



**HAL**  
open science

## Tellurium and selenium sorption kinetics and solid fractionation under contrasting estuarine salinity and turbidity conditions

Teba Gil-Díaz, Jörg Schäfer, Virginia Keller, Elisabeth Eiche, Lionel Dutruch, Claudia Mössner, Markus Lenz, Frédérique Eyrolle

### ► To cite this version:

Teba Gil-Díaz, Jörg Schäfer, Virginia Keller, Elisabeth Eiche, Lionel Dutruch, et al.. Tellurium and selenium sorption kinetics and solid fractionation under contrasting estuarine salinity and turbidity conditions. *Chemical Geology*, 2020, 532, pp.119370 -. 10.1016/j.chemgeo.2019.119370 . hal-03488405

**HAL Id: hal-03488405**

**<https://hal.science/hal-03488405>**

Submitted on 21 Dec 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License



35 Radioactive tellurium (Te) is produced during nuclear fission reactions in non-negligible quantities.  
36 All Te radionuclides have a 13-16% probability of being produced from  $^{239}\text{Pu}$ - and  $^{235}\text{U}$ -based fuels  
37 compared to ~11% for Cs and ~10% for I radionuclides (unpublished data calculated from Element  
38 Collection Inc. and Sonzogni 2013). There is little information on the specific Te species released  
39 from nuclear power plant (NPP) accidents, potentially presenting both (i) volatile/intermediate  
40 (Morewitz 1981), and (ii) refractory character (e.g., forming metal/oxide compounds; Kleykamp 1985;  
41 Izrael 2002 and references therein). Though different NPP accidents display different emission  
42 patterns, Te radionuclides were released into the environment during both April-1986 Chernobyl  
43 (CNPP) and March-2011 Fukushima Daiichi (FDNPP) accidental events (Steinhauser et al. 2014). In  
44 these cases, short-term half-life Te radionuclides (e.g.,  $^{132}\text{Te}$  half-life of 3.2 days) produced important  
45 atmospheric radioactive emissions ( $^{132}\text{Te}$ : ~1150 PBq at CNPP and ~180 PBq at FDNPP) comparable  
46 to  $^{137}\text{Cs}$  and  $^{131}\text{I}$ , the most monitored radionuclides after NPP accidental events (~85 PBq and ~1700  
47 PBq at CNPP, ~37 PBq and ~160 PBq at FDNPP, respectively; Steinhauser et al. 2014). Emitted Te  
48 radionuclides were still detected in the atmosphere one month after the FDNPP accident reflecting  
49 their non-negligible environmental persistence and potential worldwide atmospheric dispersion (Baeza  
50 et al. 2012; Ishikawa et al. 2014; Leppänen et al. 2013). In fact, radioactive Te has been detected in  
51 FDNPP fallouts (Saegusa et al. 2013) and in seawater from Monaco, after CNPP (May 1986), yet with  
52 relatively low  $^{129}\text{Te}$  activities in the dissolved ( $0.13 \text{ Bq L}^{-1}$ ) and particulate ( $1.18 \text{ mBq L}^{-1}$ ) phases  
53 (Whitehead et al. 1988). The latter study further suggested for the first time the moderate particle-  
54 reactive behaviour of radioactive Te and its potential intake by marine bivalves, thus, risk of entering  
55 environmental food chains (i.e., up to  $340 \text{ Bq kg}^{-1} \text{ DW}$  in mussel soft tissues; Whitehead et al. 1988).

56 On the other hand, radioactive selenium (Se) is a widely known fission product of nuclear  
57 reactions. It can be released into the environment during several steps of the nuclear fuel cycle  
58 comprising NPP wastewaters and spent nuclear fuel, with recent research focusing specifically on  $^{79}\text{Se}$   
59 mobility (half-life of  $\sim 10^5 \text{ y}$ ) from waste storage and nuclear waste disposal areas (Aguerre and  
60 Frechou 2006; Asai et al. 2011; Hamed et al. 2017). Selenium is considered a highly soluble, mobile,  
61 biologically essential and toxic trace element with a more comprehensive biogeochemical cycle (e.g.,  
62 Tan et al. 2016; Winkel 2016) than that of Te. Due to their overall chemical similarity (both  
63 chalcogens/Group 16 elements), the environmental behaviour of Te is generally assumed to be similar  
64 to that of Se (Belzile and Chen 2015).

65 Given the massive dispersion of past NPP accidental releases through both aquatic and atmospheric  
66 compartments, the development of management plans for hypothetical future accidental NPP events  
67 requires knowledge on radionuclide behaviour including adsorption kinetics under environmentally-  
68 representative conditions. Worldwide, many NPPs are located on fluvial-estuarine systems, for which  
69 little is known on Te (Wu et al. 2014; Duan et al. 2014; Biver et al. 2015) and Se (Measures and

70 Burton 1978; Cutter 1989; Bizsel et al. 2017) environmental dispersion and biogeochemical  
71 behaviour.

72 This study aimed at determining Te and Se reactivity in estuarine salinity and turbidity gradients  
73 through isotopically-labelled sorption experiments (kinetics and isotherms) using natural bulk  
74 sediments and natural water matrices. Parallel selective extractions of particles previously exposed to  
75 isotopically-labelled Te and Se address solid fractionation for both, inherited and spiked  
76 concentrations. The results were further compared to dynamic environmental conditions (i.e.,  
77 environmental timescales of semi-diurnal tidal variations, seasonal migration of the estuarine  
78 maximum turbidity zone, etc.). This comparison allowed to assess and predict for the first time the  
79 environmental fate and potential dispersion of short-lived Te vs long-lived Se radionuclides in case of  
80 a hypothetical accidental NPP liquid discharge in the fluvial-estuarine system of the Gironde Estuary  
81 (SW France hosting two NPPs: the Blayais NPP and the Golfech NPP, Gil-Díaz et al. 2018).

82

## 83 **2. Material and Methods**

### 84 **2.1. Experimental design**

85 Sorption experiments simulated four experimental conditions representative of the Gironde Estuary  
86 salinity and turbidity gradients: two contrasting water matrices (salinities 0 and 32) and two  
87 solid/liquid ratios (100 mg L<sup>-1</sup> and 1000 mg L<sup>-1</sup> DW). Freshwater from the Garonne River and  
88 seawater from the Arcachon Bay, were filtered with 0.45 µm Teflon filters (FHLC, Merck Millipore  
89 Ltd.). Freshwater sediments were sampled at Portets (~30 km upstream from Bordeaux) on the  
90 Garonne River. The water content was evaluated by comparing the masses of precise volumes of wet  
91 and dry sediment aliquots.

92 Spike solutions were prepared by dissolution of elemental <sup>125</sup>Te (99.89% purity; Cortecnet, France)  
93 and <sup>77</sup>Se (99.20% purity; Cortecnet, France) in HCl (2% Suprapur®, Merck) and HNO<sub>3</sub> (2%  
94 Suprapur®, Merck), respectively, heated at 70°C until dissolution. This method is known to produce  
95 oxidized species, i.e., well-known reaction for the formation of Se(VI) (Van Dael et al. 2004).  
96 Isotopically-labelled Te and Se solutions were further oxidised with H<sub>2</sub>O<sub>2</sub> (30 µL L<sup>-1</sup> 30% J.T. Baker  
97 ultrapure) in the different water matrices to favour the oxidation state of <sup>125</sup>Te(VI) and <sup>77</sup>Se(VI) (e.g.,  
98 Edwards et al. 1959; Horner and Leonard 1952), followed by an equilibration period of 24h. Slurries  
99 were prepared from the fresh sediments and unspiked water matrices and equilibrated during 24h, to  
100 avoid potential effects of sediment-water interactions during the sorption experiment (e.g., other ionic  
101 exchanges related to matrix properties influencing spiked Te or Se adsorption).

102 Sorption kinetics were performed with nominal concentrations of 5 µg L<sup>-1</sup> of <sup>125</sup>Te(VI) and 100 µg  
103 L<sup>-1</sup> of <sup>77</sup>Se(VI). These spike concentrations are higher than those expected in most natural systems but

104 were required for analytical purposes. All sorption experiments were performed in acid-washed 50 mL  
105 centrifuging polypropylene (PP) tubes with 3 replicates per experimental condition. Sorption  
106 experiments were placed on an automatic overhead shaker (REAX 20 Heidolph Instruments) and  
107 sampled at  $t = 0, 2, 4, 8, 24$  and  $48\text{h}$  ( $N=3$ ). These relatively short-term experimental conditions are  
108 considered to be in accordance with the environmental timescales of highly dynamic environments  
109 such as those occurring in continent-ocean transition systems. Temperature ( $21.1 \pm 0.4\text{ }^\circ\text{C}$ ), pH ( $7.50 \pm$   
110  $0.45$ ) and oxic ( $104 \pm 0.5\%$  saturation) conditions, were monitored and remained stable throughout the  
111 experiment. In parallel, blank tubes containing only spiked water solutions were used to control  $^{125}\text{Te}$   
112 and  $^{77}\text{Se}$  potential losses onto PP walls over time.

113 Adsorption isotherms were performed for two SPM concentrations ( $100\text{ mg L}^{-1}$  and  $1000\text{ mg L}^{-1}$ )  
114 with initial concentrations of dissolved  $^{125}\text{Te}$  of  $0.1, 0.25, 0.5, 1, 2.5, 5\text{ }\mu\text{g L}^{-1}$  and initial concentrations  
115 of dissolved  $^{77}\text{Se}$  of  $0.5, 5, 10, 25, 50, 75, 100\text{ }\mu\text{g L}^{-1}$  ( $N=2$ ) and sampled after  $48\text{h}$ . Due to analytical  
116 constraints (i.e., salt tolerance of the ICP-MS), especially at the low concentration ranges, these  
117 experiments were only performed in freshwater conditions.

118 In both kinetics and isotherm experiments, dissolved Te ( $\text{Te}_d$ ) and dissolved Se ( $\text{Se}_d$ ) were  
119 monitored. Particulate concentrations were only determined for isotherm experiments using freshwater  
120 slurries with  $1000\text{ mg L}^{-1}$  SPM for mass balance calculations. In all cases, the dissolved phase was  
121 separated from the particulate phase by centrifugation ( $10\text{ min}$  at  $4000\text{ rpm}$ ; Hettich Rotofix 32A  
122 centrifuge) and filtered ( $0.2\text{ }\mu\text{m}$  Minisart® cellulose acetate) into acid-washed PP  $15\text{ mL}$  tubes. These  
123 were then acidified with  $\text{HNO}_3$  ( $1/1000\text{ v/v}$ ; J.T. Baker ultrapure,  $14\text{ M}$ ) and stored at  $4^\circ\text{C}$  in the dark  
124 until analysis.

125

## 126 **2.2. Parallel selective extractions and total digestions**

127 High SPM concentrations ( $2 - 4\text{ g L}^{-1}\text{ DW}$ ) in freshwater ( $S = 0$ ) and seawater ( $S = 32$ ) were left to  
128 equilibrate for  $48\text{h}$  in spiked solutions of nominal  $10\text{ }\mu\text{g L}^{-1}$  of  $^{125}\text{Te}$  and  $100\text{ }\mu\text{g L}^{-1}$  of  $^{77}\text{Se}$ . All  
129 sediments were recovered by centrifugation (Hettich ROTOFIX 32A), oven dried ( $70^\circ\text{C}$ , constant  
130 weight) and grinded in agate mortars, then aliquoted and extracted with parallel selective extractions  
131 (two replicates per extraction mode, Table 1). The targeted operationally defined solid fractions were:  
132 F1 – easily exchangeable and/or carbonate fraction (acetate solution extracting carbonates, Mn  
133 oxyhydroxides, sulphates and organic matter phases; Bordas and Bourg 1998; Kersten and Förstner  
134 1987), F2 – reducible Fe/Mn oxides (ascorbate solution extracting Mn oxide and amorphous Fe oxide  
135 phases; Kostka and Luther 1994), F3 – oxidisable fraction ( $\text{H}_2\text{O}_2$  extraction of organic matter and  
136 labile/amorphous sulphide phases; Tessier et al. 1979; Ma et Uren 1995) and F4 – reactive and  
137 “potentially bioaccessible” fraction ( $\text{HCl } 1\text{M}$  acid extraction of amorphous and crystalline Fe and Mn  
138 oxides, carbonates, amorphous monosulphurs and phyllosilicate phases; Huerta-Díaz and Morse 1990;

139 Gasparon and Matschullat 2006). In addition to the latter, acid extraction with HNO<sub>3</sub> 1 M (F4N) was  
140 performed on a separate aliquot to discard the Cl effect or specific acid effect on F4 obtained from  
141 HCl 1 M leaching. All reagents used were of high purity grade except H<sub>2</sub>O<sub>2</sub> (p.a. grade). High Te  
142 contamination of ~35 µg L<sup>-1</sup> was observed in the extraction blanks of F3 potentially from the H<sub>2</sub>O<sub>2</sub>  
143 solution or the added ammonium acetate. This contamination is suspected to have been adsorbed into  
144 other than H<sub>2</sub>O<sub>2</sub>-extracted solid fractions (given the Te behaviour, see results), thus not affecting the  
145 inherited Te identified in F3 fraction. All extractions were performed in acid-washed (HNO<sub>3</sub> 10%) PP  
146 Falcon 50 mL conical centrifuge tubes (Fisher Scientific). Three blanks of each extraction were  
147 performed. Currently, no Certified Reference Materials (CRM) are available for Te and Se selective  
148 fractions. Residual fractions were calculated as the difference between the acid-soluble fraction (F4 or  
149 F4N) and the total adsorbed particulate concentration.

