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# 1 A REVIEW ON CESIUM DESORPTION AT 2 THE FRESHWATER-SEAWATER 3 INTERFACE

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- 25
- 26
- 27

## 1           **Introduction**

2  
3   The pollution of marine ecosystems by radionuclides is a major concern for society since  
4   the beginning of the nuclear era. It may be due to different sources including: *in-situ*  
5   releases from coastal nuclear power-plants, accidents associated with nuclear vessels  
6   (vessels, missiles), Naturally Occuring Radioactive Materials (NORMs) related to oil or  
7   gas production and direct or indirect global releases associated with nuclear tests or  
8   accidents on installations. A direct input is provided by atmospheric fallout and/or  
9   offshore releases (Fukushima), while an indirect input is due to the transport by rivers,  
10   collecting radionuclides from watersheds consequently to atmospheric fallout. Finally,  
11   submarine groundwater discharge may constitute a very specific direct input (Sanial et  
12   al., 2017).

13  
14  
15   Cesium radioactive isotopes ( $^{134}\text{Cs}$  and  $^{137}\text{Cs}$ ) have been extensively monitored in the  
16   environment due to their significant radioecological hazard (Garnier-Laplace et al.,  
17   2011) and their persistence (half-life of 2.4 and 30.2 years respectively). They are  
18   produced through uranium fission within nuclear reactors and thus can be found in both  
19   accident or authorized releases.

20   In the case of accidents and atmospheric nuclear testing, radiocesium has been spread  
21   over large spatial scales by the way of atmospheric deposition (Mattsson and Moberg,  
22   1991), but rivers constitute an additional input to the sea (Trapeznikov et al., 1994;  
23   Yamashiki et al., 2014). These rivers bring radiocesium through the releases of  
24   reprocessing and power plants as well as by the runoff of contaminated watersheds like  
25   in Chernobyl or Fukushima (Walling and He, 1999; Garcia-Sanchez and Konoplev, 2009;

26 Sakaguchi et al., 2018 ). Cesium exists in rivers as dissolved Cs<sup>+</sup> with small tendency to  
27 form colloids (Onishi et al., 1981; Eyrolle and Charmasson 2004) but is mainly  
28 transported in particular form (Takahashi et al., 2017) because of its high affinity for  
29 clay minerals ( Torstenfelt et al., 1982; Fan et al., 2014;)

30

31 At the river-sea interface, the important changes in physico-chemical conditions  
32 including ionic strength, solution composition and pH may induce the desorption of Cs  
33 from particles to the dissolved phase. A direct consequence is the shift of its distribution  
34 coefficient K<sub>d</sub> (ratio between solid and liquid activities, L/Kg), decreasing from 6,66.10<sup>3</sup> -  
35 1,35.10<sup>5</sup> in freshwater (Tomczak et al., 2019) to 4,5.10<sup>2</sup> -2.10<sup>3</sup> in seawater (IAEA, 2004;  
36 Tagami and Uchida, 2013)

37

38 This desorption has been highlighted in laboratory experiments and *in-situ* studies,  
39 through the monitoring of dissolved activities ( Matishov et al., 2006 ; Kakehi et al.,  
40 2016) or sediment inventories (Kusakabe et al., 2013). It is well recognized that clay  
41 minerals are the most important solid phase for the adsorption of radiocesium, but a  
42 fraction may also be attached to organic material, at least in contaminated watersheds  
43 near Fukushima (Naulier et al., 2017). For clays, illite is the most important and strong  
44 absorbent but kaolinite, smectite and vermiculite are also active, as well as biotite for  
45 phyllosilicate (Okumura et al., 2018)),

46 The negatively charged basal oxygen surfaces found on clay planar sites can form strong  
47 inner-sphere complexes with monovalent cations with low hydration energy, such as  
48 K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> (Sposito et al., 1999). These sites have usually low affinity due to  
49 their low selectivity (Wauters et al., 1996), but they adsorb Cs<sup>+</sup> more efficiently than the  
50 other cations due to its lowest hydration energy (Nakao et al., 2014). This cation uptake  
51 can be effective within a few hours (Onishi et al., 1981). Other sorption occurred on edge

52 sites, hydrated interlayer sites or frayed edge sites, corresponding to weathering fronts  
53 of micaceous minerals (Okumura et al., 2018). Finally, interlayer sites are not accessible  
54 to hydrated cations with large effective ionic radii, but are accessible to easily  
55 dehydrated cations such as Cs<sup>+</sup> (Zachara et al., 2002). This binding could result in a  
56 strong fixation, similar to those of native stable Cs already present in the mineral (Yin et  
57 al., 2016). However, binding on both planar and interlayer sites are partially reversible,  
58 and the increase of competitive ions in seawater ( K<sup>+</sup>, Na<sup>+</sup> or NH<sub>4</sub><sup>+</sup>) moves the  
59 equilibrium towards a release of Cs<sup>+</sup>, providing an additional input to the dissolved  
60 phase.

61 If desorption process at the freshwater-seawater interface has been already  
62 demonstrated, there is no consensus on the potential quantity of Cs that can be desorbed  
63 depending on the salinity. According to Sakaguchi et al (2018): “the desorbed value  
64 remains open for discussion”. Furthermore, the influence of the major cations on the  
65 desorption efficiency is not completely clear. According Yin et al (2016), questions remain  
66 on how each site is likely to desorb and on the various associated kinetic rates.

67

68 This paper provides a review on experimental laboratory studies conducted on Cs  
69 desorption in seawater. It aims to precise this process by identifying the values that can  
70 be expected according to the salinity, by characterizing the parameters of influence and  
71 by underlining unknowns for an eventual modelling work.

72

73

## 74 **1 Material and methods**

### 75 **1.1 Literature search**

76

77 All laboratory experiments exposing particles to a Cs (stable or radioactive)  
78 contamination in freshwater or seawater and then desorbing in seawater media were  
79 examined. The information required were the distribution of Cs between the solid  
80 and the dissolved phase.

81 Searches were performed to list all experimental studies carried out on stable and  
82 radioactive cesium desorption from particles samples in salt water. We included peer-  
83 reviewed and conferences papers, thesis and technical reports from 1950 to present.  
84 The databases used were Google Scholar, Scopus, and the CRIS (Centre de  
85 ressources en informations scientifiques et techniques) of IRSN.

86 Searches were performed using the keywords: "Caesium", "cesium", and "desorption",  
87 "remobilization", "leaching", "distribution" and "saltwater", "seawater", "sea",  
88 "salinity". Studies reporting distribution of radiocesium between solid and liquid  
89 phases in the field were not considered because of the lack of information on duration  
90 of desorption, delay between adsorption and desorption as well as the salinity of the  
91 media. We focused only on experimental laboratory approach that explicitly  
92 addressed cesium desorption in saltwater (minimal salinity of 1). Three studies  
93 which did not provide the fraction of desorbed Cs from samples after the desorption  
94 experiment (or a way to obtain it such as graphs,  $K_d$ , or activities in both phases  
95 before and after experiment) were excluded. The completeness of the results obtained  
96 was considered as satisfactory when no more relevant references on the topic could  
97 be found in the selected studies. This is the "snowballing approach" proposed by  
98 (Sayers, 2007).

99

## 100 1.2 Database construction

101 A bibliographic database was created to list all publications concerning cesium  
102 desorption from particles samples in saltwater according to the enounced modalities,  
103 leading to a total of 32 publications (Table 1).

