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Iodine uptake in brown seaweed exposed to radioactive liquid discharges from the reprocessing plant of ORANO La Hague

FIEVET Bruno^a, VOISEUX Claire^a, LEBLANC Catherine^b, MARO Denis^a, HEBERT Didier^a, SOLIER Luc^a, GODINOT Claire^{a*}

^aInstitut de Radioprotection et de Sûreté Nucléaire, PSE-ENV/SRTE, Laboratoire de Radioécologie de Cherbourg-Octeville, France

^bSorbonne Université, CNRS, UMR 8227, Integrative Biology of Marine Models, Station Biologique de Roscoff, Roscoff, France

* corresponding author

Claire GODINOT. IRSN, Laboratoire de Radioécologie, Rue Max Pol Fouchet, BP10, 50130 Cherbourg-en-Cotentin, France. claire.godinot@irsn.fr.

Abstract

Iodine-129 is present in controlled liquid radioactive waste routinely released in seawater by the ORANO nuclear fuel reprocessing plant in La Hague (Normandy, France). Brown algae are known for their exceptional ability to concentrate iodine from seawater. They also potentially emit volatile iodine compounds in response to various stresses, such as during emersion at low tide. For these reasons, brown seaweed is routinely collected for radioactivity monitoring in the marine environment. Despite the high concentration ratio the exact mechanism of iodine uptake is still unclear. Chemical imaging by laser desorption/ionization mass spectrometry provided evidence that iodine is stored by kelps as I⁻. In this study we investigate *in vivo* iodine uptake in kelps (*Laminaria digitata*) with an emphasis on seawater iodine chemical speciation. Our results showed that kelp plantlets were able to take up iodine in the forms of both IO₃⁻ and I⁻. We also observed transient net efflux of I⁻ back to seawater but no IO₃⁻ efflux. Since the seaweed stores I⁻ but takes up both IO₃⁻ and I⁻, IO₃⁻ was likely to be converted into I⁻ at some point in the plantlet, or through the action of associated microorganisms. One major outcome of our experiments was the direct observation of the kelp-based biogenic conversion of seawater IO₃⁻ into I⁻. On the basis of both IO₃⁻ and I⁻ uptakes by the seaweed, we propose new steps in the possible iodine concentration mechanism used by kelp.

Keywords: radioactive iodine, uptake, kelp, chemical speciation

1 Introduction

Though a minor element in seawater, iodine is mainly present on Earth dissolved in the oceans (Carpenter, 2003; Carpenter et al, 2021; Chance et al, 2014; Wong, 1991). In the terrestrial environment, it is present at very low levels in soils, water and plants, but in vertebrates, it is involved in the crucial functions of the thyroid gland as organically bound in thyroid hormones (Fuge & Johnson, 2015). Iodine is also present as multiple volatile compounds involved in a complex geochemical cycle between the oceans and the atmosphere. The high reactivity of iodine is considered to play a key role in atmospheric chemistry and possibly the climate, at least in coastal environments (Carpenter et al, 2021; Carpenter et al, 2013; Kolb, 2002; Saiz-Lopez et al, 2012). In addition to stable ¹²⁷I, iodine has 36 radioactive isotopes, and with the exception of ¹²⁹I (half-life of 15.7 10⁶ years), most iodine radioisotopes quickly decay (half-lives of a few days). Two main iodine radioisotopes are generated by

42 human activities. ^{131}I is a short-lived (half-life of 8.5 days) fission by-product of ^{235}U in nuclear electricity
43 production, and high activities are also used in medicine for cancer radiotherapy. ^{129}I is generated in
44 nuclear reactors, and because of its very slow decay rate, it is a major residual iodine radioisotope in
45 the nuclear fuel cycle, which adds to naturally occurring ^{129}I (cosmic ray spallation of Xe in the
46 atmosphere and spontaneous fission of natural uranium). It is also present in fallout from past
47 atmospheric nuclear weapons testing and major powerplant accidents. ^{129}I is present in controlled
48 liquid radioactive waste routinely released in seawater by the ORANO nuclear fuel reprocessing plant
49 in La Hague (Normandy, France) and the annual amounts released are between 1 and 2 TBq.yr⁻¹ (Fiévet
50 et al, 2020). Discharging liquid ^{129}I waste into seawater results in isotopic dilution in naturally-present
51 stable ^{127}I . The background isotopic ratio $^{129}\text{I}/^{127}\text{I}$ is in the range $[10^{-13}-10^{-12}]$ and reaches $[10^{-7}-10^{-6}]$ in
52 seawater in the English Channel (Hou et al, 2007). Considering a concentration of dissolved ^{127}I in
53 seawater of 0.5 μM , this means ^{129}I activities in the range $[0.05-0.5]$ Bq.m⁻³. However, higher seawater
54 ^{129}I activities could be expected in the close vicinity of the ORANO plant outlet.

55 Brown algae are known for their exceptional ability to concentrate iodine from seawater. The ratio
56 of iodine content between kelps (i.e. Laminariales) and seawater reaches 10^5 , especially in young
57 plantlets (Leblanc et al, 2006). Moreover, brown algae are also known to release volatile iodine
58 compounds in response to various stresses, such as during emersion at low tide (Ball et al, 2010;
59 McFiggans et al, 2010; McFiggans et al, 2004; O'Dowd et al, 2002; Whitehead et al, 2009). Wherever
60 brown seaweed is exposed to ^{129}I discharges in seawater, the radioisotope could return to the
61 terrestrial environment via an airborne route, namely via the wind and aerosols. For these reasons,
62 brown seaweed is routinely collected in the marine environment in the English Channel to monitor
63 radionuclide concentrations, and in particular that of ^{129}I (Fiévet et al, 2020). In a previous study on
64 radionuclide transfers between seawater and biota, we observed that the bioavailability of ^{129}I
65 appeared to decrease with distance from the source of input (the ORANO La Hague plant outlet). We
66 emphasized the role of the chemical speciation of dissolved iodine in seawater (Fiévet et al, 2021).
67 Iodine uptake by Laminariales, and more generally brown algae, is hypothesized to be mediated by
68 enzymes from the vanadium-haloperoxidase (VHPO) family, through the specific oxidation of iodide
69 (Küpper et al, 1998). Dissolved iodine is naturally present in seawater in the forms of iodide (I^-) and
70 iodate (IO_3^-). Although iodate is the dominant chemical form because of pH and redox potential in
71 seawater, both chemical forms are present in various proportions (Carpenter et al, 2013; Hou et al,
72 2007; Wong, 1991). The conversion mechanisms between iodine species are still unclear because
73 iodate does not spontaneously reduce to iodide in natural seawater for thermodynamic reasons (Hou
74 et al, 2007). Nevertheless this reaction between iodate and iodide takes time to reach equilibrium
75 (Luther et al, 1995), around two weeks according to estimates (Carpenter, pers. Comm.). Now,
76 depending on the chemical form of ^{129}I discharged by the reprocessing plant, the question arises as to
77 its bioavailability for seaweed. The PUREX process
78 (<https://www.cea.fr/Documents/monographies/Procédé-PUREX.pdf>) operated at the ORANO
79 reprocessing plant results in the liquid release of ^{129}I as iodide. As such, it is assumed to be a potential
80 substrate for VHPOs, being incorporated by kelps. But as conversion into $^{129}\text{IO}_3^-$ occurs in seawater, it
81 may become unavailable for the enzyme. In summary, two crucial questions should be answered to
82 better understand ^{129}I uptake by brown seaweed in the marine environment around the reprocessing
83 plant of ORANO La Hague: 1- Which form of iodine is bioavailable for uptake by brown seaweed? 2-
84 Does it evolve with time and distance from the outlet once released in seawater by the plant? More
85 generally, the exact mechanism of iodine uptake is still unclear, and was challenged by chemical
86 imaging results confirming a major apoplastic storage location (Lebeau et al, 2021). Assessing which
87 chemical form of seawater iodine is taken up by kelps in the marine environment should contribute to
88 the exploration of its bioaccumulation mechanism.