150 Total sediment concentrations were determined differently for particulate Te (Te<sub>p</sub>) and particulate  
151 Se (Se<sub>p</sub>). Mineralisation of sediment for Te analysis was achieved using a tri-acid digestion with  
152 HNO<sub>3</sub> + HCl + HF as described elsewhere (e.g., Schäfer et al. 2002). Briefly, samples of 30 mg were  
153 digested in closed PP tubes (DigiTUBE<sup>®</sup>, SCP Science) on a heating block (2 h at 110 °C) using 750  
154 µL HNO<sub>3</sub> (14 M Suprapur<sup>®</sup>, Merck), 1.5 mL HCl (10 M Suprapur<sup>®</sup>, Merck) and 2.5 mL HF (29 M  
155 Suprapur<sup>®</sup>, Fisher). After an evaporation step at 120°C, re-dissolution of the samples was performed  
156 with 250 µL HNO<sub>3</sub> (14 M) and heating. After cooling, the samples were brought to 10 mL using Milli-  
157 Q water (18.2 MΩ).

158 For the analysis of Se<sub>p</sub> (volatile at >70°C, not compatible with the above-described tri-acid  
159 digestion) total microwave-assisted digestions (START 1500, MLS GmbH) were performed with 40 -  
160 50 mg of sediment aliquots (Eiche et al. unpublished) already dried (50°C drying oven) and  
161 homogenised (agate mortar). Briefly, 3 mL HNO<sub>3</sub> (sub-boiled acid-distilled 65%, p.a. grade, VWR  
162 Chemicals), 0.5 mL H<sub>2</sub>O<sub>2</sub> (30% Rotipuran<sup>®</sup>, Carl Roth), 0.25 mL HF (40% Suprapur<sup>®</sup>, Merck KGAA  
163 Darmstadt) and 0.5 mL ultrapure Milli-Q water were added. The temperature program was: 18°C min<sup>-1</sup>  
164 to 75°C, followed by 7°C min<sup>-1</sup> to 110°C, then 8°C min<sup>-1</sup> to 150°C and 6°C min<sup>-1</sup> to 210°C, with a  
165 constant temperature of 210°C during 10 min before completely cooling down over night. After  
166 digestion, samples were transferred into PTFE vessels and evaporated on a hotplate to dryness at 70°C  
167 (no Se evaporation at this temperature), recovered with 270 µL of HNO<sub>3</sub> (65% Suprapur), heated at  
168 70°C for 1h and made up with ultrapure Milli-Q water to a final volume of 6 mL.

169

### 170 **2.3. Tellurium quantification**

171 Dissolved Te in samples from freshwater kinetics and isotherms experiments were directly  
172 analysed by ICP-MS (X-Series II, Thermo Fisher Scientific) using external calibration. Seawater  
173 matrices were diluted in 2% HNO<sub>3</sub> (J.T. Baker ultrapure, 14 M) and quantified with external

174 calibration in an adapted salty matrix. In all cases, recoveries were between 85 – 91% for NIST 1643f  
175 CRM (N=4) with a detection limit (LOD) of 0.01  $\mu\text{g L}^{-1}$  (N=10). Given this LOD, the spiked  
176 concentrations and the dilution effect, it is assumed that pre-existing inherited  $^{125}\text{Te}$  in the kinetics and  
177 isotherm samples is negligible in the water matrices as expected concentrations are in the range of 1 ng  
178  $\text{L}^{-1}$  (Filella 2013; Belzile and Chen 2015). The latter is corroborated by upstream freshwater analyses  
179 (Gil-Díaz et al. 2019a).

180 Digestates of particles from the isotherm experiments using 1000  $\text{mg L}^{-1}$  SPM in freshwater were  
181 quantified with an QQQ-ICP-MS (Agilent 8800, Basel, Switzerland) using an external calibration with  
182  $^{103}\text{Rh}$  as internal standard to correct for matrix effects. Tellurium was measured in oxygen-shift mode  
183 using  $\text{O}_2$  as collision gas ( $^{125}\text{Te} + ^{16}\text{O} \rightarrow ^{141}\text{TeO}$ ). A certified reference material (NCS 73307) was used  
184 for quality check-up of the total digestions showing mean  $\pm$  SD recovery values of  $94 \pm 17\%$  (N=3).

185 Particulate Te in total digestions and selective extractions were quantified by TripleQuad-ICP-MS  
186 (TQ ICP-MS; iCAP-TQ, Thermo®) using external calibration. Given the very low inherited  $\text{Te}_p$   
187 concentrations ( $\sim 0.04 \text{ mg kg}^{-1}$ ), natural/inherited Te ( $\text{Te}_{\text{nat}}$ ) was quantified from  $^{126}\text{Te}$  measured in  
188 KED-mode (He), correcting for  $^{86}\text{Sr}^{40}\text{Ar}$ ,  $^{110}\text{Cd}^{16}\text{O}$  and  $^{110}\text{Pd}^{16}\text{O}$  interferences (Filella and Rodushkin  
189 2018) with respective monoelemental solutions (influencing  $<0.1\%$ ) and  $^{126}\text{Xe}$  from analytical blanks  
190 ( $2\% \text{ HNO}_3$ ). Spiked/experimental  $^{125}\text{Te}$  ( $\text{Te}_{\text{ex}}$ ) was determined by TQ ICP-MS in mass-shift  $\text{O}_2$ -mode  
191 (iCAP-TQ, Thermo®). Certified reference materials were used for instrumental quality check-up  
192 (freshwater NIST 1643f) and total digestions (stream sediment NCS 73307). Recoveries were  $95 \pm 5\%$   
193 (N=5) in the KED-mode,  $89 \pm 10\%$  (N=5) in the  $\text{O}_2$ -mode for NIST 1643f and  $99 \pm 14\%$  (N=4) in the  
194 KED-mode and  $70 \pm 19\%$  (N=4) in the  $\text{O}_2$ -mode for NCS 73307. Inherited Te was quantified from  
195 both Te-spiked SPM and Se-spiked SPM (i.e., no influence from potential  $^{125}\text{Te}$  spike effect). In  
196 selective extractions,  $\text{Te}_{\text{nat}}$  concentrations ranged from 5-fold (in F2 extractions) to 200-fold (in F4  
197 extractions) above LOD ( $0.1 \text{ ng L}^{-1}$ , N=10).

198

## 199 **2.4. Selenium quantification**

200 Dissolved Se concentrations from sorption kinetics and isotherms were quantified by ICP-MS  
201 (XSeries 2, Thermo Fisher Scientific, KIT, Germany) using external calibration, CCT-mode (collision  
202 cell with He:H<sub>2</sub> mixture at 92%: 8% to minimise  $^{40}\text{Ar}^{37}\text{Cl}$  interferences) and  $^{103}\text{Rh}/^{115}\text{In}$  as internal  
203 standards. Analytical quality control was followed with certified drinking water (CRM-TMDW) and  
204 freshwater (NIST 1643f) standards showing recoveries ranging between 98 – 106% for the former  
205 (N=16) and 100-102% for the latter (N=16), with a LOD of  $0.06 \mu\text{g L}^{-1}$  (N=10). Natural  $\text{Se}_a$   
206 concentrations were  $0.14 \pm 0.03 \mu\text{g L}^{-1}$  in freshwater (N=32) and  $\sim 0.31 \mu\text{g L}^{-1}$  for seawater  
207 (unpublished).

208 Total  $^{77}\text{Se}$  digestions from the 1000 mg L<sup>-1</sup> SPM isotherm experiment were quantified by QQQ-  
209 ICP-MS (Agilent 8800, Basel, Switzerland) using external calibration with  $^{103}\text{Rh}$  as internal standard  
210 and oxygen-shift mode collision gas for  $^{77}\text{Se}$  ( $^{77}\text{Se} + ^{16}\text{O} \rightarrow ^{93}\text{SeO}$ ) to avoid, amongst others, doubly  
211 charged Rare Earth Element (REE) interferences (mainly  $^{154}\text{Sm}^{++}$ ,  $^{154}\text{Gd}^{++}$ ). The CRM NCS 73307  
212 showed recoveries of total digestions ranging from 70 to 134% (N=3).

213 Analyses of Se in selective extractions, namely particulate inherited/natural Se ( $\text{Se}_{\text{nat}}$ ) and  
214 spiked/experimental Se ( $\text{Se}_{\text{ex}}$ ) were quantified with the O<sub>2</sub>-mode of the TQ ICP-MS (iCAP-TQ,  
215 Thermo®) using external calibration, eliminating the known polyatomic interferences (e.g.,  $^{40}\text{Ar}^{37}\text{Cl}$ ,  
216  $^{154}\text{Sm}^{++}$  and  $^{154}\text{Gd}^{++}$  in  $^{77}\text{Se}$ ,  $^{78}\text{Kr}$ ,  $^{156}\text{Gd}^{++}$  and  $^{156}\text{Dy}^{++}$  in  $^{78}\text{Se}$ ,  $^{81}\text{Br}^1\text{H}$  and  $^{82}\text{Kr}$  in  $^{82}\text{Se}$ ) on both inherited  
217 ( $^{78}\text{Se}$ ,  $^{80}\text{Se}$ ,  $^{82}\text{Se}$ ) and spiked ( $^{77}\text{Se}$ ) isotopes. Particulate  $\text{Se}_{\text{nat}}$  was quantified from both Te-spiked and  
218 Se-spiked slurries. Analytical quality check showed recoveries of  $95 \pm 3\%$  for NIST 1643f and  $85 \pm$   
219  $2\%$  for NIST 1640a. Total adsorbed  $\text{Se}_{\text{ex}}$  was calculated from the difference between initially spiked  
220 and final  $\text{Se}_{\text{d}}$  after 48h.

221

## 222 2.5. Distribution coefficient (K<sub>d</sub>)

223 Tellurium and Se partitioning between dissolved and particulate concentrations was evaluated from  
224 the kinetic experiments at equilibrium by using the particle-water distribution coefficient (K<sub>d</sub>),  
225 described in Sung (1995). Briefly, K<sub>d</sub> (in L kg<sup>-1</sup>) is the particulate (mg kg<sup>-1</sup>) to dissolved (mg L<sup>-1</sup>)  
226 concentration ratio (Equation 1). The relative contribution of the particulate concentration (X<sub>p</sub>) of a  
227 given element X to the total (dissolved + particulate) concentration of the same element (X<sub>T</sub>, Equation  
228 2) is expressed as the fraction of X<sub>p</sub> (F<sub>p</sub>, expressed in percentage, Equation 3).

$$229 \quad K_d = X_p/X_d \quad (1)$$

$$230 \quad X_T = X_p \cdot \text{SPM} + X_d \quad (2)$$

$$231 \quad F_p(\%) = (X_p \cdot \text{SPM})/X_T = (K_d \cdot \text{SPM})/(1 + K_d \cdot \text{SPM}) \quad (3)$$

232 where X<sub>p</sub> is expressed in mg kg<sup>-1</sup>, X<sub>d</sub> in mg L<sup>-1</sup>, X<sub>T</sub> in mg L<sup>-1</sup> and SPM in kg L<sup>-1</sup>. This K<sub>d</sub> should also  
233 match the slope of the isotherm experiments.