104 Different kinds of information were extracted from this database and reported into  
105 sections described hereunder. Some are presented in Table 1:

- 106 • Paper information and objectives of the experiment: This section includes reference  
107 information such as title, year and authors of the publication.
- 108 • Sampling location information: Geographical information on the sampling sites as  
109 well as available information on main physico-chemical parameters: grain-size,  
110 cation exchange capacity (CEC), organic content and clay content. It is important to  
111 note that samples can be different and include suspended particles in the water  
112 column, sediments or soils. The results obtained on samples that were modified are  
113 not taken into account (sieving of grain-size or removal of specific mineral phases;  
114 Ouaniche, 1984; El Assy et al., 1991).
- 115 • Experimental design: This section focused on the materials and methods information  
116 such as the conditions of cesium uptake and the isotope used. Four main  
117 experimental designs were found and differentiated for our work (see the scheme of  
118 their classification on Figure 2).
  - 119 ✓ 1) desorption of Stable Cesium (**SCs**) corresponding to  $^{133}\text{Cs}$  naturally  
120 incorporated into the mineral material of the particles (not spiked). A  
121 good example of the experiment is provided by Takata et al. (2015).
  - 122 ✓ 2) desorption of RadioCesium (**RCs**) from particles which have been  
123 exposed to  $^{134}\text{Cs}$  or  $^{137}\text{Cs}$  in the field (Yamasaki et al., 2016).

124 ✓ 3) desorption of RadioCesium from particles spiked ( $^{134}\text{Cs}$  or  $^{137}\text{Cs}$ ) in  
125 Laboratory and in Freshwater media (**RCs.Lab.Fw**; ex. Onodera et al.,  
126 2017).

127 ✓ 4) desorption of RadioCesium from particles spiked in Laboratory in  
128 Saltwater media at salinity $>1$  (**RCs.Lab.Sw**; ex. Oughton et al., 1997).

129

130 • Experimental conditions: this section reports experimental parameters such as  
131 salinity, ratio between sample mass and volume of seawater, use of natural or  
132 artificial seawater, duration of the sorption and desorption phases.

133 • Results collection methodology: All the results concerning the distribution of cesium  
134 between the solid and the dissolved phases after exposition to saltwater were  
135 collected. When a study reported multiple values corresponding to change of the  
136 experimental conditions or of the sample used, all results were also collected. Results  
137 were homogenized into a percentage of Cs activity (or concentration for stable Cs)  
138 desorbed in seawater. The section reports the methodology used to obtain this  
139 percentage which are values: (i) directly provided by the authors, (ii) calculated from  
140 graphical extraction with plot digitizer, (iii) calculated from activities of (iv) the  
141 sample or from the  $K_d$  provided by the authors.

142

## 143 **2 Global overview of the database**

144

### 145 **2.1 Worldwide and historic concerns on radiocesium desorption at river-** 146 **sea interfaces**

147

148 The 32 studies selected correspond to 68 samples and a total of 502 experimental results.  
149 87% of these samples were sediments, 10% suspended particles and 3% soils. The  
150 sediments were collected mostly in river (56 %), sea or bays (30%), or estuaries (14%).  
151 The majority of studies (14) were interested in the fate of radiocesium sorbed onto soils  
152 after atmospheric depositions due to global fallout or nuclear accidents. Also, most of the  
153 sediment or suspended particle samples were collected at the output of contaminated  
154 watersheds as shown by the locations of the sites (figure 1), mostly related with the  
155 Fukushima accident or with nuclear power-plant releases. Only one study reported data  
156 directly in relation with the Chernobyl accident (Davison et al., 1993). Four specific  
157 studies were also conducted in the Arctic Sea in relation with the dumping of radioactive  
158 material (17000 containers and 19 vessels) and the potential release from high activity  
159 sediments.  
160 The aim of the other works (5) was related to the understanding of stable elements  
161 transfer at the river-sea interface, using of their radioactive analogs.

162

## 163 **2.2 Influence of the experimental design**

164 The values of Cs desorption percentage are reported in Figure 2. They relate the initial  
165 activity onto the particles, i.e. 100% indicates that all radiocesium was released into  
166 dissolved phase. They are directly issued from the document or calculated according  
167 different methodologies (Table 1). When this value in % was not given in the study, it  
168 was calculated as following:

$$169 \quad \%des = 1 - \frac{A_{solid\ final}}{A_{solid\ initial}} \times 100 \quad (1)$$

170 Or

$$171 \quad \%des = 1 - \frac{A_{liquid\ final} * V_{liq\ final}}{A_{solid\ initial} * M_{solid}} \times 100 \quad (2)$$

172 Where  $A_{solid\ initial}$  and  $A_{solid\ final}$  are the massic activities (Bq/kg) of the sample before  
173 and after desorption,  $A_{liquid\ final}$  the dissolved activity after the desorption experiment  
174 (Bq/L),  $M_{solid}$  the mass of sample used (kg) and  $V_{liq\ final}$  the mass of water in the media  
175 (L).

176

177 The design of the experiment may have an influence on the results. Indeed, while the  
178 desorption protocol was similar between experiments, the Cs sorption (in the lab or in  
179 the environment) was very different. This could lead to different desorption dynamics  
180 depending on the solid to liquid ratio used for the contamination (Onodera et al., 2017),  
181 or the ionic composition of the spiked medium as shown by Benes et al. (1992) in  
182 freshwater. Consequently, results were separated into 4 different experimental designs  
183 defined in section 1.2, and the distribution of the percentage of desorption obtained are  
184 presented in Figure 2.

185 The range of desorption rate for experiments SCs and RCs varied greatly since they are  
186 limited between 0 and respectively 10 and 64%. They present however the same modal  
187 class at 2-6%. On the other hand, experiments RCs.Lab.Fw and RCs.Lab.Sw show wider  
188 and multimodal distributions, extending from 6 to 86 % and 7 to 88%.

189 Our aim is to evaluate the state of knowledge and major uncertainties on the fate of  
190 radiocesium at the river-sea interface. We will focus on the RCs and RCs.Lab.Fw  
191 experiments because SCs concerns stable Cs and RCs.Lab.Sw sorption phase occurs in  
192 seawater. These two experiments answer to different questions described below. They  
193 were designed to give an order of magnitude of the Cs released after a sorption in  
194 freshwater, and they did not look at the influence of various physico-chemical  
195 parameters.

196 The experimental design RCs includes (but not only) riverine particles or sediments  
197 issued from contaminated watersheds (Sakaguchi et al., 2018) or contaminated directly

198 in the river (Standring et al., 2002). These particles are likely to be transported from  
199 river to sea especially during a flood event (Takata et al., 2015).

200 The experimental design RCs.Lab.Fw aims to reproduce the fate of suspended particles  
201 or bottom sediments contaminated after a radioactive release directly into freshwater  
202 (river), but desorption is still considered into seawater (Ciffroy et al., 2003). In general,  
203 such experiment is more difficult to carry out because it requires an additional sorption  
204 phase using radioactive sources. This could explain the lower number of available  
205 results.

### 206 **3 Overview on experiments**

207

208 Results of the RCs experiments follow a log-normal distribution (Fig. 2 and 3). The  
209 percentages of desorption range between 0 and 65%, but the modal class 2-6% gathers  
210 more than 47% of the experimental results (93/197). Furthermore, it should be noted  
211 that values above 30% are issued from three studies only, and two of them used  
212 sediments from Bombay Harbour (Desai et al., 1994; Patel, 1978). These authors  
213 reported little information on their samples. The last and maximal value of 65 % comes  
214 from the Ravenglass estuary (Stanners and Aston, 1982).

215 In contrary, results of RCs.Lab.Fw do not follow any classical distribution (Fig 2 and 4)  
216 and present many modes. Low desorption below 10% concerned only particles with solid  
217 to liquid ratios at or above 10000 mg/L. This concentration is already above most of those  
218 observed in rivers, even in floods (Meybeck and Moatar, 2014; Sadaoui et al., 2016). The  
219 highest desorption value (86%) was found for particles from the Tamar estuary (Bale,  
220 1987).