89 In this study, we investigate *in vivo* iodine uptake in *L. digitata* with an emphasis on chemical
90 speciation between iodide vs iodate. We also use radioactive $^{131}\text{I}^-$ as a tracer of unidirectional iodide
91 influx to estimate iodide turnover in seaweed as well as the relationship with seawater iodide
92 concentration. We also report an isotopic ratio $^{129}\text{I}/^{127}\text{I}$ measured in the marine environment in the
93 vicinity of the outlet of the ORANO reprocessing plant in La Hague. Iodine-129 activity and stable iodine
94 concentrations were determined in total dissolved iodine in seawater and as total iodine extracted
95 from two species of brown seaweed, *L. digitata* and *Fucus serratus* collected in Goury (6 Km from the
96 plant outlet). Finally, laboratory experiment results and data from the natural environment are put
97 into perspective to attempt to better understand radioactive iodine transfers between seawater and
98 brown seaweed.

99 2 Material and methods

100 2.1 Algal material

101 For iodine uptake experiments, plantlets of *Laminaria digitata* [0.05-3 g] were collected on the
102 rocks in Goury (Normandy, France) at low tide (spring-tides) and transferred to the laboratory (LRC,
103 IRSN, Cherbourg, France) for maintenance in an aquarium. The temperature was set to that of the
104 natural environment upon collection (12.5 °C), the water was aerated and recirculated. About 200 g of
105 total biomass (plantlets and young sporophytes, see below) was kept in a 60 L tank in natural light, and
106 the seawater was replaced every week with pre-cooled fresh seawater. The iodine concentration in
107 seawater (see 2.2.2) was checked to ensure no depletion occurred.

108 For ^{131}I experiments, we used both whole plantlets and tissue disks. In the latter case, disks of about
109 0.04-0.05 g (diam. 14 mm) were punched out of the blade of young sporophytes (20-40 cm long;
110 collected and maintained as described above) of *L. digitata* by die-cutting. Algal disks were then kept
111 in filtered seawater (seawater collected in Goury, filtered at 0.45 μm ; Millipore ref. HAWG0700) until
112 iodine leakage stopped, as indicated by the monitoring of iodine concentration in seawater (with one
113 disk in 10 mL of seawater: no iodine leakage was observed after 1 hour).

114 For the environmental monitoring of $^{129}\text{I}/^{127}\text{I}$, adult sporophytes of *L. digitata* (1-1.5 m in length)
115 and *Fucus serratus* (30-70 cm in length) were collected monthly at low tide at Goury for 37 months
116 (see supplementary material S2-1 for sampling location).

117 2.2 Determination of I^- and IO_3^- in seawater

118 2.2.1 Separation of seawater I^- and IO_3^-

119 After sample filtration (0.45 μm , Millipore ref. HAWG0700), seawater I^- and IO_3^- were separated by
120 anion exchange chromatography (AEC) using Bio-Rad AG1-X4 resin and mini-spin columns according
121 to (Hou et al, 2001; Zhang, 2015). Briefly, AG1-X4 resin (provided in Cl^- form) was conditioned into NO_3^-
122 form as follows: 1- a first wash in NaClO 5% removed any residual I^- from the fresh resin. 2- Cl^- was
123 replaced by NO_3^- in NaNO_3 2M. 3- Excess NO_3^- was finally flushed with MilliQ water (Millipore). About
124 0.5 cc of conditioned resin (NO_3^- form) was added to mini Bio-spin columns (Bio-Rad #7326207) and
125 allowed to drain by gravity. Then 3 more 0.9 mL washes of MilliQ water were applied and left to drain
126 prior to starting AEC on filtered (0.45 μm) seawater as follows: 1- two 0.9 mL seawater samples were
127 passed through the resin to replace the mobile phase. 2- The bottom of the column was closed with
128 the stopper tip, another 0.9 mL sample was added and the top was closed with the cap. The column
129 was flipped twice and agitated horizontally for 1 hour on a 3D-platform shaker (Polymax) at slow
130 speed. 3- The bottom stopper tip and the top cap were removed and the mobile phase was allowed to
131 drain in a 1.5 mL centrifuge tube. The flow-through contained IO_3^- anions whilst I^- anions stayed
132 trapped on the resin. Total dissolved iodine concentration was measured (see 2.2.2) before the AEC (I^-

133 + IO₃⁻) and in the column flow-through (IO₃⁻), I⁻ was calculated as the difference. We checked the
134 accuracy of the separation with the standard addition method using KI, KIO₃ and both together.

135 2.2.2 Determination of iodine concentration

136 Total dissolved iodine (as I⁻ and/or IO₃⁻) concentration in seawater was determined by
137 spectrophotometry according to (Sandell & Kolthoff, 1937) in the range [0.04-0.30] μM. Seawater
138 samples were filtered (0.45 μm, Millipore ref. HAWG0700) and diluted in MilliQ water to fit within that
139 range. The color reaction was prepared in a 1.5 mL centrifuge tube with 500 μL of either seawater or
140 an AEC-treated seawater sample (diluted), 50 μL NaCl (10% g/g), 500 μL As₂O₃ (0.1 M) and transferred
141 to a water bath at 30°C. Then 125 μL of (SO₄)₄Ce(NH₄)₄ · 2 H₂O, (0.02 M) was added and the reaction was
142 allowed to run for exactly 20 min at 30°C in the water bath. Absorbance at 420 nm was then measured
143 in 1 mL disposable cuvettes in a spectrophotometer. A calibration curve was carried out with standard
144 solutions between 0.039 μM and 0.316 μM (dilutions of 1.31 g·L⁻¹ KI in MilliQ water solution). The
145 repeatability of the method showed that the uncertainty of the results was ± 5%. Total iodine
146 concentration before (I⁻ + IO₃⁻) and after (IO₃⁻) separation by AEC (see 2.2.1) was determined in order
147 to obtain the I⁻ concentration based on the difference. We checked the accuracy of the quantification
148 with the standard addition method using KI, KIO₃ and both together. The reliability of method was
149 further checked by comparing the results obtained by spectrophotometry with duplicates analyzed by
150 ICPMS measurements on some of our samples.

151

152 2.3 Measurement of net iodine flux between seaweed and seawater

153 Plantlets of *L. digitata* (pooled to about 2 g) were incubated in beakers with 50-75 mL of filtered
154 seawater (0.45 μm, Millipore ref. HAWG0700) at the same temperature as in the host aquarium (12.5
155 ± 1.0 °C), with bubbling. Seawater samples were collected over time (a picture of the incubation setup
156 is provided in the supplementary material S1-1). The sample volume was 0.5 mL for total dissolved
157 iodine (I⁻ + IO₃⁻) and 3 mL for AEC separation. Beakers without seaweed plantlets served as controls for
158 changes in iodine concentrations into the filtered seawater used due to adsorption onto the beakers
159 surface. No changes in iodine concentrations were observed in those beakers. At some point in the
160 experiment, seawater was spiked either with KI, KIO₃ or both. Upon completion of each experiment,
161 the plantlets were patted dry between absorbent paper sheets and weighed. Concentrations of both
162 I⁻ and IO₃⁻ in the water were plotted as a function of time.

163 2.4 Measurement of unidirectional ¹³¹I⁻ influx in seaweed

164 Iodine-131 as KI was purchased from CIS Bio International (I-131-S-2) and the activity information
165 was provided by the manufacturer with the calibration date (Act.=1.11E+08 Bq; Vol.=0.67 cc;
166 ¹³¹I/¹²⁷I=4.64E+08). Because of constraints in accurate nuclear metrology (geometry calibration),
167 unidirectional radioactive ¹³¹I influx was measured on tissue disks punched out of *L. digitata* blade as
168 previously published (Küpper et al, 1998; Shaw, 1959). Tissue disks were incubated in seawater spiked
169 with ¹³¹I in the form of KI. The disks were rapidly patted dry on absorbent paper, transferred to a plastic
170 container and counted for 60 sec on a hyper pure GeHP gamma detector. The measurement procedure
171 lasted 1.5 min and the disks were then returned to the incubation medium to carry on the uptake
172 kinetics experiment. Radioactive iodine disk content was then plotted as a function of time and it was
173 found to be linear for 15 min. The activity in seawater was found to be constant for short-term
174 experiments (15 min). We investigated the relationship between the ¹³¹I uptake by the disks and iodine
175 concentration in seawater. For that purpose, seawater iodine concentration was increased by addition
176 of KI to 1, 3, 10, 50, 500 μM and spiked with ¹³¹I (230 Bq·mL⁻¹). The slope of the 15 min linear ¹³¹I uptake
177 allowed the iodine permeability of the disks to be estimated (in nmol·min⁻¹·g⁻¹) since the exchange

178 surface was constant. Plotting the iodine permeability as a function of seawater concentration allowed
179 for the derivation of the values of Vmax and Km according to the Michaelis-Menten model as
180 previously described by (Küpper et al, 1998). The Michaelis-Menten model was fitted using Microsoft
181 Excel™ Solver function.