234

## 235 2.6. Adsorption isotherm models

236 The exchange of a substance between the dissolved and particulate phases reaches a dynamic  
237 equilibrium (i.e., equal sorption and desorption rates) after sufficient contact time (Foo and Hameed  
238 2010). Appropriate modelling and thermodynamic considerations provide insights into the adsorption



239 mechanisms (i.e., physisorption vs chemisorption), surface properties and sorption strength (Foo and  
240 Hameed 2010, and references therein).

241 The Langmuir empirical model is the most common two-parameter isotherm employed to describe  
242 monolayer chemical saturation onto finite sites with no lateral interactions between adsorbed  
243 molecules (no “steric hindrance”; Langmuir 1918). The mathematical equation for the Langmuir  
244 isotherm (Equation 4) is complemented with the dimensionless constant ( $R_L$ ) also known as the  
245 separation factor or equilibrium parameter (Equation 5) defined by Weber and Chakravorti (1974):

$$246 \quad X_p = (X_{pmax} \cdot K_L \cdot X_d)/(1 + K_L \cdot X_d) \quad (4)$$

$$247 \quad R_L = 1/(1 + K_L \cdot X_{d0}) \quad (5)$$

248 where  $X_p$  is the concentration of element X in the particulate phase at equilibrium ( $\text{mg kg}^{-1}$ ), calculated  
249 from the difference in dissolved concentrations between the initial spiked ( $X_{d0}$ ) and the equilibrium  
250 ( $X_d$ ) concentrations ( $\mu\text{g L}^{-1}$ , converted to particulate concentrations with the corresponding SPM  
251 ratio),  $X_{pmax}$  is the maximum charge of X in the SPM and  $K_L$  is the constant of Langmuir ( $\text{L } \mu\text{g}^{-1}$ ).  
252 Values of  $R_L$  indicate the adsorption nature of the isotherm as unfavourable ( $R_L > 1$ ; i.e., highly soluble  
253 elements), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) and irreversible ( $R_L = 0$ ; i.e., high affinity for the  
254 particulate phase; Weber and Chakravorti 1974).

255 The Freundlich empirical model was the first one to describe heterogeneous (i.e., non-uniform  
256 distribution) multilayer adsorption on a non-homogeneous surface (Freundlich 1907). The  
257 mathematical expression of the Freundlich isotherm (Equation 6) represents the adsorption intensity  
258 by the  $K_F$  constant (i.e., the higher the value the higher the affinity for the particulate phase) and the  
259 surface heterogeneity with the  $c$  value (i.e., the closer to zero the more heterogeneous; Foo and  
260 Hameed 2010). When  $c = 1$ , the relationship between  $X_p$  and  $X_d$  is linear and  $K_F = K_d$  (distribution  
261 coefficient).

$$262 \quad X_p = K_F \cdot X_d^c \quad (6)$$

263

## 264 **3. Results**

### 265 **3.1. Tellurium sorption kinetics and isotherms**

266 Sorption kinetics of dissolved Te ( $\text{Te}_{ex}$ ) was rapid (>40% in less than 3 min., Figure 1a)  
267 independent from salinity, but highly dependent on the solid/liquid ratios, showing ~90% sorption in  
268  $1000 \text{ mg L}^{-1}$  SPM within 3 min. Equilibrium between the dissolved and particulate phases was  
269 achieved at  $\geq 48\text{h}$  in  $100 \text{ mg L}^{-1}$  SPM and in <5h for  $1000 \text{ mg L}^{-1}$  SPM (Figure 1a). Experimental  
270 blanks (i.e., no SPM) showed no measurable  $\text{Te}_{ex}$  loss or adsorption onto tube walls throughout the

271 whole experiment duration. Estimated particulate concentrations were used to calculate partitioning  
272 coefficients for  $Te_{ex}$  at 48h of adsorption time, showing  $\log_{10} K_d$  values in freshwater of  $4.94 \pm 0.02$  L  
273  $kg^{-1}$  for  $100\text{ mg L}^{-1}$  and  $5.31 \pm 0.01$  L  $kg^{-1}$  for  $1000\text{ mg L}^{-1}$ , whereas in seawater  $K_d$  values were  $4.98 \pm$   
274  $0.02$  L  $kg^{-1}$  for  $100\text{ mg L}^{-1}$  and  $4.96 \pm 0.09$  L  $kg^{-1}$  for  $1000\text{ mg L}^{-1}$ .

275 Sorption isotherms showed non-linear correlations at low SPM concentrations ( $100\text{ mg L}^{-1}$ , Figure  
276 1b) following a Langmuir isotherm. Langmuir parameters were  $K_L = 3.91\text{ L } \mu g^{-1}$  and  $b = 50.7\text{ mg } kg^{-1}$   
277 with a separation factor of “favourable” to “very favourable” due to  $R_L$  variations between 0.72 and  
278 0.05. Nevertheless, higher SPM content of  $1000\text{ mg L}^{-1}$  showed a linear behaviour representative of a  
279 Freundlich isotherm (Figure 1c) with relatively low heterogeneity ( $c = 1$ ). The value of  $\sim 0.02\text{ mg } kg^{-1}$   
280 at the intercept represented the inherited  $Te$  in the SPM, thus, included in the  $Te_p$  concentrations.  
281 Calculated  $Te_p$  concentrations were in accordance with directly analysed  $Te_p$  (<15% difference, within  
282 analytical error) from  $1000\text{ mg L}^{-1}$  experimental isotherm sediments.

283

### 284 3.2. Selenium sorption kinetics and isotherms

285 Selenium sorption kinetics ( $Se_{ex}$ , Figure 2a) was less rapid than that of  $Te_{ex}$  (Figure 1a), showing  
286 <10% sorption after 3 min of exposure. There seems to be an effect of both salinity (i.e., higher  
287 sorption in seawater) and SPM concentration (i.e., higher sorption in  $1000\text{ mg L}^{-1}$ ), reaching  
288 solid/liquid equilibrium in <24h for  $1000\text{ mg L}^{-1}$  with max. 25% sorption. Precise sorption kinetics and  
289 equilibrium time for  $100\text{ mg L}^{-1}$  (max. 5% sorption) were uncertain, as all  $Se_d$  values were close to the  
290 experimental blank concentrations with 4% variability shown by the standard deviation. Experimental  
291 blanks showed no measurable  $^{77}Se$  loss or adsorption onto tube walls along the experiment. Estimated  
292  $\log_{10} K_d$  values at 48h were:  $2.51 \pm 0.08$  L  $kg^{-1}$  for  $100\text{ mg L}^{-1}$  and  $2.42 \pm 0.04$  L  $kg^{-1}$  for  $1000\text{ mg L}^{-1}$   
293 in freshwater, whereas in seawater they were  $2.87 \pm 0.10$  L  $kg^{-1}$  for  $100\text{ mg L}^{-1}$  and  $2.57 \pm 0.04$  L  $kg^{-1}$   
294 for  $1000\text{ mg L}^{-1}$ .

295 Sorption isotherms for both SPM conditions ( $100\text{ mg L}^{-1}$  and  $1000\text{ mg L}^{-1}$ ) showed similar  
296 concentrations and linear correlations, representative of a Freundlich isotherm (Figure 2b). The value  
297 at the intercept of  $\sim 0.26\text{ mg } kg^{-1}$  represented inherited  $Se$  included in the  $Se_p$  values. Calculated  $Se_p$   
298 concentrations tended to be  $\sim 30\%$  higher than those directly measured for  $1000\text{ mg L}^{-1}$  SPM isotherm  
299 samples.

300

### 301 3.3. Selective extractions

302 Selective extractions from both freshwater ( $S=0$ ) and seawater ( $S=32$ ) experiments of independent  
303  $^{125}Te$  and  $^{77}Se$  spikes showed differences between spiked and inherited concentrations as well as

304 distinct fractionation patterns for both elements (Figure 3). Relative contributions of each extracted  
305 fraction to total (inherited or spiked) Te and Se concentrations were expressed in percentages (Figure  
306 3). Total concentrations used for Te calculations were 0.05 mg kg<sup>-1</sup> for Te<sub>nat</sub> whereas 2.68 mg kg<sup>-1</sup> in  
307 S=0 and 3.20 mg kg<sup>-1</sup> in S=32 for respective Te<sub>ex</sub> concentrations. Total Se<sub>nat</sub> concentrations ranged  
308 between 0.37-0.53 mg kg<sup>-1</sup> and average Se<sub>ex</sub> was 25.7 mg kg<sup>-1</sup> in both, freshwater and seawater.

309 The acid-soluble fractions showed the highest Te<sub>nat</sub> contribution (~50% in F4 and ~30% in F4N,  
310 Figure 3a) for freshwater experiments and were 10-20% lower in seawater experiments. Average Te<sub>nat</sub>  
311 contribution was 14% in the H<sub>2</sub>O<sub>2</sub> fraction (F3, associated to organic matter), <2% in both, the easily  
312 exchangeable or carbonate fractions (F1) and the amorphous Mn/Fe oxide fraction (F2; Figure 3a). In  
313 contrast, Te<sub>ex</sub> sorbed preferentially (average ~60%) to the acid-soluble mineral phases (F4-F4N),  
314 comprising amorphous and crystalline Fe and Mn oxides, carbonates, amorphous monosulphurs (e.g.,  
315 acid volatile sulphides and FeS) and phyllosilicate phases. The latter also implies a ~40% retention of  
316 Te<sub>ex</sub> in the residual fraction. Up to 10% of Te<sub>ex</sub> was sorbed in the F1-acetate (easily exchangeable or  
317 carbonates fraction) and F2-ascorbate (Mn/Fe oxides) extracted fractions, obtaining a lower, <0.2%  
318 extraction with the oxidisable fraction (F3-H<sub>2</sub>O<sub>2</sub> organic matter and labile/amorphous sulphide  
319 phases). In any case, low differences (~5%) were observed between freshwater-adsorbed and  
320 seawater-adsorbed Te<sub>ex</sub> except for acid-soluble fractions where this difference varied from 20 to 30%.

321 Selective extractions for Se<sub>nat</sub> showed highest contributions (≥85%) in the F3-H<sub>2</sub>O<sub>2</sub> fraction  
322 (targeting organic matter and labile/amorphous sulphide phases) of SPM exposed to contrasting  
323 salinities (Figure 3b). Acid-soluble fractions obtained from 1M HCl showed 2-fold lower Se<sub>nat</sub>  
324 extractions than 1M HNO<sub>3</sub>. Ascorbate solutions extracted concentrations of Se<sub>nat</sub> similar to that of  
325 HCl-extracted aliquots, and the lowest Se<sub>nat</sub> fractions occurred in acetate extractions (~1%, Figure 3b).  
326 Spiked concentrations were also highly extracted in the F3-H<sub>2</sub>O<sub>2</sub> fraction, representing 95-105% of  
327 total sorbed Se<sub>ex</sub>. Noteworthy, the second most important fraction was the F2-ascorbate fraction,  
328 extracting ~60% of Se<sub>ex</sub>, presumably from amorphous Mn/Fe oxide mineral phases. This amount of  
329 Se<sub>ex</sub> extracted was higher than that in the acid-soluble fractions F4 and F4N, both extracting ~20% of  
330 Se<sub>ex</sub>. Only 12% of Se<sub>ex</sub> was leached in the easily exchangeable/carbonate fraction (F1-acetate  
331 extraction). Differences between freshwater-adsorbed and seawater-adsorbed Se<sub>ex</sub> were <10%.

332

## 333 4. Discussion

### 334 4.1. Tellurium reactivity and solid fractionation in estuarine salinity and turbidity gradients

335 Results from sorption isotherms suggest a relatively high Te affinity for the particulate phases, as  
336 previously reported for Te radionuclides (Whitehead et al. 1988) and natural Te in the Changjiang  
337 Estuary (Wu et al. 2014). The observed log<sub>10</sub> K<sub>d</sub> values for experimentally adsorbed Te are similar to

338 typical Te  $\log_{10}$  Kd values in the Garonne-Gironde fluvial-estuarine system (Gil-Díaz et al. 2019a)  
339 ranging from 4.9 to 5.3 L kg<sup>-1</sup>. These values are up to one order of magnitude greater than those of  
340 natural As (3.5 – 4.8 L kg<sup>-1</sup>) and Sb (3.8 – 4.8 L kg<sup>-1</sup>; Gil-Díaz et al. 2018) suggesting that the  
341 solubility/mobility of both natural and experimentally adsorbed Te is lower than that of natural As and  
342 Sb. Experimentally adsorbed Se showed even lower partitioning (2.4 – 2.9 L kg<sup>-1</sup>, this study) with ~2  
343 orders of magnitude lower than those of Te, suggesting that Se and Te solubility in environmental  
344 matrices may be very different.