221

222

### 223 3.1 Influence of salinity

224

225 There is no significant statistical relation between the salinity and the desorbed fraction  
226 or  $K_d$ , when the results of the 32 studies related to RCs and RCs.Lab.Fw experiments  
227 are plotted together (Fig 5). However, most of these studies tested just one salinity value,  
228 and only two of them reported results over a range of salinity. In RCs experiments,  
229 Sakaguchi et al. (2018) tested two salinities (16.5 and 33) using successive desorption  
230 experiments, and each time the desorption at the 33 salinity medium increases by a  
231 factor 1.5-2 compared to those at 16.5. Patel (1978) found a linear relation between  
232 salinity and the amount of desorbed Cs for two different samples of the Bombay Harbour  
233 for salinities ranging between 9.5 and 38.

234 For RCs.Lab.Fw, Reynolds and Gloyna (1964) found a positive linear relation between  
235 released Cs and salinity, whereas Ciffroy et al. (2003) and Bale (1987) found that the  
236 same fraction of Cs is desorbed for low (respectively 13 and 10) and high salinity (34),  
237 similarly to a threshold over which salinity had no more influence on the fraction of  
238 desorbed Cs. It must be noted however that in both studies, the desorbed fraction  
239 increased significantly in the range 0 to 10 of salinity.

240 It is impossible from these various results to parametrize a relation between the salinity  
241 and desorption of Cs from the particles. This might be due to the various solutions  
242 chemistry used for these experiments, ranging from natural seawater to monoionic  
243 solutions of  $\text{Na}^+$ . Indeed, the use of monoionic solutions ( $\text{Na}^+$ ,  $\text{K}^+$ ) as desorption medium  
244 leads to different effects. Mukai et al. (2018), Onodera et al. (2017), and Desai et al.  
245 (1994) observed that for the use of  $\text{K}^+$  solutions always reached a plateau in the Cs  
246 desorption, which was similar whatever the range of  $\text{K}^+$  concentrations, respectively  $10^{-5}$   
247 to 1 M, 0.01 to 1 M and 0.01 to 1.6 M. On the other hand, desorption increased linearly  
248 with  $\text{Na}^+$ , using respective ranges of  $10^{-5}$  to 1M, 0.47 to 1M, and 0.01 to 1.6 M. By

249 comparison, the mean concentrations of  $K^+$  and  $Na^+$  in seawater at 35 salinity are 0.01  
250 and 0.47M, and their molar ratio is 47.

251

252

253 These authors explained their results by the fact that  $Na^+$  has a higher hydration energy  
254 and the capacity to enhance the interfoliar layer of clays, releasing thus the Cs stored on  
255 these sites. On the other hand,  $K^+$  has a lower hydration energy and cannot release this  
256 Cs. It is only involved in the cation exchange reaction occurring on surficial sites.

257

258 In addition, Mukai et al., (2018), and Onodera et al., (2017) both found that an increase  
259 of  $K^+$  concentration from 0.001 to 0.01 M (seawater) combined with  $Na^+$  (at 1M or 0.47 M)  
260 decreased the desorption by a factor 2 (60% to 30% for Onodera) or even 4 (80% to 20%  
261 for Mukai et al), which is also the amount of desorption observed with natural seawater  
262 in their experiment.

263 These authors and Desai et al., (1994), argue that the “shrinking” or “collapsing” effect of  
264  $K^+$  on the interfoliar gap of clays (Mela, 1962) inhibits Cs release from these interfoliar  
265 sites. Increasing salinity undoubtedly influences the desorption due to  $Na^+$  and  $K^+$  and  
266 their mechanisms discussed above. However, while desorption increases linearly with  
267  $Na^+$  alone, addition of  $K^+$ , around 0.001 to 0.01M range (corresponding to concentrations  
268 in seawater of salinity 3.5-35) leads to a desorption plateau, due to its shrinking  
269 properties on clay. These results suggest that the desorption no longer significantly  
270 increases once a minimal salinity has been reached (>3.5). This is in agreement with  
271 Figure 5 showing that  $K_d$  are similar in seawater regardless of salinity. This could also  
272 explain the salinity threshold found by Ciffroy et al. (2003) and Bale (1987).

273 Care must thus be taken on desorption results obtained only with Na<sup>+</sup> solution at high  
274 concentrations which would lead to an overestimation of the amount of desorbed Cs due  
275 to the absence of the inhibitive effect of K<sup>+</sup>.

276

277

### 278 **3.2 Influence of the duration of the desorption phase**

279

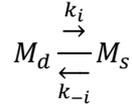
280 Studies performing experiments in the form of successive desorption (Sakaguchi 2018;  
281 Berthail, 2015; Ouaniche, 1984; Yamasaki et al 2016) were not taken into account as  
282 each time that a new desorption media is added, equilibrium is moved, allowing  
283 additional Cs to be released.

284 Durations of desorption phase for RCs ranged between half an hour and 8 months. The  
285 desorption was not more important by extending the experiment over one week (Takata  
286 et al 2015), one month (Otosaka and Kobayashi, 2013) or two months (Standring et al.  
287 (2002). Only Stanners & Aston (1982) found that the amount of released Cs is still  
288 increasing after few days in their experiments.

289 The desorption phase for RCs.Lab.Fw ranged between ten minutes and ten days. The  
290 five studies of RCs.Lab.Fw experiments looking at desorption over time showed a fast  
291 increase of release within the first hours and then a plateau. The timescales of these five  
292 studies differed and we integrated rate laws in order to compare the desorption rates  
293 (Jannasch et al., 1988; Simonsen and Saetra, 2019). This approach assumes that trace  
294 element uptake and release, including Cs, are the sum of a complex series of first order  
295 reversible reactions (Okumura et al, 2018; Jannasch et al., 1988) .

296 M<sub>d</sub> and M<sub>s</sub> being the metal in dissolved and solid phases, each reaction can be written as  
297 :

298



299 Each first-order reaction should verify the linearized equation :

300

$$301 \quad -\ln\left(\frac{[M_d] - [M_d]_e}{[M_t] - [M_d]_e}\right) = (k_i + k_{-i}) \cdot t \quad (3)$$

302 where  $[M_d]_e$  is the metal in dissolved phase at equilibrium and  $M_t$  the total metal in the  
303 solid-liquid system. Demonstration of the equation is available in Simonsen and Saetra,  
304 (2019) and Jannasch et al. (1988).

305 Plotting the left member of equation (3) in function of time provides the slope.

306 Because the number of experimental data points ( $n \approx 5$ ) for each desorption studies was  
307 too small, multiple linearization was not possible and the equation was derived only one  
308 time for each experiments (16) with the available points. Observations ranged between  
309 0.17 and 168 hours. One analytical curve by experiment is then plotted using  
310 exponential transformation of equation (3). The 16 curves are presented in Figure 6.

311

312

313 The integration allows to define 3 cases (Figure 6):

- 314 • The equation was verified but a significant intercept (different from zero) exists  
315 (7/16 experiments; black curves)
- 316 • The equation was not verified (slope not significant at 0.05 error) and a  
317 significant intercept exists (7/16; dotted blue curves)
- 318 • The equation was not verified (2/16) and there is no significant intercept at 0.05  
319 error (dotted red curves)

320

321 The significant intercept observed on 14 studies proves the existence of one or more  
322 desorption processes at a timescale inferior to one hour (Jannasch et al., 1988). The

323 fraction of Cs released by these fast processes on the total released is  $86 \% \pm 13$  (mean of  
324 the intercepts). The non-significant slopes (9/16; case 2 and 3) can be due to the fact that  
325 an increasing number of data within the plateau relatively to those in the rising limb  
326 minimizes the trend.

327 These observations lead to the conclusion that Cs desorption in this kind of experimental  
328 design is governed by one or more processes on a timescale inferior to one hour releasing  
329 in average 86% of the available Cs, and less frequently by an additional (or more)  
330 reaction on timescales inferior to 7 days. This justify the use of at least two reactions for  
331 an accurate representation of desorption process for timescales over one hour.

332 In modeling, these reactions are usually taken into account through two successive  
333 desorption kinetics involving surficial and interlayer sites of clays, they have led to a  
334 two box model (or more) used for both saltwater and freshwater (e.g. Comans and  
335 Hockley, 1992).