182 A longer time intake experiment was carried out over 14 days with a 0.1 g plantlet kept in a 10 L
183 tank to estimate iodine turnover by the algae. The procedure was the same as for tissue disks with the
184 plantlet patted dry and lying in a plastic dish for gamma counting. The activity of the seawater (30
185 Bq.mL⁻¹ seawater) was maintained constant by adding ¹³¹I to compensate for intake by the plantlet as
186 well as ¹³¹I decay. The very large volume of the tank compared to the small size of the plantlet ensured
187 that no total iodine depletion occurred in seawater. The biological half-life of iodine in *L. digitata*
188 plantlet was estimated as $t_{b1/2} = \ln(2)/k$ by fitting the data to equation $Act_t = Act_0.[1-\exp(-k.t)]$ (with
189 t=time; Act=¹³¹I activity at time t; k=time constant) with the Solver function of Microsoft Excel™ (we
190 don't need to implement ¹³¹I decay since the radioisotope activity is artificially maintained constant in
191 seawater).

192 2.5 Measurement of iodine-129 activity in seawater

193 120 L-seawater samples were collected monthly at Goury for 37 months, and filtered at 0.45 µm
194 (Millipore, Durapore membrane ref. HVLP2932A). Total dissolved iodine concentration was
195 determined in an aliquot as described above (2.2.2). A known amount of stable iodine (0.500 g KIO₃)
196 was added to the 120 L as a carrier and to allow for the calculation of the extraction yield. Dissolved
197 iodine in the forms of I⁻ and IO₃⁻ were merged by the addition of 120 g Na₂SO₃ at pH 2 (HCl-36%) to
198 reduce IO₃⁻ into I⁻. Total I⁻ was then precipitated by the addition of 6 g AgNO₃. The AgI precipitate was
199 recovered in 500 mL with MilliQ water and then solubilized by the addition of 35 g L+ascorbic acid
200 (C₆H₈O₆) at pH 10 (NaOH 5N). The solution containing dissolved iodine was then transferred into a
201 separation funnel and covered with 100 mL 1,2,4-Trimethylbenzene (TMB). HNO₃ 65% was added until
202 pH 2 was reached, and NaNO₂ added whilst pH was maintained with HNO₃ to oxidize iodide into I₂. The
203 funnel was vigorously shaken to trap I₂ in the organic phase and then left to decant. The aqueous phase
204 was recovered and another 50 mL TMB was added to further extract I₂. The two TMB organic phases
205 were pooled (150 mL) and washed twice with 100 mL MilliQ water (the water was discarded). Extracted
206 iodine was finally recovered from the organic phase by adding 20 mL of NaOH 0.5 N; Na₂SO₃ 0.2 M to
207 reduce I₂ into I⁻. The separation funnel was vigorously shaken, allowed to settle, and the 20 mL aqueous
208 phase was recovered in a plastic vial where traces of TMB adhered to the plastic wall. The aqueous
209 phase was finally transferred into a clean 20 cc geometry. The final 20 cc geometry contained initial +
210 added stable iodine and unknown iodine-129. Iodine-129 activity was determined by gamma
211 spectrometry in the 20 cc geometry previously calibrated with a standard solution (IL29-ELSF15
212 #4793/4, provided by CEA/DAMRI), using a hyper pure GeHP gamma detector (29,78 keV double ray,
213 emission rate 57,3%, detection limit = 0.05 Bq in the final sample with a counting time of 80 000 s, 0.03
214 Bq in the final sample with a counting time of 240 000 s). A quenching curve was obtained by
215 incrementing stable iodine concentration in the standard IL29-ELSF15 solution using the same 20 cc
216 geometry: the quenching by stable iodine was lower than 15% (15% at 600 mg iodine, 5% at 200 mg
217 iodine). Stable iodine concentration in the 20 cc geometry was determined by potentiometric method
218 using an Orion 96-53 ionplus® Series Iodide Electrode according to the manufacturer's instructions.
219 The iodine concentration in the geometry was used to correct the results for the extraction yield and
220 for gamma counting quenching. Extraction yield was in the range [70%-80%]. Final results were
221 expressed in Bq.m⁻³ for ¹²⁹I and in µM for stable ¹²⁷I. The isotopic ratio ¹²⁹I/¹²⁷I could then be calculated
222 in seawater for total dissolved iodine (I⁻ + IO₃⁻; with 1 Bq ¹²⁹I = 1.186E-09 mol).

223 2.6 Iodine-129 activity measurement in seaweed

224 In parallel with seawater, iodine-129 activity was determined in *L. digitata* and *F. serratus* samples
 225 collected monthly (see **Erreur ! Source du renvoi introuvable.**), dried at 90°C and finely ground as
 226 described in (Bouisset et al, 1999; Lefevre et al, 2003). In both species, stable total iodine concentration
 227 was determined in parallel on aliquots by the CNRS/SCA (Service Central d'Analyses, Vernaison,
 228 France). Seaweed dry material was mineralized in Schöniger combustion flasks and the solutions were
 229 analyzed using ion exchange chromatography with electrochemical detection (the quantification limit
 230 was 0.25 µg.L⁻¹ iodine). Final results were expressed in Bq.Kg⁻¹ dry weight for ¹²⁹I and in mg.Kg⁻¹ dry for
 231 stable ¹²⁷I. The isotopic ratio ¹²⁹I/¹²⁷I could then be calculated in dry seaweed material).

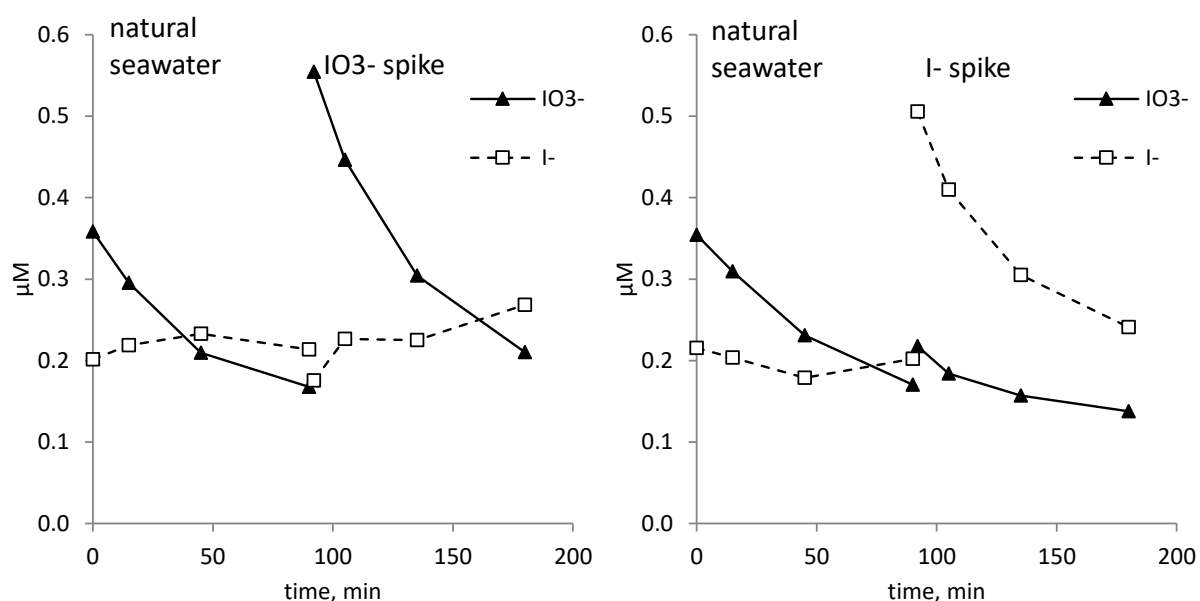
232

233 3 Results

234 3.1 Which form of inorganic iodine in seawater is taken up by *Laminaria digitata*?