345 Tellurium partitioning may also be compared to that of Cs, given (i) their potential common  
346 sources from weathering/remobilisation processes in the watershed (Gil-Díaz et al. 2019a), and (ii)  
347 their considerable radioactivity after accidental events (Steinhauser et al. 2014), making them relevant  
348 for radionuclide dispersion models. While the observed Te partitioning suggests relatively constant  
349  $\log_{10}$  Kd of ~ 4.9 L kg<sup>-1</sup>, the reported Cs  $\log_{10}$  Kd values range from <4.7 L kg<sup>-1</sup> in river systems  
350 (Ciffroy et al. 2009) to typical values of  $\log_{10}$  Kd 5.1 to 6.8 L kg<sup>-1</sup> in the Garonne-Gironde fluvial  
351 system (Gil-Díaz et al. unpublished). Furthermore, Te  $\log_{10}$  Kd values are similar for both freshwater  
352 and seawater matrices with a maximum decrease of only 0.3 L kg<sup>-1</sup> in the seawater, similar decreases  
353 to that observed for Sb in the Gironde Estuary (i.e., 0.2 L kg<sup>-1</sup>; Gil-Díaz et al. 2018). In contrast, the  
354 difference in Cs  $\log_{10}$  Kd between freshwater and seawater is 1.4 L kg<sup>-1</sup> under experimental conditions  
355 (Oughton et al. 1997). Therefore, one would expect only little desorption of Te along estuarine salinity  
356 gradients, compared to Cs mobilisation. This major difference in estuarine geochemical behaviour  
357 represents important information for the development of continent-ocean transition models  
358 anticipating potential Te and Cs radionuclide dispersion after accidental NPP releases. This  
359 observation also implies different biological transfers of Te and Cs, depending on the dissolved  
360 concentrations and bioaccessible fractions from the particle phase.

361 Assuming Te adsorption under natural conditions and at natural, low concentrations (i.e. less Te  
362 available for adsorption) one would expect the limited Te available to preferentially adsorb onto sites  
363 with high binding energy. Under experimental conditions, when relatively abundant dissolved Te  
364 exceed the number of strong binding sites, the different Te species would adsorb onto different sites,  
365 according to the respective binding strengths, starting with the high binding energy sites. However, the  
366 sorption isotherms of dissolved Te onto the particulate phase fits a Langmuir (chemisorption-driven)  
367 behaviour for both the low SPM ratio (~100 mg L<sup>-1</sup>; Figure 1b) and the high SPM condition (1000 mg  
368 L<sup>-1</sup>; Figure 1c), suggesting homogeneous monolayer adsorption of Te at equal bonding energy sites  
369 until saturation (Foo and Hameed 2010). This observation implies that, in the present experiment, the  
370 amount of dissolved Te available for adsorption did not exceed the number of strong bonding energy  
371 sites available, and thus may be representative of sorption processes under natural conditions. This  
372 saturation would be achieved at ~50 mg kg<sup>-1</sup> for Garonne River SPM which, together with kinetic  
373 results suggest that, in the maximum turbidity zone (MTZ) of the Gironde Estuary (SPM ≥ 1000 mg L<sup>-1</sup>

374 <sup>1</sup>; Sottolichio and Castaing 1999), a hypothetical Te<sub>d</sub> concentration of 50 µg L<sup>-1</sup> could be retained to  
375 ~90% within <3 min. Nearly all Te<sub>d</sub> (98%) would adsorb to the SPM in less than 2 h (Figure 1a).  
376 However, environmental concentrations of dissolved Te are found within the ultra-trace levels (e.g.,  
377 Belzile and Chen 2015), and in the case of potential NPP accidents released Te masses would be  
378 expected to be orders of magnitude lower than those needed to reach saturation. In fact, a maximum of  
379 68 000 000 Bq m<sup>-3</sup> of <sup>137</sup>Cs (equivalent to ~20 ng L<sup>-1</sup>) has been detected in early April in surface  
380 waters adjacent to the FDNPP, decreasing to 10 000 Bq m<sup>-3</sup> (equivalent to ~3 pg L<sup>-1</sup>) in early 2012  
381 (Buesseler et al. 2017). Therefore, assuming that the amounts of Te released would be similar in  
382 magnitude (or lower) than those of <sup>137</sup>Cs, nearly all Te<sub>d</sub> radionuclides potentially released/produced in  
383 the Gironde Estuary would be highly retained in the particulate phase, even in seawater conditions.  
384 The latter is in accordance with the scavenged behaviour of Te observed in open ocean profiles of the  
385 Pacific and Atlantic Oceans, the East China Sea and the Angola and Panama Basins (Lee and Edmond  
386 1985; Yoon et al. 1990; Wu et al. 2014).

387 The F4 acid-soluble fraction (attributed to the sum of amorphous and crystalline Fe and Mn oxides,  
388 carbonates, amorphous monosulphurs and phyllosilicate phases) is commonly considered to represent  
389 the fraction potentially bioaccessible to organisms (Australian and New Zealand sediment quality  
390 guidelines; ANZECC and ARMCANZ 2000). Based on this idea, the extractions suggest that ~30% of  
391 Te<sub>nat</sub> in the SPM and ~60% of the experimentally added Te<sub>ex</sub> retained in the particulate phase would be  
392 potentially bioaccessible. Accordingly, these fractions could impact filter-feeding organisms such as  
393 economically relevant bivalves (i.e., oysters) with unknown implications for the food chain.  
394 Interestingly, this observation also suggests that ~40% of the experimentally adsorbed Te<sub>ex</sub> could not  
395 be recovered by 1M acid extraction, i.e. would be bound to the so-called residual fraction, typically  
396 attributed to minerals that are considered as relatively insoluble under respective conditions (Gupta  
397 and Chen 1975). Adsorption of Te<sub>ex</sub> to both, the bioaccessible (60%) and residual (40%) fractions  
398 implies interaction with different mineral surfaces, which would not be consistent with the Te<sub>ex</sub>  
399 adsorption isotherm fitting the Langmuir model, unless different fractions showed relatively similar  
400 surface properties regarding Te sorption. Differences in Te dissolution between 1M HCl (F4) and 1M  
401 HNO<sub>3</sub>-based (F4N) extractions (~20% higher in HCl, Figure 3) observed for both naturally and  
402 experimentally-adsorbed Te, suggest that HCl may have stronger extraction efficiency than HNO<sub>3</sub>,  
403 although previous work has reported similar stability and solubility in both HCl and HNO<sub>3</sub> solutions  
404 (Inorganic Ventures 2016).

405 Furthermore, these results appear to be in opposition with the higher Te adsorption observed in  
406 SPM in seawater conditions compared to that in freshwater (3.20 vs 2.70 mg kg<sup>-1</sup>, respectively). In  
407 fact, the relatively low acid-soluble extractions obtained from SPM exposed to seawater compared to  
408 freshwater conditions suggest that Te binds somehow strongly in seawater conditions (i.e., not related  
409 to easily exchangeable binding sites). This observation is in accordance with the observed negative

410 correlation between the labile fraction of  $Te_p$  and the salinity gradient in the Changjiang Estuary (Duan  
411 et al. 2014). Nevertheless, further research is required to verify these hypotheses and the specific  
412 binding modes of Te to amorphous and crystalline Fe and Mn oxides, amorphous monosulphurs and  
413 phyllosilicate phases.

414 Low extraction of  $Te_{nat}$  from the exchangeable/carbonate (<10% in F1), the amorphous Fe/Mn  
415 oxide fraction (<10% in F2) and the organic matter fraction (~14% in F3) are consistent with  $Te_{nat}$   
416 extractions in marine SPM from the East China Sea (Duan et al. 2014). In fact, Duan et al. (2014)  
417 observed 13% and 11% Te in the exchangeable and carbonates fraction (i.e., from an acetate-solution  
418 extraction), 11% in the Fe–Mn oxides (i.e., from a hydroxylamine-based solution) and 15% in the  
419 organic matter fraction (i.e., from  $H_2O_2$ -solution extraction), leaving ~50% in the so-called “residual”  
420 fraction. Similarly, the residual fraction (accounted as the difference between total Te and that in F4)  
421 of the Garonne River SPM carried ~50% in freshwater-exposed SPM and 70% in seawater-exposed  
422 SPM of  $Te_{nat}$ .

423 For the experimentally adsorbed  $Te_{ex}$  simulating potential anthropogenic Te release into the natural  
424 environment the results suggest that up to ~99% would be fixed onto SPM within few hours,  
425 depending on SPM concentrations. After sediment deposition in the estuarine banks and bed during  
426 tidal slacks, the onset of early diagenetic processes might potentially release (i) up to 10% of  $Te_{ex}$  due  
427 to reductive dissolution of reactive Fe and Mn oxyhydroxides as simulated by ascorbate extractions  
428 (F2), and (ii) less than 1% of  $Te_{ex}$  adsorbed to organic matter ( $H_2O_2$  extraction, F3). The relatively low  
429 F3 fraction obtained for  $Te_{ex}$  compared to that of  $Te_{nat}$  (14%) may suggest that Te physisorption or  
430 chemisorption onto particulate organic matter may be smaller than Te fixation by active incorporation  
431 (absorption). The observed results are applicable to Te(VI) sorption behavior, which is assumed to be  
432 representative of environmental conditions as Te(VI) is generally more abundant than Te(IV) in  
433 aquatic systems (Lee and Edmond 1985; Yoon et al. 1990), representing up to 5-fold the abundance of  
434 Te(IV) in the Changjiang Estuary (Wu et al. 2014). The precise Te species released to the environment  
435 after a NPP accident are unknown, potentially varying between events due to specific accident  
436 conditions. In fact, the presence and concentration of radionuclide species in the nuclear fuel depend  
437 on several factors including fuel composition and fuel burnup (Kleykamp 1985). Nevertheless, both  
438 Te(IV) and Te(VI) equally adsorb to Fe(III) hydroxides and Te(IV) to illite mineral phases (Harada  
439 and Takahashi 2009; Qin et al. 2017). Thus, this work may serve as a preliminary approach to  
440 radionuclide Te dispersion fate scenarios in the Gironde Estuary.

441 In a scenario of Te radionuclide dispersion after hypothetical NPP accidental events the above  
442 considerations suggest a dominant role of the estuarine SPM in Te retention and dispersion  
443 independent from the hydrological situation. Therefore, relatively few Te radionuclides would be  
444 bioavailable strongly limiting potential transfer to the atmosphere due to bio-methylation processes

445 (Chasteen and Bentley 2003) within the estuarine reaches. Both, relatively low ( $\sim 100 \text{ mg L}^{-1}$ ) and high  
446 ( $>1000 \text{ mg L}^{-1}$ ) SPM concentrations would result in almost total sequestration of Te due to adsorption  
447 of Te radionuclides on suspended particles. The environmental persistence of Te radionuclides  
448 depends on both, half-lives (e.g., ranging between 3.2 days for  $^{132}\text{Te}$  to  $\sim 3$  months for  $^{127\text{m}}\text{Te}$  for the  
449 most relevant ones) and fission yield (i.e., the probability of being produced from nuclear fission  
450 reactions). The combination of both parameters may result in estuarine Te radionuclide half-lives of  
451 several months. In any case, average particle residence times in the Gironde Estuary (1-2 years,  
452 Castaing and Jouanneau 1979), are clearly greater than the aforementioned radionuclide timescales,  
453 suggesting that the maximum decay would take place inside the estuary, except for specific  
454 hydrodynamic conditions allowing for massive particle expulsion to the coastal ocean (few days per  
455 year; Allen et al. 1980; Castaing and Allen 1981). The main decay products are radioactive or stable  
456 iodine daughter nuclides (e.g.  $^{129}\text{I}$  with  $1.57 \cdot 10^7$  y half-life) which will then likely be mobilised to the  
457 water column (or pore waters) due to their relatively high solubility.