336 The kinetic of the first reaction is given by the slope coefficient between time 0 (origin)  
337 and the first point of measure. These overall rates ( $k_1+k_{-1}$ ) obtained for the 16 studies  
338 range between  $1.10^{-4}$  and  $1.10^{-3} \text{ s}^{-1}$  (half-reaction time,  $t_{1/2}$ , of 0.2 to 2 hours) similar to  
339 those obtained in freshwater (Ciffroy et al., 2003; Benes et al., 1992; Comans and  
340 Hockley, 1992). They are theoretically related to surficial sites. The second reaction,  
341 theoretically related to interlayer sites, presents overall rates ranging between  $5.10^{-6}$  and  
342  $1.10^{-5} \text{ s}^{-1}$  (half-reaction time of two days to one week) in seawater, half an order of  
343 magnitude above those in freshwater ( $1.10^{-6}$  to  $5.10^{-6}$ ); (Benes et al., 1992; Comans and  
344 Hockley, 1992; Ciffroy et al., 2003).

345 These two reactions are considered to occur consecutively (Comans and Hockley, 1992;  
346 Oughton et al., 1997; Ciffroy et al., 2001) or in parallel (Benes et al., 1992; Yamamoto et  
347 al., 2015). Since the fast desorption rate of surficial Cs is usually two orders of  
348 magnitude higher, most of the slowly released pool of Cs within interlayers must remain

349 available even if the reactions are in parallel. In any case, this difference is not so much  
350 important for timescales inferior to one week and does not change the goodness of fit of  
351 the models (Benes et al., 1992; Borretzen and Salbu, 2002).

352

### 353 **3.3 Influence of the cesium distribution into particles prior to desorption**

354

355 The existence of different sites with their own affinity for Cs implies that preliminar  
356 distribution of cesium on these sites influences the quantities and the dynamics of  
357 desorbed Cs. When plotting the values of  $K_d$  obtained after desorption in seawater from  
358 experiment RCs.Lab.Fw in function of their  $K_d$  after adsorption in freshwater (8 studies;  
359 Fig 7) we observe a positive and significant correlation ( $R^2=0.43$ , p-value = $2.10 \cdot 10^{-14}$ ) and a  
360 decrease by a factor 6 in seawater. This leads to the hypothesis that particles presenting  
361 high affinity with cesium in freshwater (high  $K_d$ ) partially keep this affinity in seawater.  
362 Consequently, we investigated factors influencing cesium repartition on material and  
363 consequences for desorption.

364

#### 365 **3.3.1 Influence of material:**

366 Authors generally refer to three components as main absorbents for  $Cs^+$  with different  
367 properties:

368 -strongly sorbing non-expansible 2:1 phyllosilicates such as micaceous mineral  
369 (biotite) or illite with relatively low cation-exchange capacity (CEC) with high affinity  
370 sites (Nakao et al., 2014).

371 -weakly sorbing expansible 2:1 phyllosilicate such as smectite with relatively high  
372 CEC (Mckinley et al., 2001).

373 - organic matter with usually high CEC (Valcke and Cremers, 1994).

374 Since particles composition is a heterogeneous mixing of mineral and organic phases in  
375 different proportions, we can expect a high spatio-temporal variability in the proportion  
376 of available sites with their own capacity to sorb Cs. Such heterogeneity may explains  
377 the discrepancies in distribution coefficients in freshwater between sites (Boyer et al.,  
378 2018; Takahashi et al., 2017). In the case where riverine particles directly reach the  
379 coastal zone (small rivers, sea with no tides), the characteristics of the particles  
380 regarding Cs fixation can be conserved in seawater, explaining the good relation of Fig 7.  
381 The important role of the nature of particulate material is highlighted in RCs.Lab.Fw, by  
382 the fact that two samples from the same river presents a similar desorption, even if they  
383 were not collected at the same time. Ferrer (1983) and Ouaniche (1984) obtained 40% of  
384 desorption in the Rhône river; Clanton (1968) and Reynolds and Gloyna (1964) also  
385 obtained 40% in Guadalupe river. Ciffroy et al (2001) used two samples from the Loire  
386 river collected over 6 months, and they found 60-80% of desorption for both.

387

### 388 **3.3.2 Influence of the contamination process**

389 Sites with high affinity (FES: Frayed Edge Site) contributes predominantly to Cs  
390 sorption at low concentrations under  $10^{-8}$ M (Sawhney, 1970; Bradbury and Baeyens,  
391 2000). However, they also present the lowest capacity (Nakao et al., 2014) and  
392 constitutes only 0.25% of the CEC of the illite (Bradbury and Baeyens, 2000). Once these  
393 sites are saturated, excess Cs goes to surficial sites with lower affinity.

394 Usually the particles spiked for the RCs.Lab.Fw experiment present higher activities  
395 than those for RCs. This potentially results in a higher fraction of Cs in surficial sites,  
396 more subject to a rapid remobilization.

397 Beyond that, an increase of solid-to-liquid ratio during the contamination phase leads to  
398 a lower desorption. Onodera et al. (2017) found that the desorbed fraction of radiocesium  
399 followed a negative power law with a ratio ranging from 0.17 g/L to 10 g/L during the  
400 spiking phase. According to the authors, a larger number of strong adsorption sites were

401 available when the solid-to-liquid ratio was higher, leading to an increase of the fraction  
402 of strongly adsorbed Cs onto particles and, as a result, desorption became more difficult.  
403 Finally, it is possible that a longer contact time with the Cs solution decreases the  
404 amount of extractable Cs from all sites (Okumura et al, 2018).

405

406 Comans and Hockley (1992) argued that radiocesium is able to migrate from basal  
407 surface sites to interlayer sites and can be incorporated into the mineral as stable Cs.  
408 This migration called “aging effect” may impact its mobility; (Madruga and Cremers,  
409 1997; Roig et al., 2007). This effect has been studied in a 1M Na<sup>+</sup> solution only by Mukai  
410 et al. (2018) on weathered biotites from Fukushima. They found that a sorption time  
411 longer than one week decreased desorbed fraction from 90% to less than 10%, compared  
412 to a one day or one week sorption. Biotite sampled at the same site, containing  
413 radiocesium post-Fukushima (RCs like experiment) desorbed the same amount of  
414 radiocesium. However, it should be noted that this experiment was conducted at pH 4.5,  
415 clearly different from those of seawater.

416

417 The aging effect has been more studied in experiments using freshwater for both the  
418 adsorption and desorption phase. Ciffroy et al (2001) found that the fraction of Cs  
419 released after 24 h decreases by a factor 2 when the duration of the contact time of the  
420 sorption phase increases from 30 min to 100 hr. Benes et al (1992) also found that a  
421 sorption phase of 5 and 21 days instead of 2 hours decreased the fraction of released Cs  
422 by a factor 1.3 and 2 respectively.

423 From these experiments it seems that a longer sorption phase allows to fix Cs more  
424 irreversibly, at least in freshwater media. These results could partly explain why the  
425 desorption in RCs experiment is usually lower than for RCs.Lab.Fw and closer to SCs  
426 experiment. Indeed the contact time for the samples used in RCs is longer because it

427 corresponds to the delay between the *in-situ* sample contamination and its desorption  
428 once the particles are exposed to seawater. This longer delay facilitates Cs migration  
429 into the mineral lattice with strong affinity.

430

431

432

## 433 4 Discussion

434

435 The objective of this review is to summarize data from literature in order to precise the  
436 efficiency of Cs desorption processes into seawater medium. We show that results issued  
437 from two main experimental designs may be used for that purpose. In the first design,  
438 RCs, particles have been exposed to  $^{134}\text{Cs}$  or  $^{137}\text{Cs}$  in the field, whereas the second one,  
439 RCS.Lab.Fw, concerns the desorption of radiocesium from particles spiked ( $^{134}\text{Cs}$  or  
440  $^{137}\text{Cs}$ ) in laboratory and in freshwater media.

