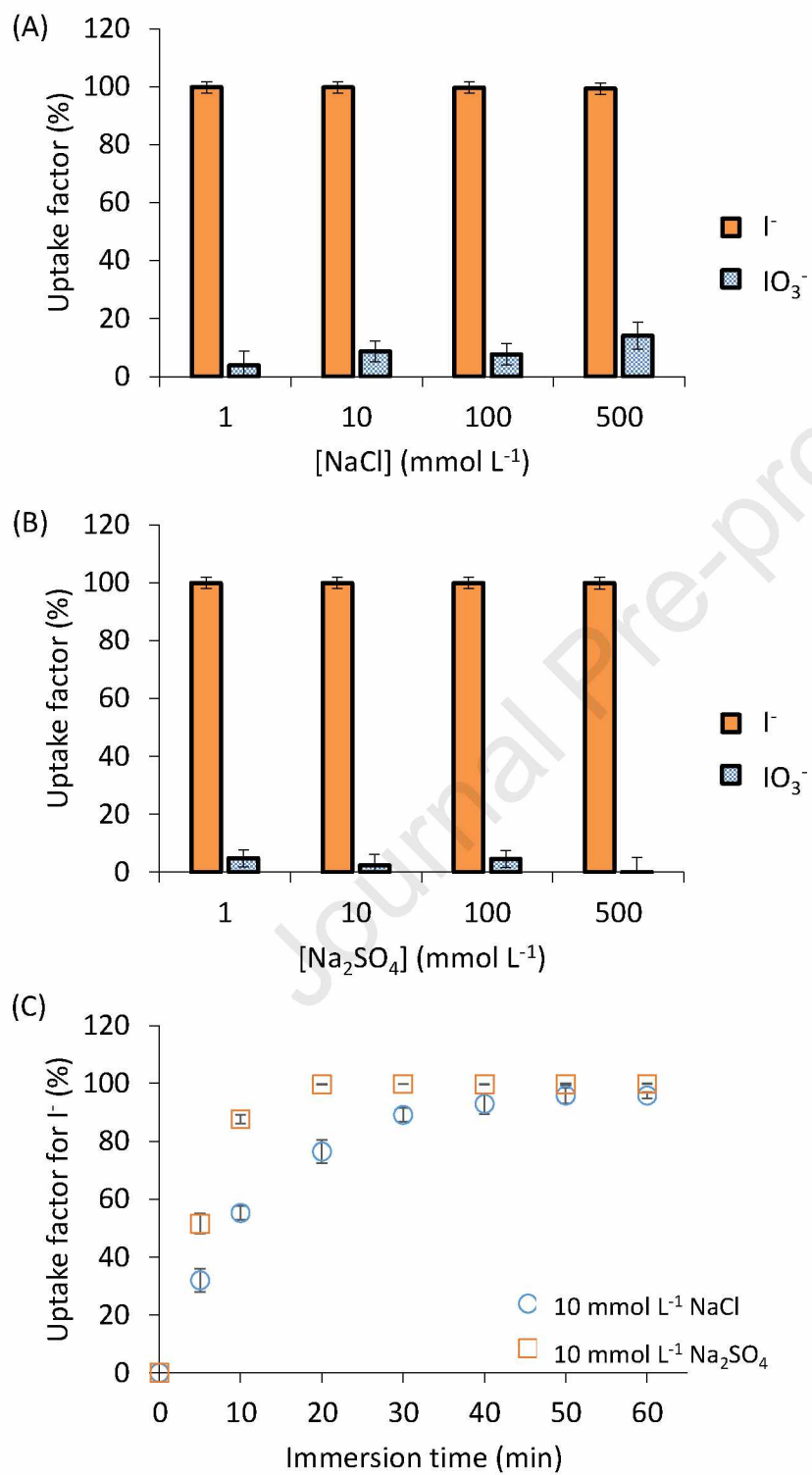


Figure 2

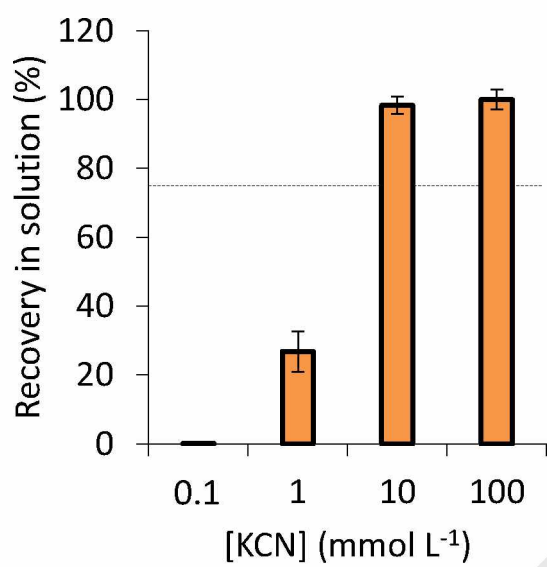


Figure 3

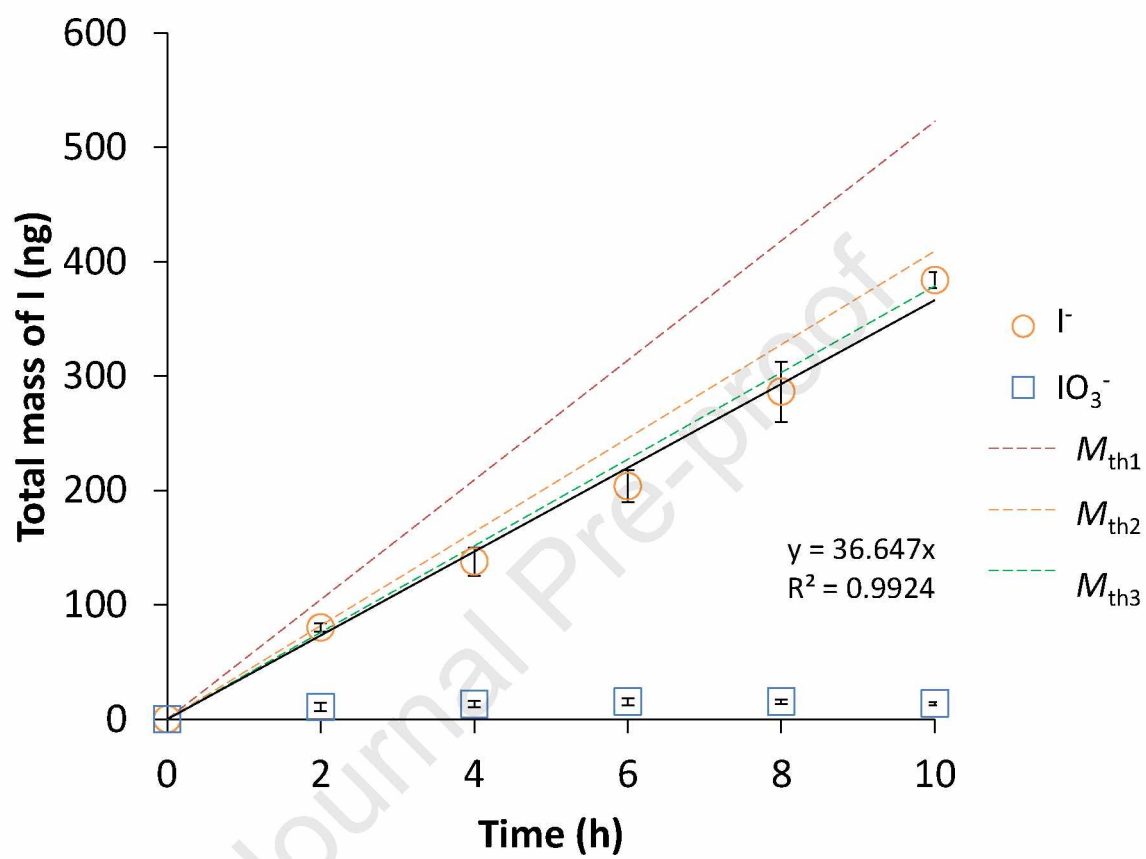


Figure 4

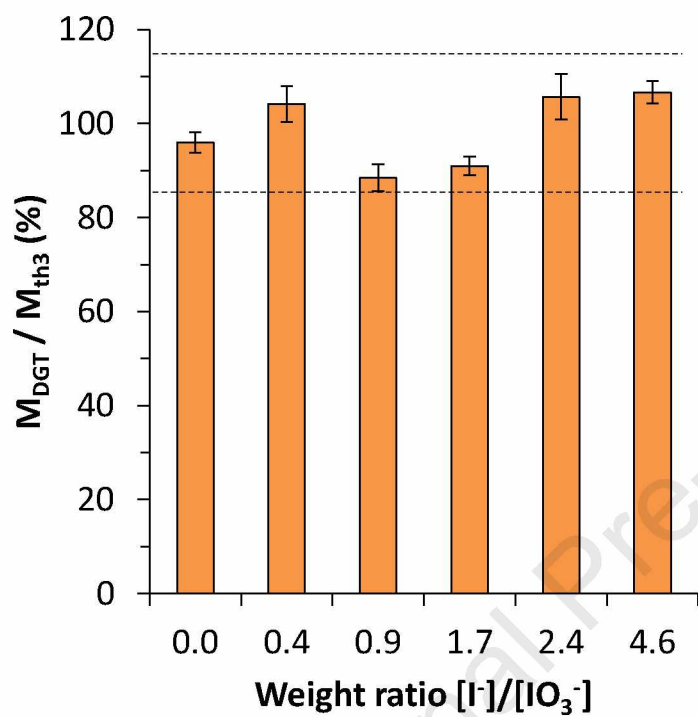


Figure 5

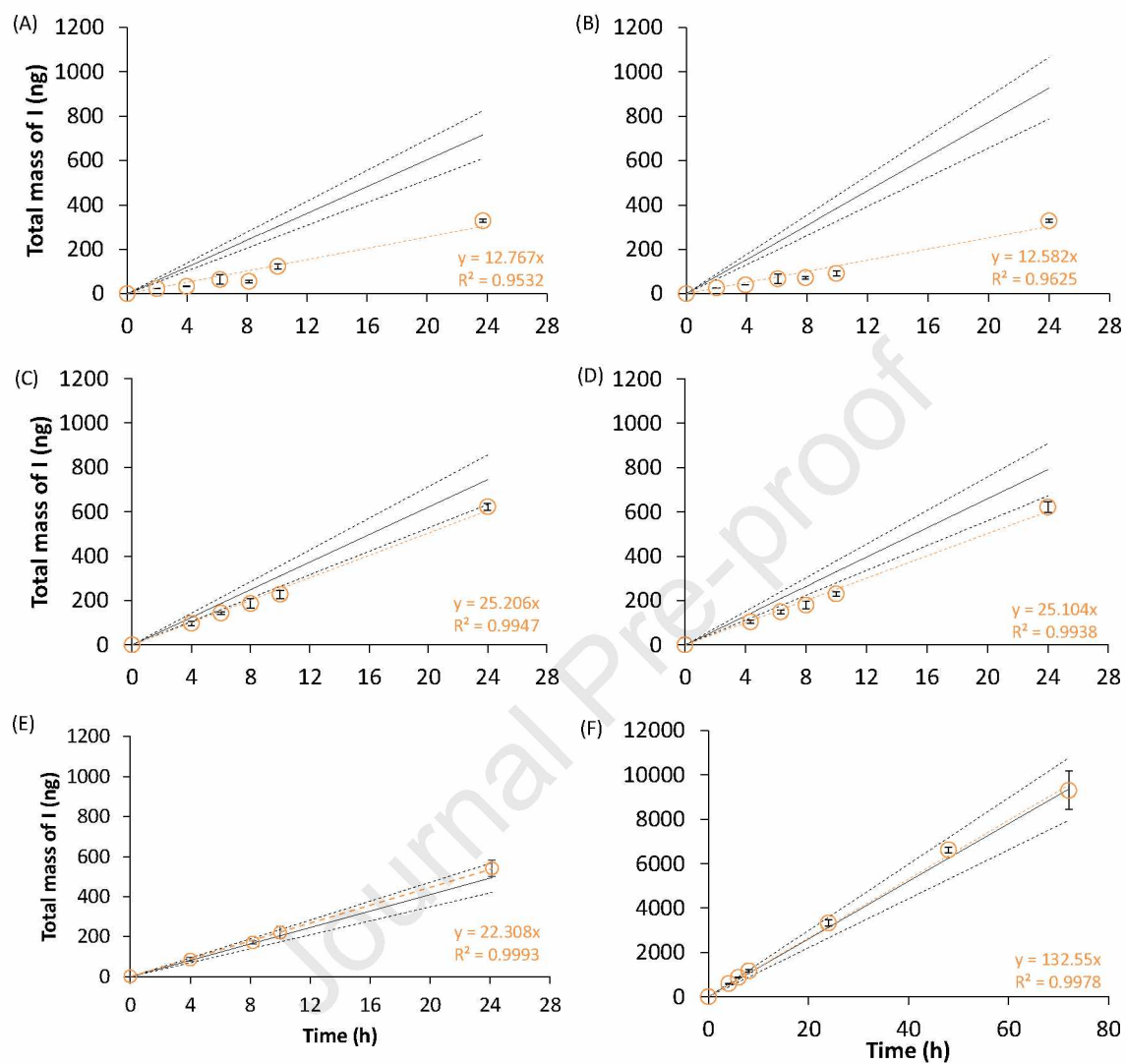


Table caption

Table 1: Continental water and seawater composition. Drinking-water physicochemical compositions provided in the bottle labels, and seawater was prepared according to Grasshoff et al. [62].