458

#### 459 **4.2. Selenium reactivity and solid fractionation in estuarine salinity and turbidity gradients**

460 The experimentally determined sorption of Se onto SPM from the Garonne River is considerably  
461 lower than that of Te, in accordance with the mobile character of Se in aquatic systems (Fernández-  
462 Martínez and Charlet 2009). The corresponding Kd values ( $\log_{10}$  Kd from 2.4 to 2.9  $\text{L kg}^{-1}$ ) are in the  
463 low Kd range of values reported for natural (stable and radioactive) Se in estuarine/coastal systems  
464 such as the San Francisco Estuary ( $\log_{10}$  Kd of 2.0 – 4.5  $\text{L kg}^{-1}$  for  $100 \text{ mg L}^{-1}$  SPM; Benoit et al.  
465 2010) and 19 Japanese coastal regions ( $\log_{10}$  Kd of 2.6 – 3.9  $\text{L kg}^{-1}$ ; Takata et al. 2016). In fact,  
466 differences between field Kd and experimental Kd for radionuclides have been also observed in  
467 environmental SPM samples (e.g., Co, Cs, Mn; Ciceri et al. 1988). These differences were explained  
468 by the contribution of the residual fraction to the calculation of field Kd (i.e., total digestions; Ciceri et  
469 al. 1988). Furthermore, Kd values are generally site-dependent as SPM mineralogy can strongly  
470 control elemental solid/liquid partitioning and Se Kd values have been observed to depend on grain  
471 size and organic matter (Takata et al. 2016). Sediments of the Gironde Estuary show characteristic  
472 particulate organic carbon (POC) contents ranging from 0.05 to 1.5% (Etcheber et al. 2007; Coynel et  
473 al. 2016) and mainly contain silts and some sands (7 - 480  $\mu\text{m}$ ; Coynel et al. 2016).

474 Marine and estuarine environments generally present higher abundances of Se(VI) over Se(IV)  
475 (Cutter 1978; Cutter and Bruland 1984; Guan and Martin 1991). The observed Se(VI) adsorption  
476 kinetics fit a pseudo-second order reaction, suggesting that the main process involving Se(VI) removal  
477 from the solution are physicochemical interactions (physisorption) with rate-limiting chemisorption  
478 surfaces (Robati 2013). This sorption pattern is in accordance with bidentate outer-sphere and  
479 monodentate inner-sphere complexes reported for selenate adsorbed on ferric-Fe(III) (hydr-)oxides

480 and clay minerals like kaolinite (Su and Suarez 2000; Peak and Sparks 2002; Nothstein 2016), despite  
481 the higher affinity of selenite (Se(IV)) inner-sphere complexes to these mineral phases (Hamdy and  
482 Gissel-Nielsen 1977; Hayes et al. 1987).

483 Such interactions are relatively weak reflecting the selective extractions results (Figure 3b), as  
484 more than half of the acid-soluble fraction (F4) is contributed by exchangeable Se forms (F1). This  
485 distribution of Se between several mineral phases is in line with Se(VI) sorption fitting Freundlich  
486 isotherms, implying heterogeneous sorption sites. In this case, stronger binding sites are occupied  
487 preferentially, decreasing the adsorption energy exponentially as they fill up (Zeldowitsch 1934).  
488 Weak interactions between dissolved Se(VI) and particle surfaces could be affected by ionic strength  
489 competition, decreasing Se(VI) sorption onto SPM (Su and Suarez 2000). However, the observed  
490 differences in Se sorption between freshwater- and seawater-exposed SPM fall within the analytical  
491 error.

492 Co-existing Se(IV) and Se(VI) forms may partly explain differences in parallel selective  
493 extractions of  $Se_{nat}$  and  $Se_{ex}$ . In fact, the selective extraction using oxidising reagents (i.e. the F3- $H_2O_2$   
494 and the F4N- $HNO_3$  fractions; Figure 3c,d) generally show a high mobilisation of Se, probably due to  
495 the oxidation of Se(IV) to the more mobile Se(VI). Strong oxidants like  $H_2O_2$ , used to chemically  
496 oxidise the organic matter, as well as  $HNO_3$  compared to HCl, can oxidise Se(IV) from carrier phases  
497 other than the target phase (Gruebel et al. 1988). Thus, although high Se content in the organic matter  
498 fraction would fit the nutrient type behaviour of Se in marine environments (e.g., Cutter and Bruland  
499 1984, Cutter and Cutter 1995), the fact that the amount of Se extracted by  $H_2O_2$  (F3) is close to 100%  
500 could also include Se extracted from other phases by oxidation (Figure 3), implying non-selectivity of  
501 the fractionation for Se. Sequential extractions in anoxic biofilms have also identified the non-  
502 selectivity of other oxidising reagents (NaOCl) targeting Se in the “organically-associated” fraction for  
503 several inorganic/organic Se species (Lenz et al. 2008). The non-selectivity of both, NaOCl and  $H_2O_2$   
504 extractions of Se was already identified for soil and sediment extractions by Gruebel et al. (1988).  
505 These observations clearly suggest that commonly applied extraction schemes (e.g., Tessier et al.  
506 1979; Ure et al. 1993) need to be updated and/or adapted before applied to specific elements, such as  
507 Se.

508 It is commonly accepted that the 1M acid-soluble fraction includes mineral phases extracted in the  
509 ascorbate fraction, thus trace element concentrations in F4 should be equal to or greater than in F2  
510 fractions (Huerta-Díaz and Morse 1990; Kostka and Luther 1994; Gasparon and Matschullat 2006).  
511 The similar  $Se_{nat}$  concentrations in both F4-HCl and F2-ascorbate fractions (Figure 3d) are in  
512 accordance with this statement, potentially suggesting that most (if not all) of the  $Se_{nat}$  in the F4-HCl  
513 fraction was extracted from the amorphous Fe/Mn oxide carrier phases (F2-ascorbate fraction). In  
514 contrast,  $Se_{ex}$  was greater in the F2-ascorbate fraction than in the acid soluble fractions (F4 and F4N,



515 Figure 3c). Interestingly, this effect of inversed extraction efficiency of parallel selective extractions  
516 (F2 vs F4) also occurred for both inherited and spiked Sb in the same SPM from the Garonne River  
517 (Gil-Díaz et al. 2019b). Thus, these results suggest an anomaly (compared to more commonly  
518 analysed elements such as Cd, Cu, Zn, Pb, etc.) for F2-ascorbate extractions of oxyanions like Se and  
519 Sb, but not Te. This effect could be potentially due to strong organic complexation of Se and Sb by the  
520 citrate present in the ascorbate solution, thus extracting higher Se and Sb concentrations,  
521 independently from the dissolution of the targeted mineral carrier phase (Gil-Díaz et al. 2019b). These  
522 observations suggest that reducing conditions and the presence of strong organic ligands, as occurring  
523 in sub-oxic early diagenetic conditions (Froelich et al. 1979), potentially enhance  $Se_{ex}$  solubility,  
524 compared to  $Se_{nat}$ .

525 Re-adsorption of Se (and As) onto non-targeted crystalline Fe hydroxides (i.e., goethite) is  
526 favoured during soil and sediment acid-based hydroxylamine extractions (reductive dissolution;  
527 Gruebel et al. 1988). Because acid 1M HCl extractions do not dissolve crystalline Fe hydroxides such  
528 as goethite and hematite (Raiswell et al. 1994), one cannot exclude Se dissolution from target minerals  
529 and re-adsorption onto non-target minerals (e.g. crystalline Fe hydroxides) in 1M HCl and 1M HNO<sub>3</sub>  
530 extractions. This effect implies that the estimation of the potentially bioaccessible Se fractions by acid  
531 extractions in sediments may be widely biased.

532 Combining the above findings, one would assume that, after a potential accidental release from  
533 NPPs in the Gironde Estuary, the majority of dissolved radioactive Se may be rapidly expelled to the  
534 coastal ocean and <30% retention in the particulate phase of the MTZ. Given the similarities between  
535 sorption isotherms and  $K_d$  at 100 mg L<sup>-1</sup> and 1000 mg L<sup>-1</sup> SPM concentrations, dissolved Se probably  
536 is dominant for a wide range of SPM concentrations and dissolved radioactive Se releases. Moreover,  
537 reducing, suboxic conditions as existing in the MTZ water column (Robert et al. 2004) may further  
538 increase Se mobility due to leaching from particles subjected to early diagenetic processes.

539 Noteworthy, this expected dominance of dissolved Se radionuclides could enhance radioactivity  
540 transfer to the biological compartment, given the nutrient behaviour of Se (Tan et al. 2016). In fact,  
541 aquatic microorganisms naturally methylate Se as a part of their detoxifying mechanisms (Cooke and  
542 Bruland 1987). In the presence of Se radionuclides, bio-methylation processes might produce  
543 radioactive volatile Se (e.g., <sup>75</sup>Se, <sup>79</sup>Se and <sup>82</sup>Se) species which must be taken into account for  
544 accidental dispersion scenarios. Such Se methylation is a seasonal process (i.e., low in winter and  
545 quantifiable in summer) with estimated average fluxes of the order of 10<sup>5</sup> g y<sup>-1</sup> for the Gironde Estuary  
546 (Amouroux and Donard 1997). Such methylation is species-dependent and can potentially show non-  
547 negligible atmospheric dispersion (Luxem et al. 2015).

548 Thus, accidental releases of dissolved Se radionuclides such as <sup>75</sup>Se (~119 d half-life), <sup>79</sup>Se (~10<sup>5</sup> y  
549 half-life) and <sup>82</sup>Se (~10<sup>19</sup> y half-life) are expected to follow the dynamics of the estuarine water

550 column (e.g. estuarine water residence times of 10 to 80 days), implying (i) continuous exportation of  
551 dissolved radioactive Se to the coast during winter/high discharge conditions, (ii) bio-availability to  
552 primary producers and the related food chain, and (iii) potential seasonal production of radioactive  
553 methylated species exported to the atmosphere.

554

## 555 **5. Conclusion**

556 Batch experiments with bulk SPM and natural freshwater/seawater matrices simulating contrasting  
557 estuarine turbidity and salinity gradients showed different sorption kinetics, particulate affinity and  
558 solid fractionation distribution for Te and Se. Experimental results strongly suggest that the fluvial-  
559 estuarine geochemical cycles of Te and Se are not comparable in terms of reactivity, solubility and  
560 bioavailability. Further knowledge on Te speciation and sorption mechanisms is required in  
561 environmental studies.

562 The solid fractionation results suggest that anthropogenic releases of dissolved Te and Se to the  
563 aquatic environment do not fully mimic inherited element distribution among SPM mineral phases.  
564 The observed differences imply that (i) particulate  $Te_{ex}$  is potentially more bioaccessible than the  
565 already present particulate  $Te_{nat}$ , and that (ii)  $Se_{ex}$  may be more easily exchangeable and mobile during  
566 early diagenetic processes than  $Se_{nat}$ . Comparison of Se solid partitioning with results of selective  
567 extractions commonly applied to other trace elements point out to two anomalies: (i) enhanced  
568 dissolution of Se species in oxidising conditions probably due to oxidation of Se(IV) to the more  
569 soluble Se(VI) and subsequent mobilisation from other solid carrier phases (non-selectivity), and (ii)  
570 potential extraction by dissolved organic complexants in addition to release from reducible mineral  
571 phases. These findings clearly show that the use of commonly applied extraction schemes to other than  
572 originally tested target elements may produce artefacts that need thorough evaluation and must be  
573 taken into account for environmental interpretations.

574 Preliminary dispersion scenarios of hypothetical releases of Te and Se radionuclides into the  
575 Garonne-Gironde fluvial-estuarine system suggest high potential adsorption of Te radionuclides onto  
576 estuarine SPM in all hydrological conditions (flood and drought). This implies long estuarine  
577 residence times for Te radionuclides (up to several months, in accordance with the half-life and  
578 activities of the radionuclides released), and the risk of seasonal upstream movement when a  
579 hypothetical accident happens in a period when the MTZ is located downstream in the estuary. In  
580 contrast, Se radionuclides would preferentially remain in the dissolved phase continuously exported to  
581 the coastal ocean within several weeks, implying a risk of transfer to primary producers and the related  
582 food chain including seafood.