441

442 In the case of field exposition, most of the values of desorption fractions are around 3%  
443 (figure 2), and this is valid for both radiocesium (RCs) and stable Cs (SCs). Furthermore,  
444 any sample of particles collected in the environment consequently to a contamination by  
445  $^{137}\text{Cs}$  or  $^{134}\text{Cs}$  (RCs experiment) released in 95% of cases one third or less of its  
446 radiocesium (Figure 3). These results have to be compared with the value proposed by  
447 IAEA for the proportion of desorbable Cs in coastal sediments: 20% (IAEA, 2004). Above  
448 20% the figure 3 shows that a plateau is effectively reached, but this value is clearly  
449 above the mode at 3% determined here.

450 Important points are that the efficiency of desorption (i.e. the fraction of Cs released)  
451 does not depend on the duration of desorption, and that an increase of salinity does not  
452 influence so much the desorbed fraction.

453

454 In RCs.Lab.Fw samples were highly contaminated and thus different mineral sites with  
455 different sorption isotherms may have stored cesium, including those with low affinity.  
456 Overall amount of released Cs is higher than for RCs experiment and could reach  
457 sometime 87%. Usually, two kinetic rates are observed and 80% of equilibrium is

458 reached in one hour. A short duration of contamination reduces the “aging” effect  
459 resulting in a consequent pool of easily released cesium.

460 Here, the percentages of desorbed Cs do not follow any regular distribution.

461 Experimental design RCs.Lab.Fw looks like an “ideal” case based on the fact that there  
462 is “no aging”, no change in equilibrium between the fixation of Cs onto particles and  
463 their arrival into brackish waters. However, it may correspond to the case where  
464 suspended particles are contaminated in freshwater and rapidly reach the sea because of  
465 short transit times in rivers. In this case, desorption could be as high as 80 %, and it is  
466 not possible to predict it regarding the irregular distribution observed here. In case of an  
467 accident, an evolution of the Cs desorbed may be thus expected with time, related to the  
468 duration of transit of the particles between their contamination and the sea.

469 This desorption is also dependent on salinity until a certain threshold. Studies showed  
470 that for salinity above 2, concentrations of  $K^+$  ( $5 \cdot 10^{-5}$  M) and  $Na^+$  (0.027 M) are in theory  
471 sufficient to desorb superficial Cs, but there was no change in desorption from 10 to 35 of  
472 salinity.

473

474 The repartition of Cs onto different sites of the mineral may thus partly explain the  
475 differences in desorbed Cs found between both experiments. The various proportions of  
476 adsorption sites between samples plus a possible aging effect are an additional source of  
477 variability. For each area of interest, we thus recommend to use a sample representative  
478 of the site for the sorption/desorption experiments, in order to properly discuss the  
479 dynamics of Cs transfer.

## 480 **5 Conclusion**

481 Desorption of radiocesium from contaminated particles was observed at any salinity  
482 above 3, and the fraction desorbed ranges widely from 0 to 86%. For particles containing

483 radiocesium due to an environmental contamination, this range extends from 0 to 64 %  
484 with a peak at 3%. Particles containing radiocesium issued from a contamination in  
485 laboratory show higher values of Cs released and a reaction implying two first-order  
486 kinetics. The first one is really short with a half-life reaction time about one hour,  
487 whereas it is of a few days for the second one. These two parallel or successive reactions  
488 must be related to sites with different affinity for Cs, and thus radiocesium distribution  
489 on mineral prior to desorption is a key factor to take into account.

490 As a result, a two kinetic box-model calibrated for each site of interest is suitable to  
491 predict more accurately desorbed cesium at the interface. However, these conceptual  
492 models should be supported by recent developments on clay mineral structures and  
493 avoid over parametrization.

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## 687 **Figures List**

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705

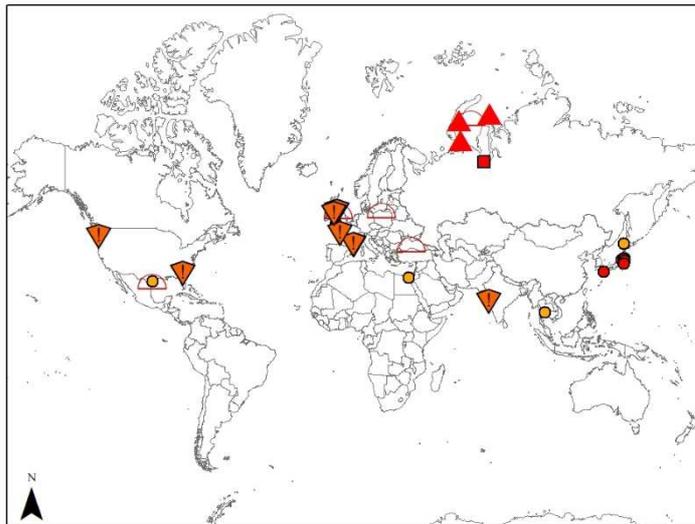
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709

## 710 **Table List**

711 **Table 1 : main information of the studies compiled in this article**



### Legend

Concerns

○ Atmospheric fallouts

▲ Dumps

● Fukushima

■ Mayak

● Other

▼ Nuclear power-plants releases

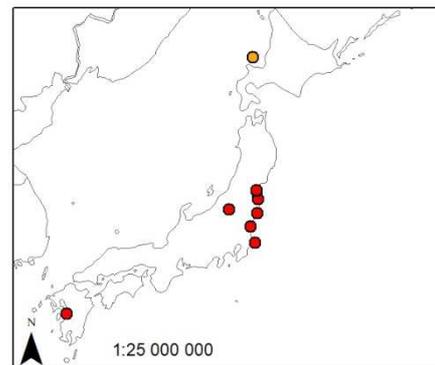
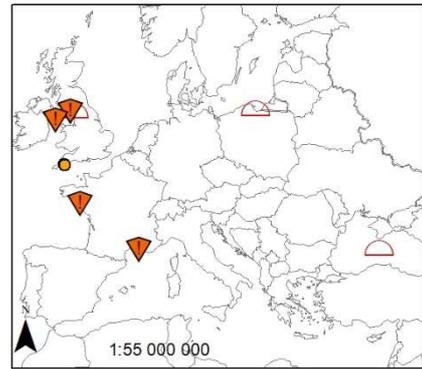


Figure 1 : Locations of the sampling sites relative to the documents reporting results on cesium desorption. The symbols refer to the sources of contamination of the particles. See Table 1 for references.