Table 2: Compilation of the experimental diffusion coefficients for IO_3^- and I^- at 25°C. Abbreviations: D^w : the diffusion coefficient in pure water; D^{gel} : the diffusion coefficient in AGE hydrogel; D^{mdl} : the diffusion coefficient in CA filter plus AGE hydrogel; D^{eff} : the effective diffusion coefficient measured by the DGT times-series method ($[\text{NaCl}] = 10 \text{ mmol L}^{-1}$; $\text{pH} \sim 5.5$); n.d.: not determined.

Table 1

Element/dissolved species	Volvic	Vittel	Seawater
Ca	0.29	5.99	13.6 mmol/L
Mg	0.33	1.73	114 mmol/L
Na	0.50	0.23	471 mmol/L
K	0.16	0.05	9.46 mmol/L
HCO ₃ ⁻	1.16	6.29	2.38 mmol/L
Cl ⁻	0.38	0.23	675 mmol/L
SO ₄ ²⁻	0.08	4.16	28.2 mmol/L
NO ₃ ⁻	0.24	0.07	mmol/L
pH	7	7.6	8.22 mmol/L
dry residue	130	1084	mg/L
Salinity			34.8

Table 2

	Diffusion coefficient ($\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	
	IO_3^-	Γ
D^w	1.08 [63]	2.05 [63]
D^{gel}	1.19 (RSD = 5 %)	2.33 (RSD = 6 %)
D^{mdl}	0.87 (RSD = 5 %)	1.61 (RSD = 5 %)
D^{eff}	n.d.	1.20 (RSD = 6 %)

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Highlights:

- A new DGT binding gel is proposed for selective iodide sampling.
- The diffusion coefficient of I species through agarose diffusive gel is reported.
- A DGT equation is developed to consider diffusive boundary layer and kinetic effects.
- The method was successfully applied to measure iodide concentrations in seawater.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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