583

584 **Declarations of interest:** none

585

## 586 **Acknowledgements**

587 This study is a scientific contribution to the French National Project AMORAD (ANR-11-RSNR-  
588 0002) from the National Research Agency, allocated in the framework program “Investments for the  
589 Future”. The authors gratefully acknowledge the financial assistance of the FEDER Aquitaine-1999-  
590 Z0061, the German Academic Exchange Service DAAD and the SNF Project 200021-178784.

591

## 592 **References**

593 Aguerre, S., Frechou, C. (2006). Development of a radiochemical separation for selenium with the aim  
594 of measuring its isotope <sup>79</sup> in low and intermediate nuclear wastes by ICP-MS. *Talanta*, 69(3),  
595 565-571.

596 Allen, G. P., Salomon, J. C., Bassoullet, P., Du Penhoat, Y., De Grandpre, C. (1980). Effects of tides  
597 on mixing and suspended sediment transport in macrotidal estuaries. *Sedimentary Geology*, 26(1-  
598 3), 69-90.

599 Amouroux, D., Donard, O. F. (1997). Evasion of selenium to the atmosphere via biomethylation  
600 processes in the Gironde estuary, France. *Marine Chemistry*, 58(1-2), 173-188.

601 ANZECC and ARMCANZ (2000). Australian and New Zealand guidelines for fresh water and marine  
602 water quality. Australian and New Zealand Environment and Conservation Council/Agriculture  
603 and Resource Management Council of Australia and New Zealand, Canberra

604 Audry, S., Blanc, G., Schäfer, J. (2006). Solid state partitioning of trace metals in suspended  
605 particulate matter from a river system affected by smelting-waste drainage. *Science of the Total  
606 Environment*, 363(1-3), 216-236.

607 Asai, S., Hanzawa, Y., Okumura, K., Shinohara, N., Inagawa, J., Hotoku, S., Suzuki, K., Kaneko, S.  
608 (2011). Determination of <sup>79</sup>Se and <sup>135</sup>Cs in spent nuclear fuel for inventory estimation of high-  
609 level radioactive wastes. *Journal of Nuclear Science and Technology*, 48(5), 851-854.

610 Baeza, A., Corbacho, J. A., Rodríguez, A., Galván, J., García-Tenorio, R., Manjón, G., Mantero, J.,  
611 Vioque, I., Arnold, D., Grossi, C., Serrano, I., Vallés, I., Vargas, A. (2012). Influence of the  
612 Fukushima Dai-ichi nuclear accident on Spanish environmental radioactivity levels. *Journal of  
613 Environmental Radioactivity*, 114, 138-145.

614 Belzile, N., Chen, Y. W. (2015). Tellurium in the environment: A critical review focused on natural  
615 waters, soils, sediments and airborne particles. *Applied Geochemistry*, 63, 83-92.

616 Benoit, M. D., Kudela, R. M., Flegal, A. R. (2010). Modeled trace element concentrations and  
617 partitioning in the San Francisco estuary, based on suspended solids concentration. *Environmental  
618 Science and Technology*, 44(15), 5956-5963.

619 Biver, M., Quentel, F., Filella, M. (2015). Direct determination of tellurium and its redox speciation at  
620 the low nanogram level in natural waters by catalytic cathodic stripping voltammetry. *Talanta*, 144,  
621 1007-1013.

- 622 Bizsel, N., Ardelan, M. V., Bizsel, K. C., Suzal, A., Demirdag, A., Sarıca, D. Y., Steinnes, E. (2017).  
623 Distribution of selenium in the plume of the Gediz River, Izmir Bay, Aegean Sea. *Journal of*  
624 *Marine Research*, 75(2), 81-98.
- 625 Bordas, F., Bourg, A. C. (1998). A critical evaluation of sample pretreatment for storage of  
626 contaminated sediments to be investigated for the potential mobility of their heavy metal load.  
627 *Water, Air, and Soil Pollution*, 103(1-4), 137-149.
- 628 Buesseler, K., Dai, M., Aoyama, M., Benitez-Nelson, C., Charmasson, S., Higley, K., Maderich, V.,  
629 Masqué, P., Morris, P.J., Oughton, D., Smith, J. N. (2017). Fukushima Daiichi-derived  
630 radionuclides in the ocean: transport, fate, and impacts. *Annual Review of Marine Science*, 9, 173-  
631 203.
- 632 Castaing, P., Allen, G. P. (1981). Mechanisms controlling seaward escape of suspended sediment from  
633 the Gironde: a macrotidal estuary in France. *Marine Geology*, 40(1-2), 101-118.
- 634 Castaing, P., Jouanneau, J. M. (1979). Temps de résidence des eaux et des suspensions dans l'estuaire  
635 de la Gironde. *Journal Recherche Océanographie IV*, 41-52.
- 636 Chasteen, T. G., Bentley, R. (2003). Biomethylation of selenium and tellurium: microorganisms and  
637 plants. *Chemical Reviews*, 103(1), 1-26.
- 638 Ciceri, G., Traversi, A.L., Martinotti, W., Queirazza, G. (1988). Radionuclide partitioning between  
639 water and suspended matter: comparison of different methodologies. *Studies in Environmental*  
640 *Science*, 34, 353-375.
- 641 Ciffroy, P., Durrieu, G., Garnier, J. M. (2009). Probabilistic distribution coefficients (K<sub>d</sub>) in  
642 freshwater for radioisotopes of Ag, Am, Ba, Be, Ce, Co, Cs, I, Mn, Pu, Ra, Ru, Sb, Sr and Th—  
643 implications for uncertainty analysis of models simulating the transport of radionuclides in rivers.  
644 *Journal of Environmental Radioactivity*, 100(9), 785-794.
- 645 Cooke, T. D., Bruland, K. W. (1987). Aquatic chemistry of selenium: evidence of biomethylation.  
646 *Environmental Science and Technology*, 21(12), 1214-1219.
- 647 Coynel, A., Gorse, L., Curti, C., Schafer, J., Grosbois, C., Morelli, G., Ducassou, E., Blanc, G.,  
648 Maillet, G.M., Mojtahid, M. (2016). Spatial distribution of trace elements in the surface sediments  
649 of a major European estuary (Loire Estuary, France): Source identification and evaluation of  
650 anthropogenic contribution. *Journal of Sea Research*, 118, 77-91.
- 651 Cutter, G. A. (1978). Species determination of selenium in natural waters. *Analytica Chimica Acta*,  
652 98(1), 59-66.
- 653 Cutter, G. A. (1989). The estuarine behaviour of selenium in San Francisco Bay. *Estuarine, Coastal*  
654 *and Shelf Science*, 28(1), 13-34.
- 655 Cutter, G. A., Bruland, K. W. (1984). The marine biogeochemistry of selenium: A re-evaluation.  
656 *Limnology and Oceanography*, 29(6), 1179-1192.
- 657 Cutter, G. A., Cutter, L. S. (1995). Behavior of dissolved antimony, arsenic, and selenium in the  
658 Atlantic Ocean. *Marine Chemistry*, 49(4), 295-306.
- 659 Duan, L. Q., Song, J. M., Yuan, H. M., Li, X. G., Li, N., Ma, J. K. (2014). Distribution, chemical  
660 speciation and source of trace elements in surface sediments of the Changjiang Estuary.  
661 *Environmental Earth Sciences*, 72(8), 3193-3204.

- 662 Edwards, J.O., Abbott, J.R., Ellison, H.R. and Nyberg, J. (1959). Coördination Number Changes  
663 during Oxidation-Reduction Reactions of Oxyanions. The Kinetics of the Aniline Nitrosation and  
664 of the Glycol–Tellurate Reaction. *The Journal of Physical Chemistry*, 63(3), 359-365.
- 665 Element Collection Inc.: Gray, T., Mann, N., Whitby, M. (2007). Periodic Table of Isotopes.  
666 <http://periodictable.com/Isotopes/051.123/index.p.full.html> (accessed on the 10 March 2015)
- 667 Etcheber, H., Taillez, A., Abril, G., Garnier, J., Servais, P., Moatar, F., Commarieu, M. V. (2007).  
668 Particulate organic carbon in the estuarine turbidity maxima of the Gironde, Loire and Seine  
669 estuaries: origin and lability. *Hydrobiologia*, 588(1), 245-259.
- 670 Fernández-Martínez, A., Charlet, L. (2009). Selenium environmental cycling and bioavailability: a  
671 structural chemist point of view. *Reviews in Environmental Science and Bio/Technology*, 8(1), 81-  
672 110.
- 673 Filella, M. (2013). Food for thought: a critical overview of current practical and conceptual challenges  
674 in trace element analysis in natural waters. *Water*, 5(3), 1152-1171.
- 675 Filella, M., Rodushkin, I. (2018). A concise guide for the determination of less-studied technology-  
676 critical elements (Nb, Ta, Ga, In, Ge, Te) by inductively coupled plasma mass spectrometry in  
677 environmental samples. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 141, 80-84.
- 678 Foo, K. Y., Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems.  
679 *Chemical Engineering Journal*, 156(1), 2-10.
- 680 Freundlich, H. (1907). Über die adsorption in lösungen. *Zeitschrift für physikalische Chemie*, 57(1),  
681 385-470. [Over the adsorption in solution, *Journal of Physical Chemistry*, 57, 385–471.]
- 682 Froelich, P., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin,  
683 P., Hammond, D., Hartman, B., Maynard, V. (1979). Early oxidation of organic matter in pelagic  
684 sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica*  
685 *Acta*, 43(7), 1075-1090.
- 686 Gasparon, M., Matschullat, J. (2006). Trace metals in Antarctic ecosystems: results from the  
687 Larsemann Hills, East Antarctica. *Applied Geochemistry*, 21(9), 1593-1612.
- 688 Gil-Díaz, T., Schäfer, J., Coynel, A., Bossy, C., Dutruch, L., Blanc, G. (2018). Antimony in the Lot–  
689 Garonne river system: a 14-year record of solid–liquid partitioning and fluxes. *Environmental*  
690 *Chemistry*. DOI: 10.1071/EN17188
- 691 Gil-Díaz, T., Schäfer, J., Dutruch, L., Bossy, C., Pougnet, F., Abdou, M., Lerat-Hardy, A., Pereto, C.,  
692 Derriennic, H., Briant, N., Sireau, T., Knoery, J., Blanc, G. (2019a). Tellurium behaviour in a  
693 major European fluvial-estuarine system (Gironde, France): fluxes, solid/liquid partitioning, and  
694 bioaccumulation in wild oysters. *Environmental Chemistry*. DOI: 10.1071/EN18226
- 695 Gil-Díaz, T., Schäfer, J., Filella, M., Dutruch, L., Bossy, C. (2019b). Fractionation of inherited and  
696 spiked antimony (Sb) in fluvial/estuarine bulk sediments: Unexpected anomalies in parallel  
697 selective extraction protocols. *Applied Geochemistry*, 108, 104386 (DOI:  
698 10.1016/j.apgeochem.2019.104386)
- 699 Gruebel, K. A., Leckie, J. O., Davis, J. A. (1988). The feasibility of using sequential extraction  
700 techniques for arsenic and selenium in soils and sediments. *Soil Science Society of America*  
701 *Journal*, 52(2), 390-397.
- 702 Guan, D. M., Martin, J. M. (1991). Selenium distribution in the Rhone delta and the Gulf of Lions.  
703 *Marine Chemistry*, 36(1-4), 303-316