235 A first series of experiments consisted in the incubation of *L. digitata* plantlets in natural seawater
 236 collected in Goury at the same location as the seaweed with [IO₃⁻] = 0.35 µM and [I⁻] = 0.25 µM. The
 237 changes in seawater IO₃⁻ and I⁻ concentrations showed that only IO₃⁻ appeared to decrease in the
 238 medium in the presence of the plantlet, and this was confirmed by spiking seawater with IO₃⁻ at time
 239 90 min (Figure 1 left). However, spiking seawater with I⁻ instead of IO₃⁻ clearly demonstrated that both
 240 iodine forms decreased (Figure 1 right). These experiments were replicated 6 times for I⁻ and IO₃⁻
 241 independently with the same results (supplementary materials S1-2 and S1-3).

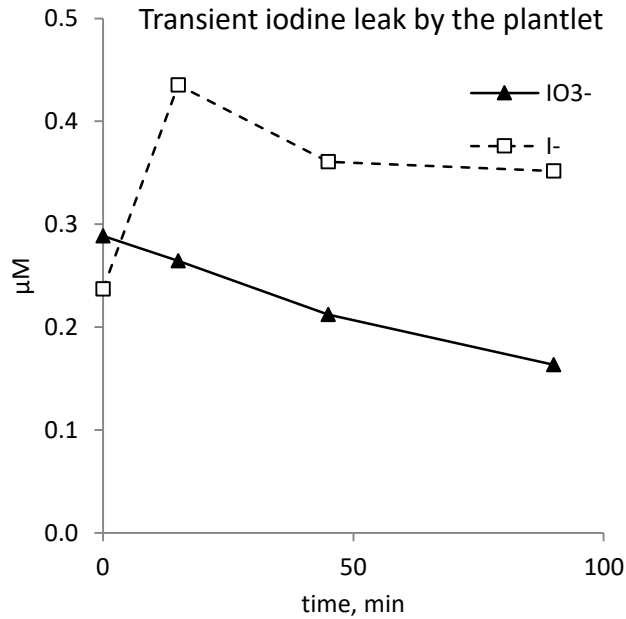
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243

244 Figure 1: Incubation of *Laminaria digitata* plantlets: changes in seawater IO₃⁻ (filled triangle) and I⁻ (open
 245 square) concentrations over time. The uncertainty of the measurements was ± 5 % (error bars omitted to ensure
 246 clarity). Seawater was spiked with IO₃⁻ (left) and I⁻ (right) after 90 min of incubation.

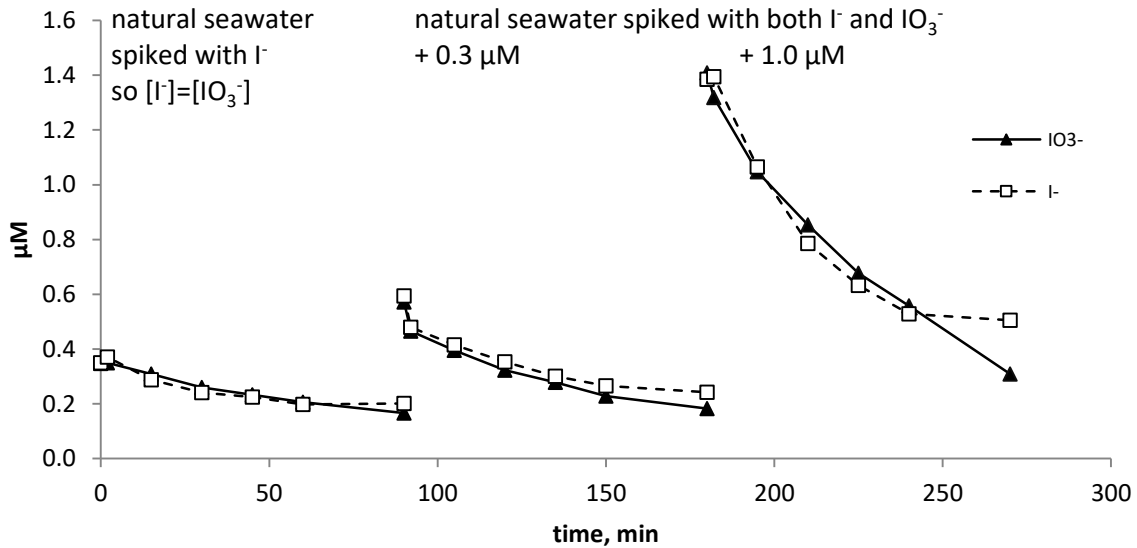
247 When replicating the experiment, the transfer of *L. digitata* plantlet to the incubation vial
 248 sometimes resulted in transient iodine leaks from the seaweed. In those cases, only I⁻ increased in
 249 seawater whilst IO₃⁻ continued to decline (Figure 2).



250

251 Figure 2: Transient iodine leak by the plantlet which only resulted in net I^- output whilst IO_3^- was still taken
 252 up (same symbols as in Figure 1, uncertainties $\pm 5\%$).

253 Since both IO_3^- and I^- seem to be taken up by *L. digitata*, the question then arose as to why the I^-
 254 concentration didn't decrease in the experiment illustrated in Fig.1 left? A simple hypothesis is that
 255 the concentrations in seawater determine which form of iodine is pumped. We repeated the
 256 experiment with different concentrations of IO_3^- and I^- in seawater, starting with the same
 257 same concentrations of both forms of iodine, and increased the levels up to $1.4 \mu\text{M}$ for each iodine species
 258 (Figure 3).

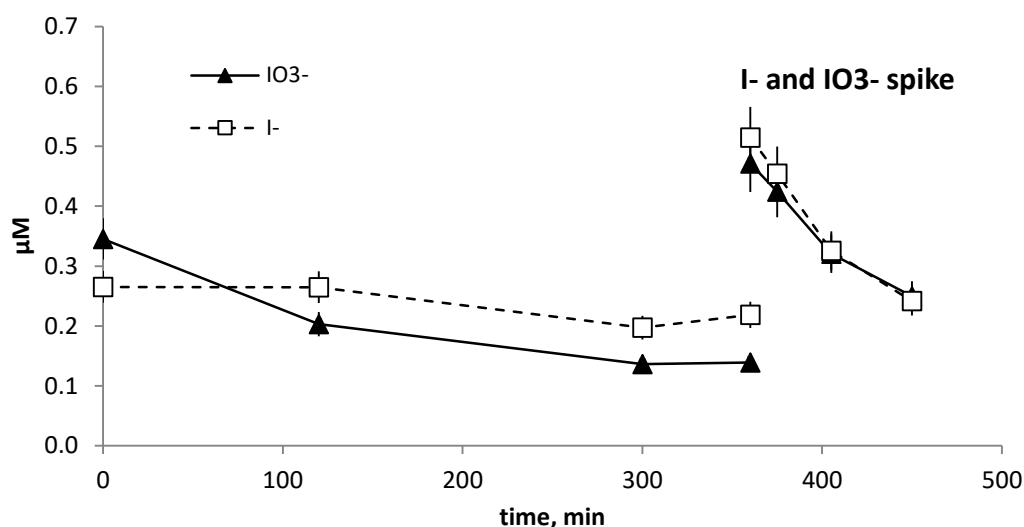


259

260 Figure 3: Incubating *Laminaria digitata* plantlets in seawater with increasing levels of IO_3^- and I^- at the same
 261 concentration (same symbols as in Figure 1, uncertainties $\pm 5\%$).

262 When both IO_3^- and I^- were present at the same concentration, their concentrations decreased
 263 equally in the presence of the plantlet. So, in the left experiment in Figure 1, was there a minimum I^-
 264 concentration below which the uptake just balanced the output? Likewise, does a minimum IO_3^-
 265 concentration exist below which this iodine form uptake just balances the output? To address this

266 point, we extended the net flux experiment for 6 hours to attempt to see the "asymptotic" seawater
 267 IO_3^- and I^- concentrations when no more net flux were observed. At the end, the net iodine uptake was
 268 re-stimulated by a fresh spike of I^- and IO_3^- . The results of this long-term kinetics are shown in Figure
 269 4.