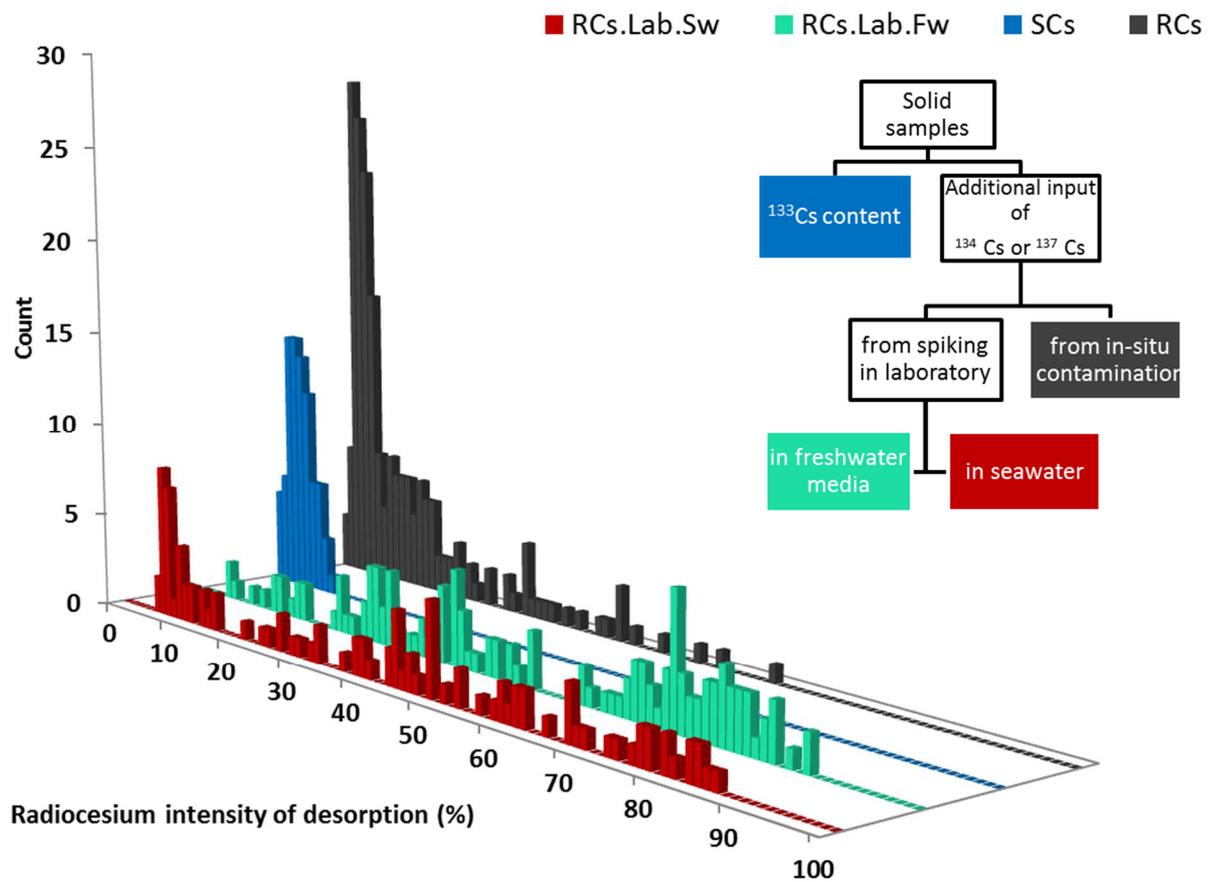


Figure 2 : Percentage of desorption distributions obtained for the 4 different experimental designs (see text for details). The scheme in the top right corner presents the classification of these designs.

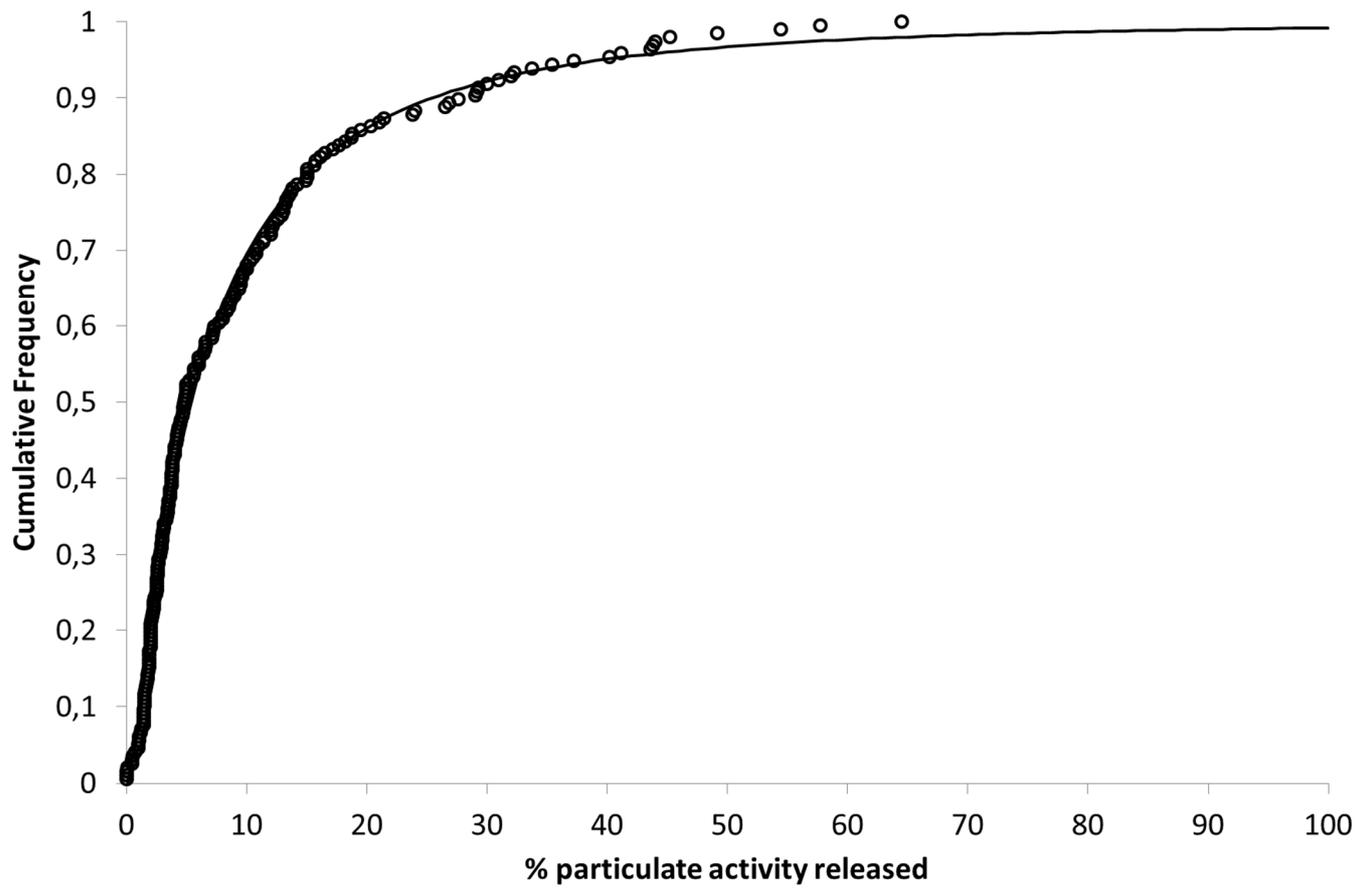
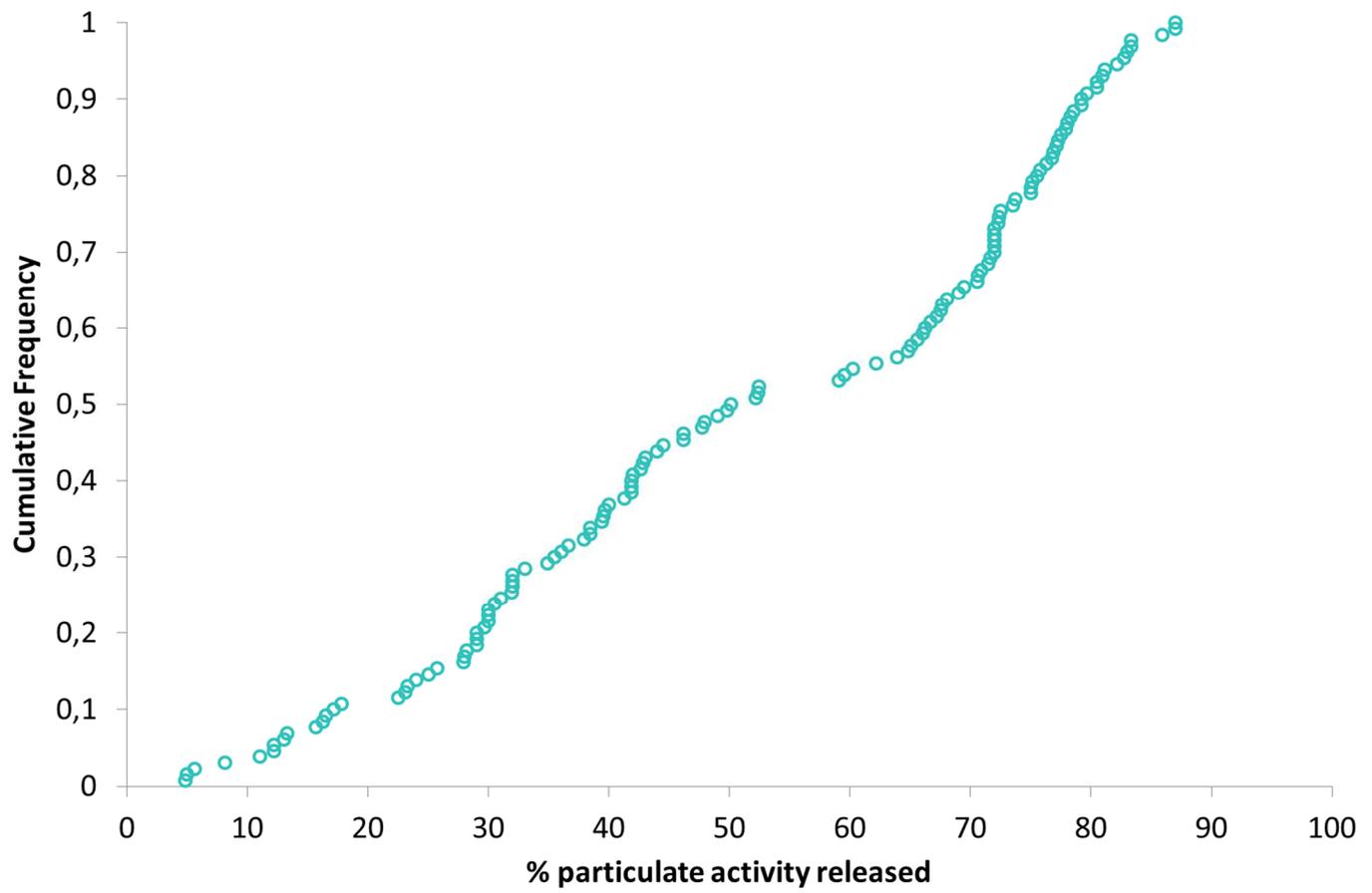