- 704 Gupta, S. K., Chen, K. Y. (1975). Partitioning of trace metals in selective chemical fractions of  
705 nearshore sediments. *Environmental Letters*, 10(2), 129-158.
- 706 Hamed, M. M., Holiel, M., El-Aryan, Y. F. (2017). Removal of selenium and iodine radionuclides  
707 from waste solutions using synthetic inorganic ion exchanger. *Journal of Molecular Liquids*, 242,  
708 722-731.
- 709 Hamdy, A. A., Gissel-Nielsen, G. (1977). Fixation of selenium by clay minerals and iron oxides.  
710 *Zeitschrift für Pflanzenernährung und Bodenkunde*, 140(1), 63-70.
- 711 Harada, T., Takahashi, Y. (2009). Origin of the difference in the distribution behavior of tellurium and  
712 selenium in a soil–water system. *Geochimica et Cosmochimica Acta*, 72(5), 1281-1294.
- 713 Hayes, K. F., Roe, A. L., Brown, G. E., Hodgson, K. O., Leckie, J. O., Parks, G. A. (1987). In situ X-  
714 ray absorption study of surface complexes: Selenium oxyanions on  $\alpha$ -FeOOH. *Science*, 238(4828),  
715 783-786.
- 716 Horner, H. J., Leonard Jr, G. W. (1952). Preparation of Telluric Acid. *Journal of the American*  
717 *Chemical Society*, 74(14), 3694-3694.
- 718 Huerta-Díaz, M. A., Morse, J. W. (1990). A quantitative method for determination of trace metal  
719 concentrations in sedimentary pyrite. *Marine Chemistry*, 29, 119-144.
- 720 Inorganic Ventures (2016). <https://www.inorganicventures.com> (accessed on the 28 July 2018).  
721 Ishikawa, T. (2014). A brief review of dose estimation studies conducted after the Fukushima  
722 Daiichi Nuclear Power Plant accident. *Radiation Emergency Medicine*, 3, 21-27.
- 723 Izrael, Y.A. (2002). *Radioactive fallout after nuclear explosions and accidents*. Elsevier, Saint  
724 Louis. Kersten, M., Förstner, U. (1987). Cadmium associations in freshwater and marine sediment,  
725 in: Nriagu, J.O., Sprague, J.B. (Eds.), *Cadmium in the Aquatic Environment*, John Wiley & Sons,  
726 Inc., pp. 51-88.
- 727 Kleykamp, H. (1985). The chemical state of the fission products in oxide fuels. *Journal of Nuclear*  
728 *Materials*, 131(2-3), 221-246.
- 729 Kostka, J. E., Luther III, G. W. (1994). Partitioning and speciation of solid phase iron in saltmarsh  
730 sediments. *Geochimica et Cosmochimica Acta*, 58(7), 1701-1710.
- 731 Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of*  
732 *the American Chemical Society*, 40(9), 1361-1403.
- 733 Lenz, M., Hullebusch, E. D. V., Farges, F., Nikitenko, S., Borca, C. N., Grolimund, D., Lens, P. N.  
734 (2008). Selenium speciation assessed by X-ray absorption spectroscopy of sequentially extracted  
735 anaerobic biofilms. *Environmental Science and Technology*, 42(20), 7587-7593.
- 736 Leppänen, A. P., Mattila, A., Kettunen, M., Kontro, R. (2013). Artificial radionuclides in surface air in  
737 Finland following the Fukushima Dai-ichi nuclear power plant accident. *Journal of Environmental*  
738 *Radioactivity*, 126, 273-283.
- 739 Lee, D. S., Edmond, J. M. (1985). Tellurium species in seawater. *Nature*, 313(6005), 782.
- 740 Luxem, K. E., Vriens, B., Wagner, B., Behra, R., Winkel, L. H. (2015, April). Selenium uptake and  
741 volatilization by marine algae. In *EGU General Assembly Conference Abstracts (Vol. 17)*.
- 742 Ma, Y., Uren, N.C., (1995). Application of a new fractionation scheme for heavy metals in soils.  
743 *Communications in Soil Science and Plant Analysis*, 26, 3291-3303.

- 744 Measures, C. I., Burton, J. D. (1978). Behaviour and speciation of dissolved selenium in estuarine  
745 waters. *Nature*, 273(5660), 293.
- 746 Morewitz, H. A. (1981). Fission product and aerosol behavior following degraded core accidents.  
747 *Nuclear Technology*, 53(2), 120-134.
- 748 Nothstein, A. K. (2016). Selenium Transfer between Kaolinite or Goethite Surfaces, Nutrient Solution  
749 and *Oryza Sativa* (Vol. 41). KIT Scientific Publishing.
- 750 Oughton, D. H., Børretzen, P., Salbu, B., Tronstad, E. (1997). Mobilisation of <sup>137</sup>Cs and <sup>90</sup>Sr from  
751 sediments: potential sources to arctic waters. *Science of the Total Environment*, 202(1-3), 155-165.
- 752 Peak, D., Sparks, D. L. (2002). Mechanisms of selenate adsorption on iron oxides and hydroxides.  
753 *Environmental Science and Technology*, 36(7), 1460-1466.
- 754 Qin, H.-B, Takeichi, Y., Nitani, H., Terada, Y., Takahashi, Y. (2017). Tellurium distribution and  
755 speciation in contaminated soils from abandoned mine tailings: comparison with selenium.  
756 *Environmental Science and Technology*, 51(11), 6027-6035.
- 757 Raiswell, R., Canfield, D.E., Berner, R.A., (1994). A comparison of iron extraction methods for the  
758 determination of degree of pyritization and the recognition of iron-limited pyrite formation.  
759 *Chemical Geology*, 111, 101-110.
- 760 Robati, D. (2013). Pseudo-second-order kinetic equations for modeling adsorption systems for  
761 removal of lead ions using multi-walled carbon nanotube. *Journal of Nanostructure in Chemistry*,  
762 3(1), 55.
- 763 Robert, S., Blanc, G., Schäfer, J., Lavaux, G., Abril, G. (2004). Metal mobilization in the Gironde  
764 Estuary (France): the role of the soft mud layer in the maximum turbidity zone. *Marine Chemistry*,  
765 87(1-2), 1-13.
- 766 Saegusa, J., Kikuta, Y., Akino, H. (2013). Observation of gamma-rays from fallout collected at  
767 Ibaraki, Japan, during the Fukushima nuclear accident. *Applied Radiation and Isotopes*, 77, 56-60.
- 768 Schäfer, J., Blanc, G., Lapaquellerie, Y., Maillet, N., Maneux, E., Etcheber, H. (2002). Ten-year  
769 observation of the Gironde tributary fluvial system: fluxes of suspended matter, particulate organic  
770 carbon and cadmium. *Marine Chemistry*, 79, 229-242.
- 771 Sonzogni, A.A. (2013). Chart of Nuclides NuDat 2.6 - National Nuclear Data Center. Brookhaven  
772 National Laboratory. <http://www.nndc.bnl.gov/nudat2/reCenter.jsp?z=51&n=68> (accessed on the  
773 10 March 2015).
- 774 Sottolichio, A., Castaing, P. (1999). A synthesis on seasonal dynamics of highly-concentrated  
775 structures in the Gironde estuary. *Comptes Rendus de l'Académie des Sciences-Series IIA-Earth  
776 and Planetary Science*, 329(11), 795-800.
- 777 Steinhauser, G., Brandl, A., Johnson, T.E. (2014). Comparison of the Chernobyl and Fukushima  
778 nuclear accidents: A review of the environmental impacts. *Science of the Total Environment*, 470-  
779 471, 800-817.
- 780 Su, C., Suarez, D. L. (2000). Selenate and selenite sorption on iron oxides an infrared and  
781 electrophoretic study. *Soil Science Society of America Journal*, 64(1), 101-111.
- 782 Sung, W. (1995). Some observations on surface partitioning of Cd, Cu and Zn in estuaries.  
783 *Environmental Science and Technology*, 29, 1303.

- 784 Tan, L. C., Nancharaiah, Y. V., van Hullebusch, E. D., Lens, P. N. (2016). Selenium: environmental  
785 significance, pollution, and biological treatment technologies. *Biotechnology Advances*, 34(5),  
786 886-907.
- 787 Takata, H., Aono, T., Tagami, K., Uchida, S. (2016). A new approach to evaluate factors controlling  
788 elemental sediment–seawater distribution coefficients ( $K_d$ ) in coastal regions, Japan. *Science of the*  
789 *Total Environment*, 543, 315-325.
- 790 Tessier, A., Campbell, P. G., Bisson, M. (1979). Sequential extraction procedure for the speciation of  
791 particulate trace metals. *Analytical Chemistry*, 51(7), 844-851.
- 792 Ure, A. M., Quevauviller, P., Muntau, H., Griepink, B. (1993). Speciation of heavy metals in soils and  
793 sediments. An account of the improvement and harmonization of extraction techniques undertaken  
794 under the auspices of the BCR of the Commission of the European Communities. *International*  
795 *Journal of Environmental Analytical Chemistry*, 51(1-4), 135-151.
- 796 Van Dael, P., Lewis, J. and Barclay, D. (2004). Stable isotope-enriched selenite and selenate tracers  
797 for human metabolic studies: a fast and accurate method for their preparation from elemental  
798 selenium and their identification and quantification using hydride generation atomic absorption  
799 spectrometry. *Journal of Trace Elements in Medicine and Biology*, 18(1), 75-80.
- 800 Weber, T. W., Chakravorti, R. K. (1974). Pore and solid diffusion models for fixed-bed adsorbers.  
801 *American Institute of Chemical Engineers Journal*, 20(2), 228-238.
- 802 Whitehead, N. E., Ballestra, S., Holm, E., Huynh-Ngoc, L. (1988). Chernobyl radionuclides in  
803 shellfish. *Journal of Environmental Radioactivity*, 7(2), 107-121.
- 804 Winkel, L. H. (2016). The global biogeochemical cycle of selenium: Sources, fluxes and the influence  
805 of climate. In *Global Advances in Selenium Research from Theory to Application: Proceedings of*  
806 *the 4th International Conference on Selenium in the Environment and Human Health* (pp. 3-4).  
807 CRC Press/Balkema.
- 808 Wu, X., Song, J., Li, X. (2014). Occurrence and distribution of dissolved tellurium in Changjiang  
809 River estuary. *Chinese Journal of Oceanology and Limnology*, 32(2), 444-454.
- 810 Yoon, B. M., Shim, S. C., Pyun, H. C., Lee, D. S. (1990). Hydride generation atomic absorption  
811 determination of tellurium species in environmental samples with in situ concentration in a graphite  
812 furnace. *Analytical Sciences*, 6(4), 561-566.
- 813 Zeldowitsch, J. (1934). Adsorption site energy distribution. *Acta Physicochimica URSS*, 1, 961-973.
- 814