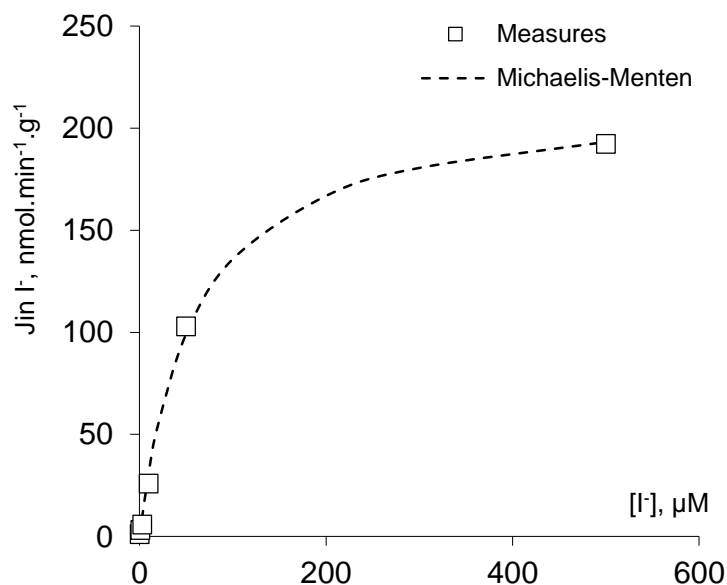


270
 271 Figure 4: Long-term kinetics experiment on net iodine flux using plantlets of *Laminaria digitata* (same symbols
 272 as in Figure 1).

273 This long-term kinetics experiment was replicated 7 times (supplementary materials S1-4) and
 274 every time, IO_3^- concentrations declined below I^- concentrations, as in the example displayed in Figure
 275 4. The average iodine concentrations (\pm SE) at time 0 were $[\text{IO}_3^-] = 0.35 \pm 0.01 \mu\text{M}$; $[\text{I}^-] = 0.31 \pm 0.06 \mu\text{M}$
 276 and at time 360 min, they were $[\text{IO}_3^-] = 0.16 \pm 0.03 \mu\text{M}$; $[\text{I}^-] = 0.29 \pm 0.03 \mu\text{M}$, (N=7).

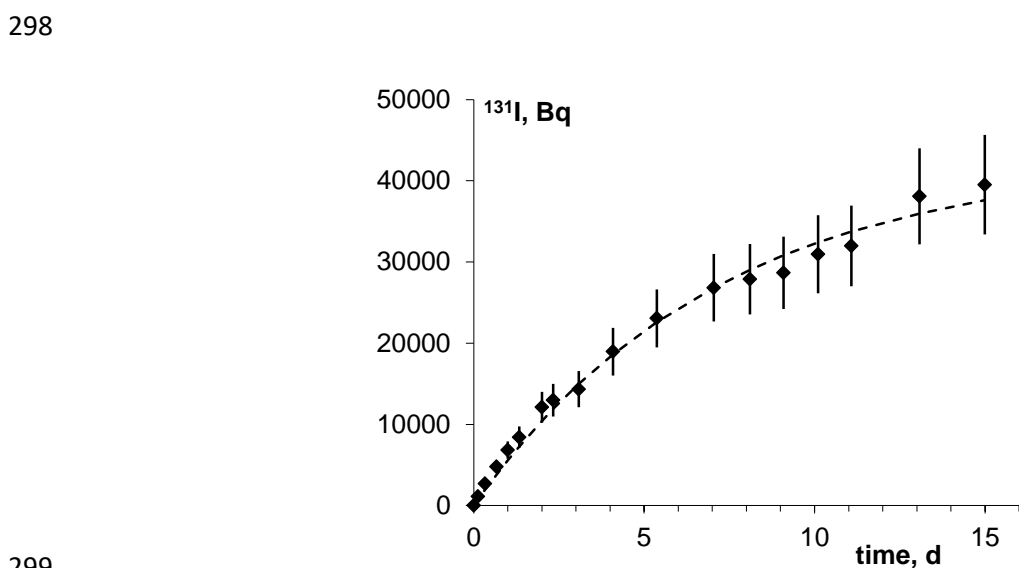
277 3.2 Tracing iodine uptake in *Laminaria digitata* with ^{131}I

278 Since both IO_3^- and I^- seemed to be taken up equally by the seaweed (provided their concentrations
 279 were high enough), using radioactive $^{131}\text{I}^-$ was considered to trace dissolved iodine uptake whatever
 280 the chemical form. We investigated the relationship between the uptake and iodine concentration for
 281 *L. digitata* using disks punched out from the thallus blade as previously described (Küpper et al, 1998;
 282 Shaw, 1959). The unidirectional flux J_{in} ($\text{nmol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$) was proportional to seaweed iodine
 283 permeability, since the disk surface was constant during the experiment. The results are presented in
 284 Figure 5 fitted with Michaelis-Menten model kinetics with apparent $K_m = 59 \mu\text{M}$ and $V_{\text{max}} = 216$
 285 $\text{nmol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. From those results, we calculate an approximate unidirectional influx capacity of ^{131}I of
 286 c.a. $100 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. This unidirectional influx can be compared to results obtained in our net fluxes
 287 experiments (Figures 1 to 4), in which we obtained influxes of around $1 \text{ nmol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. Net fluxes result
 288 from the balance between input and output fluxes. Therefore, the 2 orders of magnitude higher
 289 unidirectional input fluxes measured in our ^{131}I uptake experiment indicate that output fluxes must be
 290 very high to result in a 100 fold reduction when considering net fluxes.



291
 292 Figure 5: Relationship between unidirectional iodine influx and seawater iodine concentration for tissue disks
 293 of *Laminaria digitata*. Fitting the Michaelis-Menten model kinetics yielded $K_m = 59 \mu\text{M}$ and $V_{\text{max}} = 216$
 294 $\text{nmol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$.

295 A two-week experiment was performed to estimate the biological half-life of iodine in *L. digitata*
 296 plantlets. The ¹³¹I uptake experiment displayed in Figure 6 yielded an estimated $t_{b1/2}$ value of c.a. 5
 297 days.



299
 300 Figure 6: ¹³¹I uptake over two weeks by *Laminaria digitata* plantlet leading to the estimation of the iodine
 301 turnover in the seaweed as 5 days.

302 3.3 ¹²⁹I transfer between seawater and brown seaweed exposed to discharges from the
 303 ORANO reprocessing plant in La Hague

304 3.3.1 Seasonal changes of iodine in seawater and in brown seaweed

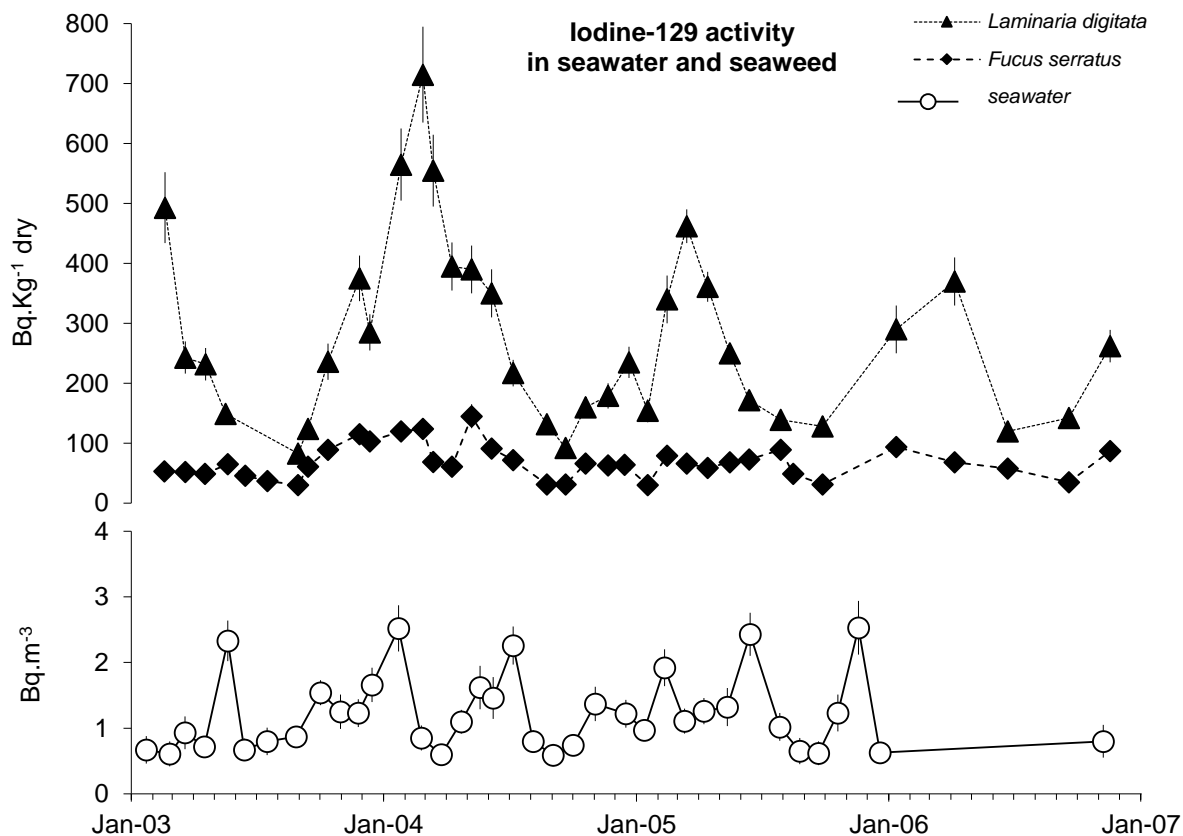
305 Seawater samples were periodically collected in Goury and analyzed for iodine chemical speciation.
 306 Additional samples were collected in different locations around the Cap of La Hague and along the
 307 coast of Brittany (Bretagne, France). The data are presented in the supplementary material (S2-2).