Figure 3 : Cumulative frequency of cesium desorption percentage and its distribution for experiment RCs



**Figure 4 : Cumulative frequency of cesium desorption percentage and its distribution for experiment RCs.Lab.Fw**

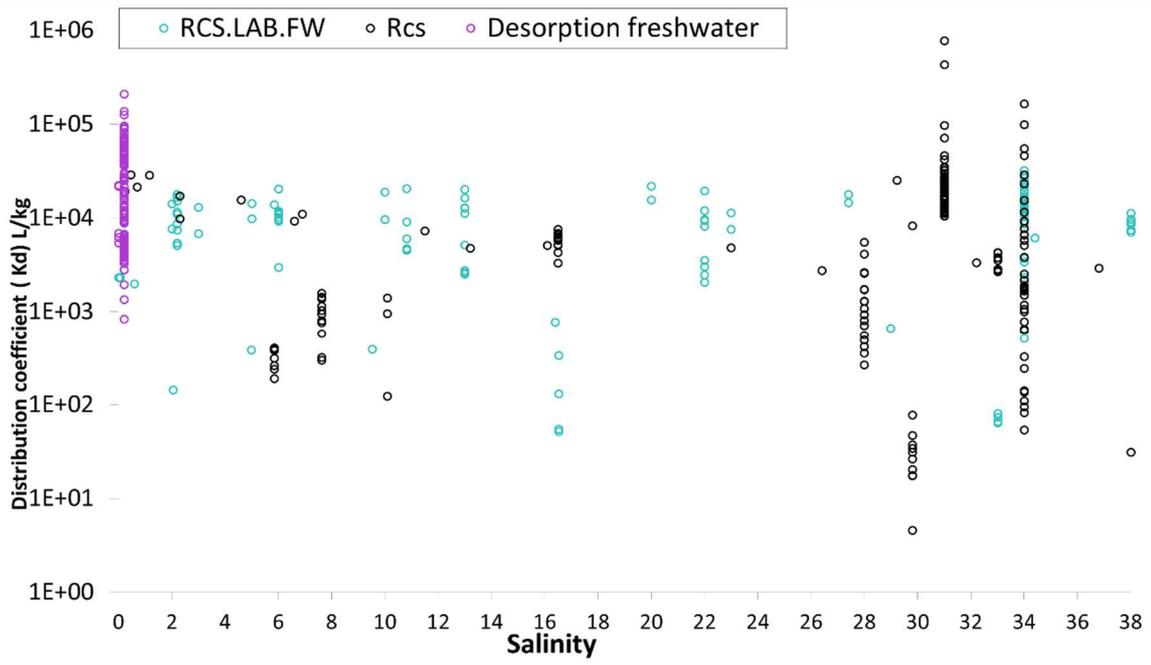


Figure 5 : Distribution coefficient of radiocesium in function of salinity for different experimental designs

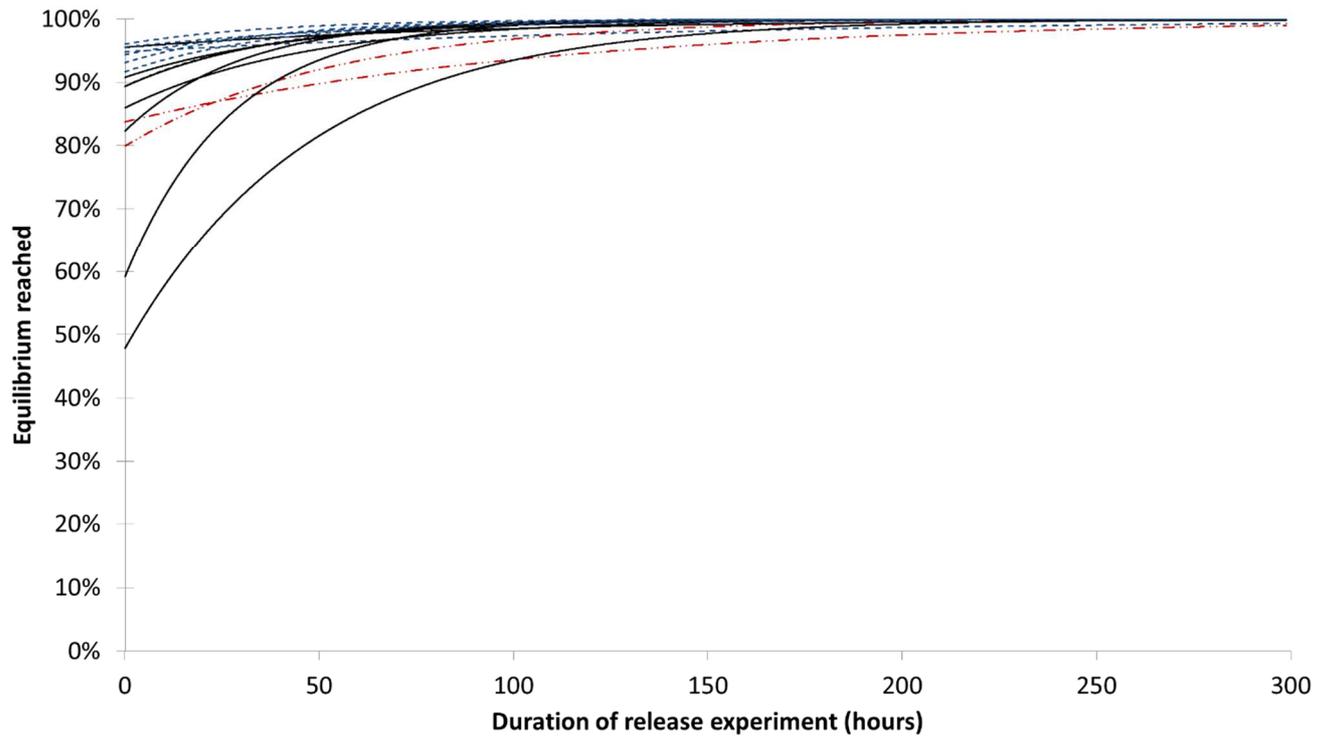


Figure 6 : Compilation of kinetic trends for cesium desorption in seawater. See text for the explanation of the different curves.