308 Since brown seaweed iodine content may vary during the seasonal cycle, it was crucial to take these
 309 changes into account when looking at radioactive iodine transfer to seaweed. Total iodine in mg.Kg^{-1}
 310 dry was determined in *L. digitata* and *F. serratus* samples were collected monthly in Goury. The data
 311 are displayed in the supplementary material (S2-3).

312 3.3.2 Iodine-129 activity in seawater and in brown seaweed

313 Iodine-129 activity determined in dissolved iodine in seawater ($\text{IO}_3^- + \text{I}^-$) and in the two brown
 314 seaweed species *L. digitata* and *F. serratus* are presented in Figure 7.

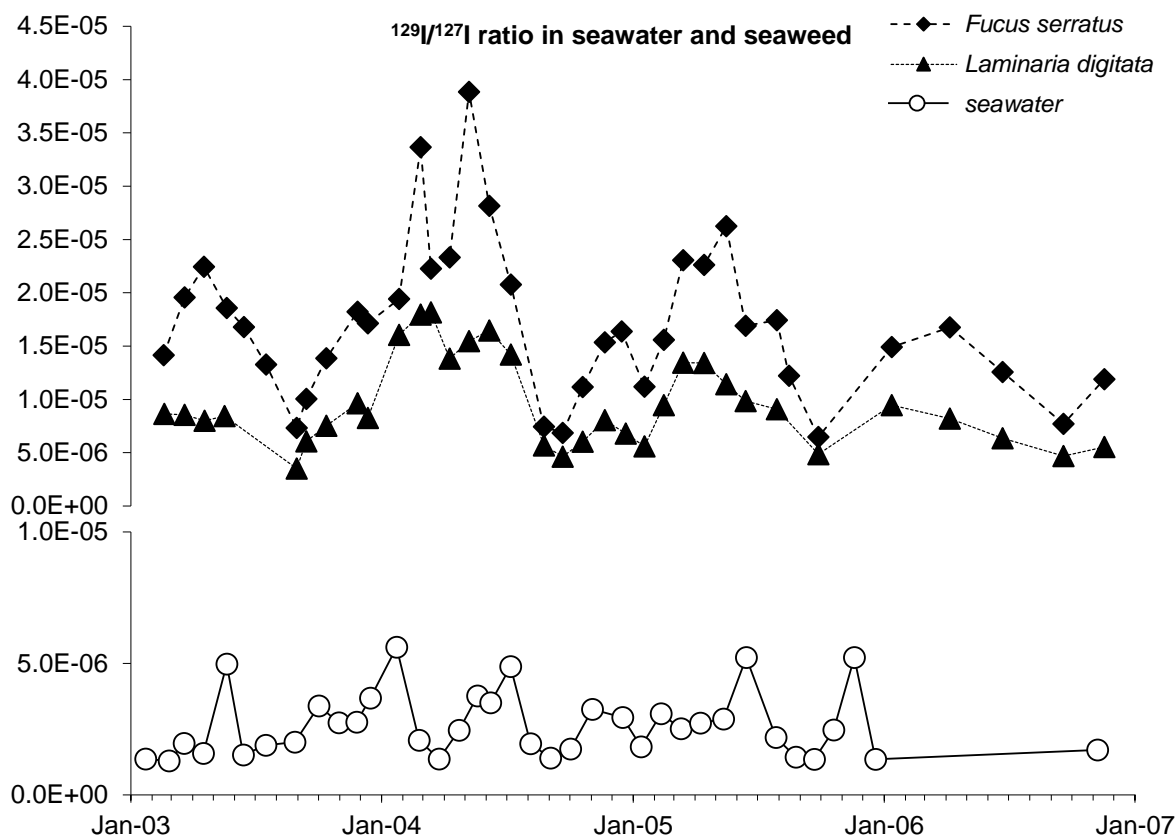
315



316

317 Figure 7: Iodine-129 activity in seawater and in brown seaweed collected in Goury, near the outlet of the
 318 ORANO reprocessing plant in La Hague. Error bars account for metrological uncertainties (2 x sigma; may be
 319 masked by symbol).

320 Because iodine content varies in seaweed over the season, expressing the radioactivity data as the
 321 isotopic ratio $^{129}\text{I}/^{127}\text{I}$ was necessary to explore ^{129}I transfer between seawater and seaweed. The ratio
 322 $^{129}\text{I}/^{127}\text{I}$ was determined in dissolved iodine in seawater ($\text{I}^- + \text{IO}_3^-$) and in *L. digitata* and *F. serratus* dry
 323 material and the data are presented in Figure 8.



324

325 Figure 8: Iodine-129 isotopic ratio in seawater and in brown seaweed collected in Goury, near the outlet of
 326 the ORANO reprocessing plant in La Hague.

327 **4 Discussion**

328 The fate of ^{129}I liquid discharged by the ORANO reprocessing plant in La Hague (Normandy, France)
 329 deserves special attention for several reasons: due to its very slow decay, this radionuclide is a major
 330 residual iodine radioisotope in the nuclear fuel cycle and a tracer of the discharges by the ORANO
 331 reprocessing plant in the environment. As part of the liquid waste released in seawater in the Alderney
 332 Race (Baillly du Bois et al, 2020; Fiévet et al, 2020), it mixes with natural stable iodine so that isotopic
 333 dilution minimizes its impact in terms of radioprotection. However, brown seaweed is known to be
 334 exceptionally efficient at bioaccumulating iodine from seawater. The recommended value for the
 335 iodine concentration factor (CF) in macroalgae is 10^4 (IAEA, 2004), and ratios of up to $4.3 \cdot 10^4$ were
 336 observed in kelps (Fiévet et al, 2021). Moreover, brown seaweed has the ability to transform
 337 accumulated iodine into volatile compounds, such as I_2 , released in response to various stresses, such
 338 as emersion at low tide (Ball et al, 2010; McFiggans et al, 2010; McFiggans et al, 2004; O'Dowd et al,
 339 2002; Whitehead et al, 2009). This process might challenge the strategy to keep ^{129}I away from humans
 340 because the isotope can return to the terrestrial environment *via* airborne routes *via* the wind and
 341 aerosols. For these reasons, although the potential contribution of this atmospheric route is not
 342 known, brown seaweed is focused on as part of radionuclide monitoring of the marine environment.
 343 Understanding the transfer of radioactive iodine released by the nuclear industry (under control) in
 344 the marine environment is not only essential for the sake of radioprotection, the fate of radioactive
 345 iodine released into the English Channel also has a much larger scope than radioprotection as a
 346 potential tracer of the complex behavior of iodine in the marine environment. The different key steps
 347 of iodine transfer from seawater to the bioaccumulation in brown seaweed are part of the bigger
 348 puzzle of the biogeochemical cycle of iodine in the ocean and its consequences on the chemistry of
 349 the atmosphere (Carpenter et al, 2021). The transfer of iodine from the ocean to the atmosphere is

350 assumed to occur through the oxidation of iodide (I^-) into diiodine (I_2) in the presence of atmospheric
351 ozone under solar radiation, but also through biological oxidation processes (Carpenter et al, 2021).
352 Iodate (IO_3^-) is the preferential chemical form of iodine in seawater, therefore its conversion into iodide
353 (I^-) is not spontaneous as regards thermodynamics (Hou et al, 2007; Wong, 1991). After decades of
354 literature on the topic, the reduction of iodate into iodide still remains poorly understood, though
355 microorganisms or marine algae clearly play a role (Carpenter et al, 2021; Wong, 1991) and this factor
356 has recently been confirmed for some marine bacteria (Reyes-Umana et al, 2022).

357 In the present study, we provide new information on the uptake mechanism of iodine by kelp (*L.*
358 *digitata*). First, our results suggest that kelp plantlets were able to take up iodine in the forms of both
359 IO_3^- and I^- with the same efficiency (Figure 1). When both iodine species were present at the same
360 concentration, they declined at equivalent rates in seawater (Figure 3). It should be emphasized that
361 our experimental conditions magnified naturally occurring phenomena due to a change in the ratio
362 between the seaweed mass and the volume of its surrounding seawater compared to the natural
363 environment. This magnification allowed us to easily assess the net IO_3^- and I^- fluxes between the
364 plantlet and seawater by measuring the decrease in those iodine species in seawater, with our
365 measurements accounting for the balance between inputs and outputs. Plantlets of *L. digitata* are very
366 sensitive and required extreme care during transfers from the natural environment and between the
367 host aquarium and the flux experiment setup. Chemical imaging data provided information on a very
368 unequal compartmentalization of iodine in the tissue of *L. digitata* plantlet. Iodine appears to be
369 preferentially concentrated in the peripheral apoplastic tissue (Lebeau et al, 2021). As such, transient
370 iodine leakage might occur when manipulating a plantlet. We assumed that plantlets underwent
371 minimal stress because after each experiment, they were returned to the host aquarium and could be
372 re-used for more experiments, and the iodine leaks sometimes observed at the beginning of the
373 experiments were only transient and brief. Indeed, a transient iodine leak by the plantlets was
374 observed in 11 out of 42 net flux experiments. In all cases it should be emphasized that only I^- leaks
375 were ever detected in seawater whilst IO_3^- always continued to decline (Figure 2). This observation was
376 an *in vivo* evidence that iodine is stored in *L. digitata* tissue as iodide (I^-), as shown by laser
377 desorption/ionization mass spectrometry (Lebeau et al, 2021). We could then interpret the results of
378 our net flux experiment on the basis of this information. When assessing IO_3^- and I^- net fluxes, we
379 expected those fluxes to stop when the inputs balanced the outputs, or when the seawater
380 concentrations were too low to meet the needs of the uptake process. In the long-term (6 hours)
381 experiment (Figure 4), a change in seawater iodine speciation was observed in the presence of *L.*
382 *digitata* plantlets. The IO_3^- concentration was initially above the I^- concentration, and this reversed
383 after 2 hours. IO_3^- declined down to around 0.15 μM whilst I^- stayed at around 0.25 μM . If the seaweed
384 only stores I^- but can take up both IO_3^- and I^- , we conclude that IO_3^- was likely to be converted into I^- at
385 some point in the plantlet (apoplast), or through the action of associated microorganisms. After 5-6
386 hours of incubation, the stable IO_3^- and I^- concentrations in seawater therefore resulted from $IO_3^- + I^-$
387 influxes and I^- outflux only. We assume that the IO_3^- stabilized in seawater because its concentration
388 was so low that the uptake mechanism was no longer able to pump this iodine form, "by exhaustion",
389 as indicated by the more than 200 fold difference between the K_M of 59 μM and the final iodine
390 concentrations of 0.15-0.25 μM we measured. Conversely, the extreme chemical gradient of I^-
391 between the seaweed and seawater and its permeability resulted in I^- outflux. I^- stabilization in
392 seawater corresponded to the balance between this I^- leak and the ability of the mechanism to take
393 up I^- . So, when the IO_3^- is low enough in seawater to exhaust its uptake, we only observe I^- recycling. A
394 major conclusion of this laboratory experiment was that we directly observed the kelp-based biogenic
395 conversion of seawater IO_3^- into I^- . Even if the quantitative contribution of the process was considerably

396 magnified with our biomass/seawater ratio, this provided direct evidence of this iodine conversion
397 mediated by brown algae and associated microorganisms observed in the marine environment.

398 Second, we also concluded that *L. digitata* plantlets can take up either IO_3^- or I^- indifferently. Iodine
399 bioaccumulation in kelps is assumed to be mediated by vanadium-dependent haloperoxidases (VHPO)
400 family (Küpper et al, 1998), and especially by vanadium-dependent iodoperoxidases (VIPO)
401 characterized in *L. digitata*, specific to iodide oxidation (Colin et al, 2005). The substrates of VHPOs are
402 halides and H_2O_2 (Colpas et al, 1996) so VIPO is assumed to oxidize I^- and not IO_3^- . The hypothetical
403 mechanism involving only VIPO-based iodide uptake in iodine bioaccumulation by kelp was recently
404 questioned by our data on the apoplastic localization of iodine storage in the plantlets (Lebeau et al,
405 2021; Verhaeghe et al, 2008). The parallel uptake of IO_3^- and I^- that we observed in our net flux
406 experiments suggests a need to further validate *in vivo* the biological function of VHPO and/or VIPO in
407 iodine bioaccumulation. However, we suggest the following speculative scheme: if iodide is the only
408 form of iodine in the storage site, as shown previously (Lebeau et al, 2021; Verhaeghe et al, 2008),
409 oxidized forms may have a favorable chemical gradient to enter the seaweed. This would rely on the
410 strong reduction capacity of the storage site in order to maintain this gradient. The question of this
411 reduction capacity inside the seaweed storage compartment is still pending, but in this scheme, the
412 driving force would be this reduction capacity of the apoplastic storage site and the uptake would only
413 rely on oxidized iodine accessing the site along a favorable chemical gradient. Natural IO_3^- in seawater
414 would be available for this, and VIPO would be there to oxidize I^- when present. It should be kept in
415 mind that a major role for the I^- bioaccumulated in the seaweed is to react with reactive oxygen species
416 to reduce oxidative stress and/or to release oxidized iodine in response to stress as a defense
417 mechanism (Küpper et al, 2008).

418 We used an ^{131}I tracer to further characterize iodine uptake in kelp. This replicated a kinetic
419 experiment (3 hours) performed many decades ago (Shaw, 1959). The isotope was added in the form
420 of $^{131}\text{I}^-$, but our net flux experiment showed that both IO_3^- and I^- uptakes exactly matched. This
421 suggested that $^{131}\text{I}^-$ unidirectional influx data were relevant to trace iodine uptake. The dependence of
422 I^- uptake on concentration followed Michaelis-Menten kinetics, as previously published with disks of
423 *L. digitata* (Küpper et al, 1998). The Michaelis-Menten kinetics confirmed the enzymatic mediation of
424 I^- uptake but our values of K_m and V_m parameters were quite different. Our K_m value of $59\ \mu\text{M}$ was
425 more than 7 times lower and our V_m value of $219\ \mu\text{M}$ was more than three times higher. We have no
426 explanation for this discrepancy except maybe the physiological condition of the disks punched out
427 from the blade of *L. digitata*. On the basis of our K_m value of $59\ \mu\text{M}$, we may speculate that at
428 concentrations more than two orders of magnitude lower, like in our flux experiments (Figure 4), the
429 uptake mechanism reached a steady state. A biological half-life of 5 days for iodine was estimated
430 based on the long-term $^{131}\text{I}^-$ uptake experiment on *L. digitata* plantlets. Although the values are
431 consistent, this was below our previous estimate of 14 days in brown seaweed based on modeling
432 using ^{129}I environmental data (*L. digitata* and *F. serratus*) in the marine environment in the vicinity of
433 the ORANO reprocessing plant in La Hague (Fiévet et al, 2021). Our laboratory experiment lasted 15
434 days, but we can't rule out that we had not reached the plateau for ^{131}I activity in the seaweed. Besides,
435 it was not surprising that the young plantlet of *L. digitata* showed small differences in iodine uptake
436 kinetics compared to adult and other brown seaweed used in our environmental modelling.