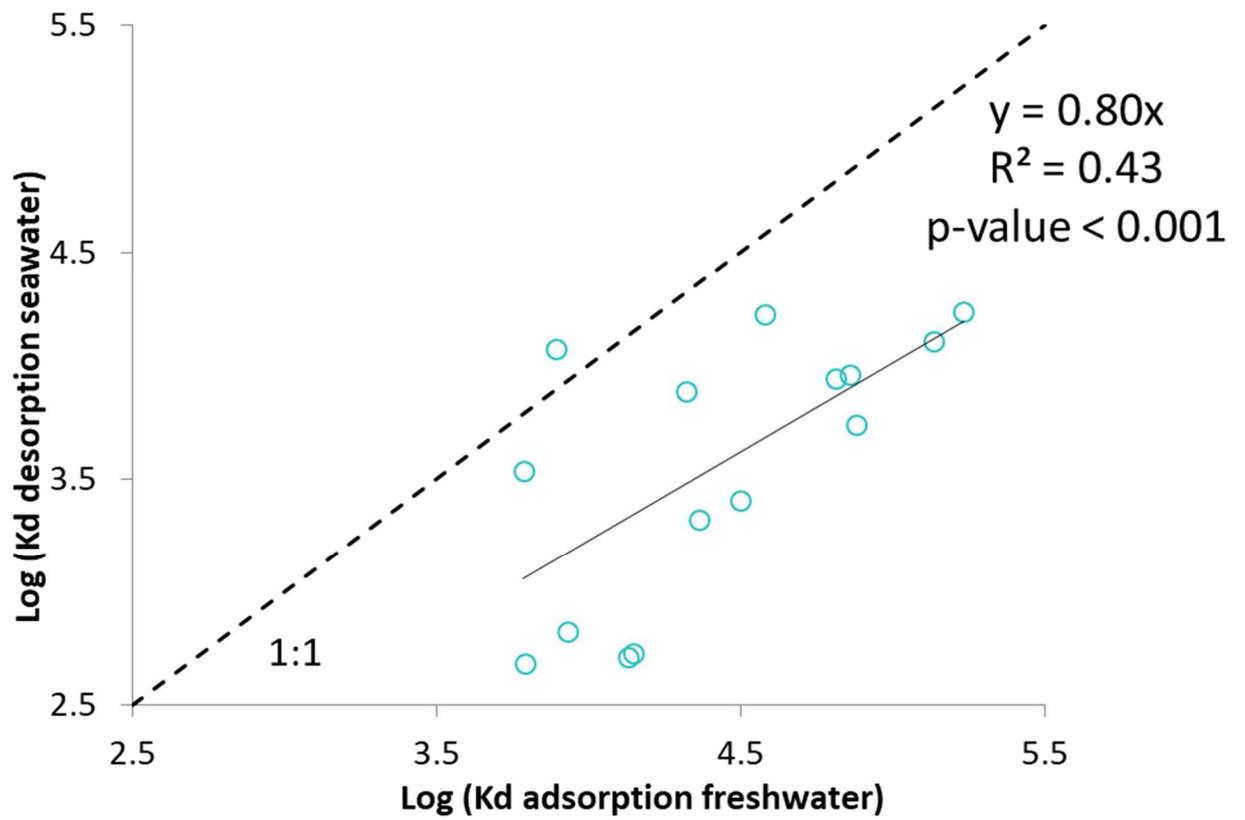


Figure 7 : Cs distribution coefficients (Kd) calculated after desorption in seawater Vs Kd calculation after laboratory sorption. See Table 1 for involved studies.

References	Sample type	Number of samples used in the study	Desorption medium	Experimental design				Studies used for linearization	Studies used for Freshwater Seawater Kd comparison	Origin of the data used in the study
				S C s	R C s	R C s · L a b · F w	R C s · L a b · S w			
(Reynolds and Gloyna, 1964)	Guadalupe river sediments	1	San Antonio bay water			X	X		X	Graphical extraction
(Clanton, 1968)	Guadalupe river sediments	1	San Antonio bay water			X		X	X	Graphical extraction
(Cheng, 1968)	Terrigenous sediments Hokkaido	1	Japanese seawater			X				Graphical extraction
(Ganguly et al., 1968)	Bombay harbour sediments	1	Bombay harbour water				X			Provided
(Robertson et al., 1972)	Columbia river sediments	1	Pacific ocean water		X					Graphical extraction
(Brisbin et al., 1974)	Savannah river sediments	1	NaCl solution		X					Reported by Onishi et al., (1981)
(Patel, 1978)	Bombay harbour sediments	2	Bombay harbour water		X					Graphical extraction
(Stanners and Aston, 1982)	Ravenglass estuary sediments	1	Irish seawater		X					Calculation from activities
(Evans et al., 1983)	Savannah river pond sediments	2	NaCl solution		X					Provided
(Ferrer, 1983)	Suspended particles Rhône river	3	Artificial seawater			X		X	X	Graphical extraction
(Ouaniche, 1984)	Rhône sediments	2	Rade de Toulon water		X	X			X	Provided
(Bale, 1987)	Tamar estuary sediments	1	Manche seawater			X			X	Graphical extraction
(El-Assy et al., 1991)	Suez canal sediments	1	Suez gulf water			X		X		Graphical extraction
(Davison et al., 1993)	Esthwaite Water lake sediments	1	Artificial seawater		X					Provided
(Desai et al., 1994)	Bombay harbour sediments	1	Bombay harbour water		X					Provided
(Kleinot, 1994)	Tamar estuary sediments	1	Artificial seawater				X			Graphical extraction
(Knapinska-Skiba et al., 1994)	Baltic sea sediments	2	Gdansk Bay water		X		X			Graphical extraction
(Oughton et al., 1997)	Kara sea sediments	4	Oslo Fjord water		X	X	X			Graphical extraction and calculations from Kd
(Fuhrmann et al., 2001)	Kara sea sediments	1	Atlantic ocean water				X			Graphical extraction
(Borretzen and Salbu, 2002)	Stepovogo Fjord sediments	1	Kara seawater				X			Graphical extraction
(Standring et al., 2002)	Mayak ponds sediments	4	Artificial seawater		X					Calculation from activities
(Topcuoğlu)	Black sea	4	Blacksea				X			Graphical extraction

et al., 2002)	sediments		water							
(Ciffroy et al., 2003)	Suspended particles Loire river	2	Atlantic ocean water			X		X	X	Graphical extraction and calculations from Kd
(Saengkul et al., 2013)	Bang Pakong estuary sediments	2	Thailand gulf water					X		Graphical extraction
(Tagami and Uchida, 2013)	Fukushima soil	1	Pacific ocean water			X				Provided
(Otosaka and Kobayashi, 2013)	Marine sediments Fukushima	2	Pacific ocean water		X					Graphical extraction
(Fan et al., 2014)	Abukama and Kuchibuto river sediments	4	Artificial seawater			X			X	Graphical extraction and calculations from Kd
(Berthail, 2015)	Nitta and Otta river sediments and Sellafield estuary sediments	3	Seawater (origin unspecified )		X					Provided
(Takata et al., 2015)	Abukama, Tone, Kuji and Naka river sediments	12	Pacific ocean water	X	X					Graphical extraction
(Yamasaki et al., 2016)	Kuma river sediments	1	Artificial seawater		X					Graphical extraction
(Onodera et al., 2017)	Suspended particles Abukama and Natsui rivers.	2	Artificial seawater, pacific ocean water and NaCl solution			X		X	X	Graphical extraction
(Sakaguchi et al., 2018)	Fukushima soil	1	Seawater nearby Kikajima island	X	X					Calculation from activities

Table 1 : main information of the studies compiled in this article