437 The apparent convergence of IO_3^- and I^- uptake by *L. digitata* plantlets observed in our net flux
438 experiments was essential for interpreting our study of radioactive iodine transfer between seawater
439 and seaweed in the marine environment under the influence of radioactive liquid discharges from the
440 ORANO reprocessing plant in La Hague. ^{129}I should be measured in seawater based on total iodine (IO_3^-
441 + I^-) to account for ^{129}I bioavailability at least for kelps. Seasonal changes in iodine concentrations in

442 seawater and in seaweed were also essential to take into account. In seawater, if we merge all total
443 ($\text{IO}_3^- + \text{I}^-$) dissolved iodine measurements we took in seawater along the coast of the English Channel
444 and Brittany (Map in the supplementary material S2-1), the average concentration (\pm SE) was $0.54 \pm$
445 $0.05 \mu\text{M}$ ($N=56$). Our recent measurements around the Cape of La Hague (supplementary material S2-
446 2) with IO_3^- and I^- partitioning showed relatively stable IO_3^- concentration whilst I^- seemed to fluctuate
447 over the year. Longer time-series measurements are required to confirm these chemical speciation
448 data, but a question already arose from these I^- data. In seawater samples collected from the shore,
449 where brown seaweed including kelp was present, our IO_3^- concentration measurements of around
450 $0.3 \mu\text{M}$ were consistent with offshore values reported in the literature (Hou et al, 2007). But our I^-
451 concentrations onshore were around $0.2 \mu\text{M}$, whilst they were in the range $[0.04-0.08] \mu\text{M}$ in the
452 middle of the English Channel. Interestingly, iodide concentrations around $0.15 \mu\text{M}$ were reported at
453 coastal sampling locations from North Germany (Hou et al, 2007). This difference in iodide partition
454 between coastal and offshore waters is in agreement with previous reviews by (Wong, 1991; Wong,
455 2001; Wong & Cheng, 2001a; Wong & Cheng, 2001b). Did the presence of local brown algae fields
456 influence the iodine chemical partition (IO_3^- vs I^-) in our coastal seawater sample? This question is now
457 under further investigation (Carrano et al, 2021). Nevertheless, total dissolved iodine concentration
458 data in seawater were used to calculate the isotopic ratio of ^{129}I in total iodine ($\text{IO}_3^- + \text{I}^-$) measurements
459 in Goury (Figure 7 and Figure 8). Iodine content in brown seaweed clearly cycled with season, with
460 higher levels in winter than in summer (supplementary material S2-3). Does a higher growth rate in
461 summer overwhelm the iodine uptake capacity of the seaweed? Does solar exposure at low tide or
462 other stresses (thallus grazing by marine organisms) result in more volatile iodine release and loss?
463 Regardless of the cause, it was critical to consider iodine seasonal fluctuations in seaweed (Ar Gall et
464 al, 2004) when investigating radioactive iodine transfer between seawater and seaweed. The isotopic
465 ratio $^{129}\text{I}/^{127}\text{I}$ in seaweeds and in seawater gave us a better understanding of iodine transfer. Up to 10-
466 fold higher isotopic ratios were found in seaweed vs seawater (Figure 8). Although the ^{129}I activities
467 were lower in *F. serratus* than in *L. digitata* (Figure 7), the $^{129}\text{I}/^{127}\text{I}$ ratio values in the former were above
468 those in the latter (Figure 8). The discrepancy between the isotopic ratio $^{129}\text{I}/^{127}\text{I}$ in seawater and brown
469 seaweed was puzzling. Our net laboratory IO_3^- and I^- flux experiments in *L. digitata* plantlets showed
470 that both forms of iodine are equally taken up by the seaweed. Therefore, a conversion of $^{129}\text{I}^-$
471 discharged by the reprocessing plant into $^{129}\text{IO}_3^-$ would not result in a change in $^{129}\text{I}^-$ bioavailability for
472 kelp, as we had however proposed in our recent review (Fiévet et al, 2021). This also invalidates this
473 hypothesis to explain why the apparent $^{129}\text{I}^-$ bioavailability declined with distance from the plant outlet,
474 as we noticed in seaweed with regards to hydrodynamic dispersion modelling (Fiévet et al, 2021). We
475 cannot currently explain the difference in the isotopic ratio $^{129}\text{I}/^{127}\text{I}$ between seawater and brown
476 seaweed. Although we cannot rule out isotopic fractionation in the uptake mechanism, it seems
477 unlikely with such a small relative difference in the nucleus mass of the two iodine isotopes. A likely
478 explanation was that, when looking at $\text{IO}_3^- + \text{I}^-$ in seawater, we missed an essential ^{129}I compartment
479 (chemical form) in the marine environment to which brown seaweed are exposed, an iodine
480 compartment that remains to be identified. The difference in the isotopic ratio $^{129}\text{I}/^{127}\text{I}$ between the
481 two seaweed species that we analyzed may provide a clue. *F. serratus* grows in the mid intertidal zone
482 whilst *L. digitata* grows at the very bottom. It means that the former emerges twice a day at low tide
483 and the latter only a few times a month during spring tides. More frequent contact with the seawater
484 surface and longer contact with the atmosphere occurs for *Fucus* than *Laminaria*. To test this
485 hypothesis in a preliminary experimental setup, we detached adult *L. digitata* from the rocks and
486 artificially maintained the seaweed in a floating net for 1 month (photo in the supplementary material
487 S2-4). At the same location, we compared ^{129}I activities in natural specimens from the bottom with
488 those from the net and observed a 50% increase (not shown). The thallus tissue was not visibly
489 degraded, and an identical ^{40}K level was taken as an indication of regular mineral balance. This

490 experiment was anecdotal and should be confirmed and further characterized. The question raised by
491 the different isotopic ratio $^{129}\text{I}/^{127}\text{I}$ between seawater and brown seaweed is still open, but the sea
492 surface and its interface with the atmosphere may be a focal point when investigating iodine transfer
493 to seaweed in the marine environment.

494 **5 Conclusion**

495 The present paper aimed to improve our understanding of iodine transfers between seawater and
496 brown seaweed in the context of radioactive liquid discharges from nuclear facilities in the marine
497 environment. We are left with a series of questions: 1- The iodine uptake mechanism in brown
498 seaweed, which yields an exceptional bioaccumulation level, unknown in any other living organism, is
499 still mysterious. The difference of five orders of magnitude in concentration with respect to seawater
500 is even a low estimate, since iodine storage compartments are probably only peripheral in the
501 apoplast, as suggested by previous results in *L. digitata* (Lebeau et al, 2021; Verhaeghe et al, 2008).
502 However, our net IO_3^- and I^- flux experiments demonstrated that both iodine chemical forms are taken
503 up by *L. digitata* plantlets. The role of iodoperoxidases identified in this species and hypothesized to
504 be key to specific iodide uptake (Colin et al, 2005) remains to be further validated *in vivo*. In this new
505 context, a reduction process is likely to be a key step for completing the picture. 2- No step in the
506 radioactive iodine biological cycle between seawater and brown seaweed is expected to change the
507 isotopic ratio, except unlikely isotopic fractionation. However, our environmental data on the isotopic
508 ratio $^{129}\text{I}/^{127}\text{I}$ in seawater and brown seaweed exposed to liquid discharges from the ORANO
509 reprocessing plant in La Hague showed an unexpected discrepancy. This means that this *in situ*
510 monitoring certainly missed a key compartment involved in ^{129}I transfer between seawater and brown
511 seaweed. The question raised in our previous review on radioactive transfers in the marine
512 environment around the reprocessing plant (Fiévet et al, 2021) regarding the non-conservative
513 hydrodynamic dispersion of ^{129}I also remains open. Although important questions remain to be
514 addressed, our laboratory experiments provided a direct observation of the ability of marine brown
515 algae to modify iodine chemical speciation in seawater and to convert seawater IO_3^- into I^- . The
516 endogenous extracellular pathways through which seaweed modify iodine chemistry in seawater
517 remain to be further investigated. This conversion is a key step in the Earth's biogeochemical iodine
518 cycle between the Ocean and the Atmosphere (Carpenter et al, 2021).

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528

529 **8 Supplementary material**

530 Additional data are provided in two files: Supplementary_Material_1.pdf and
531 Supplementary_Material_2.pdf.

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