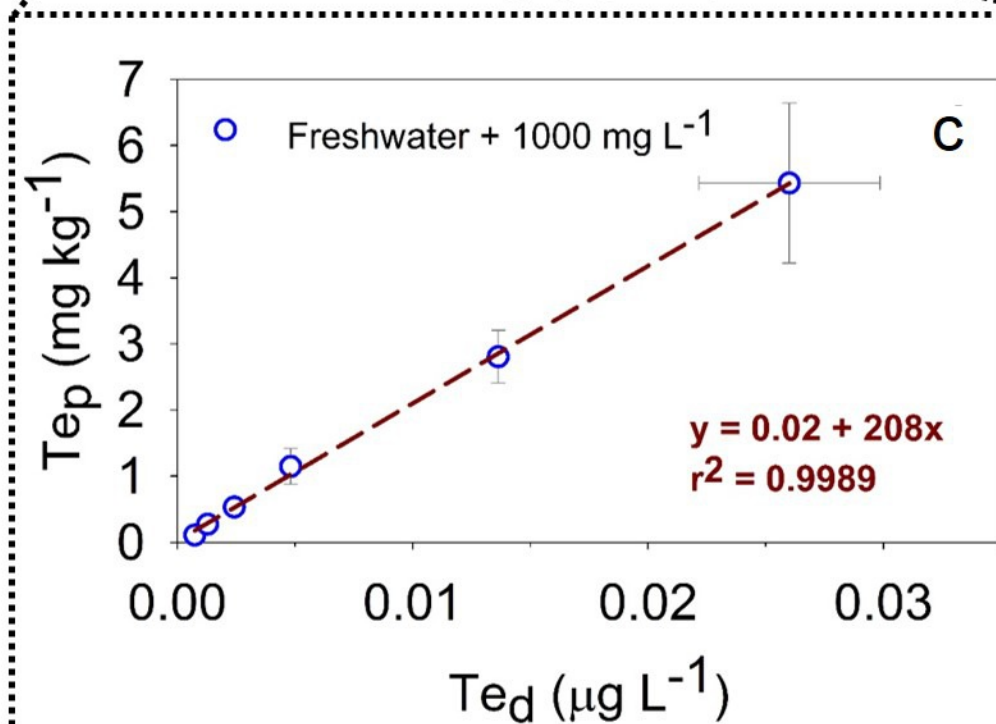
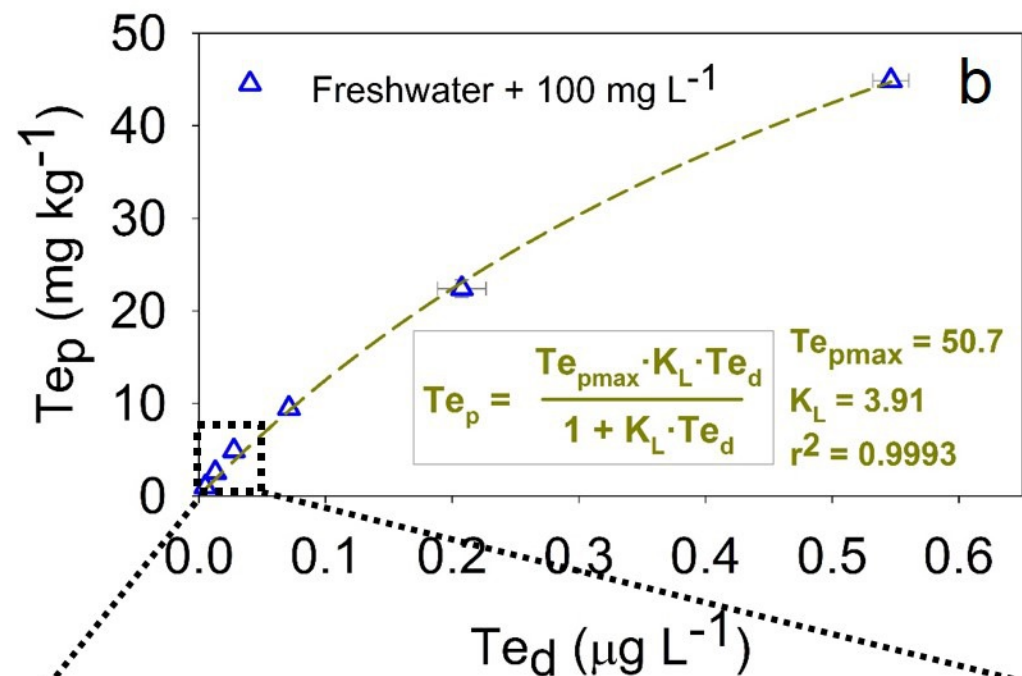
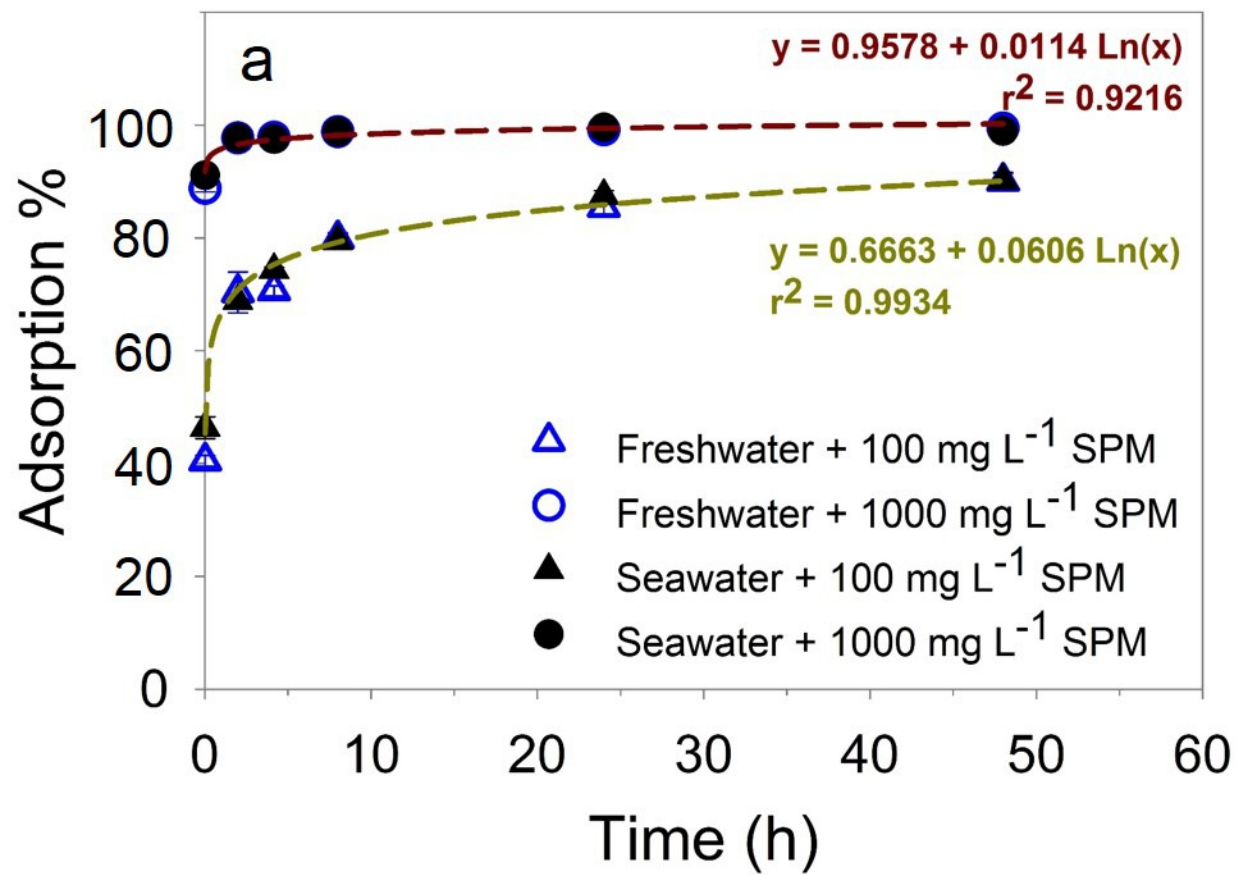


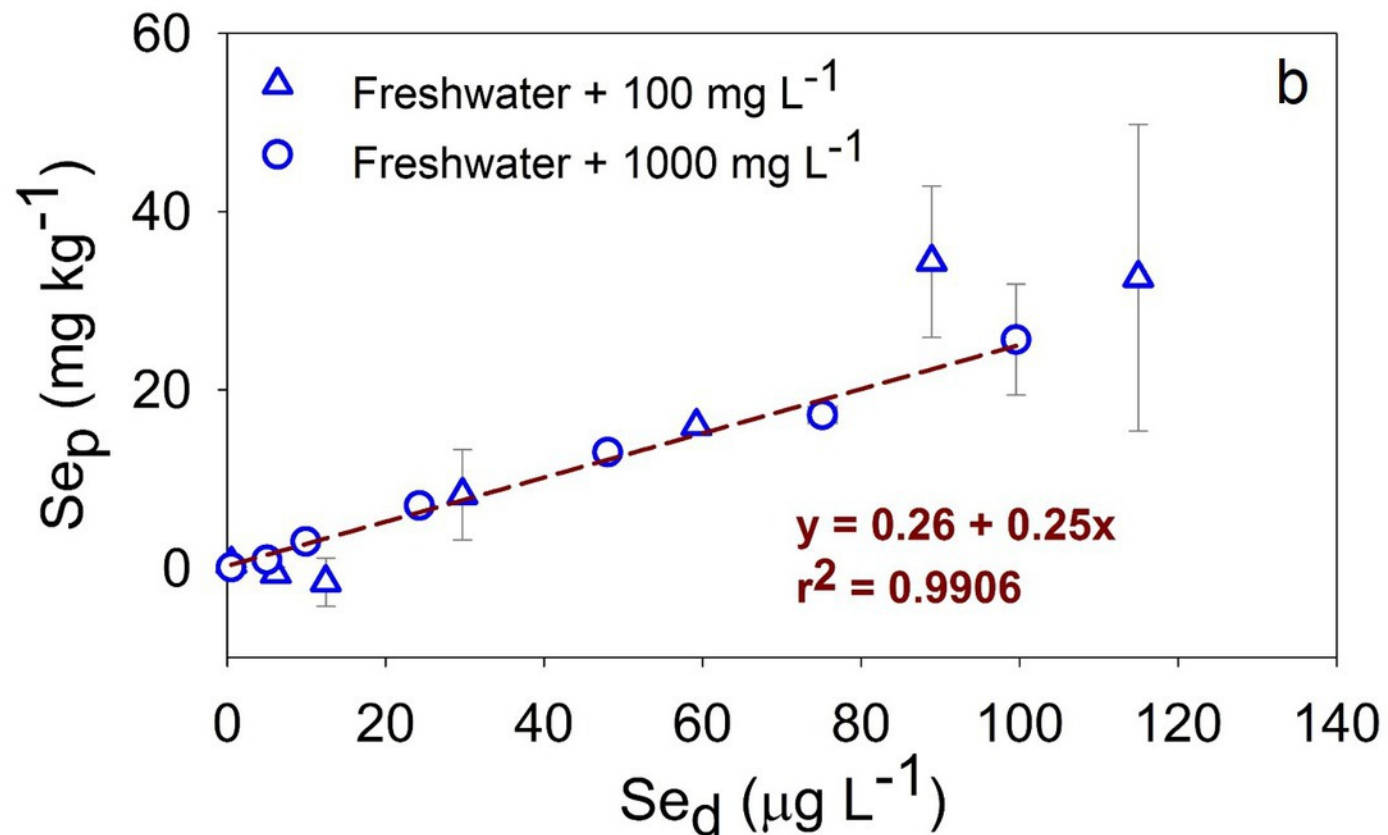
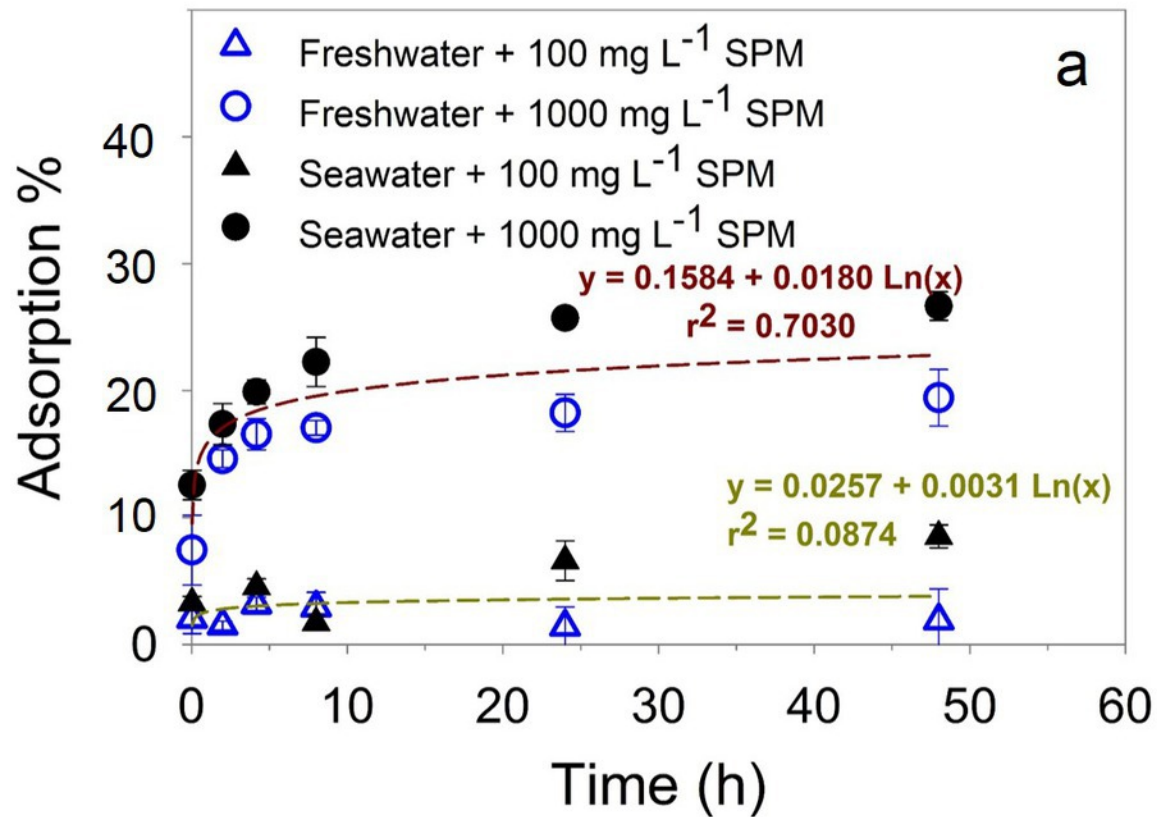
### Figure captions:

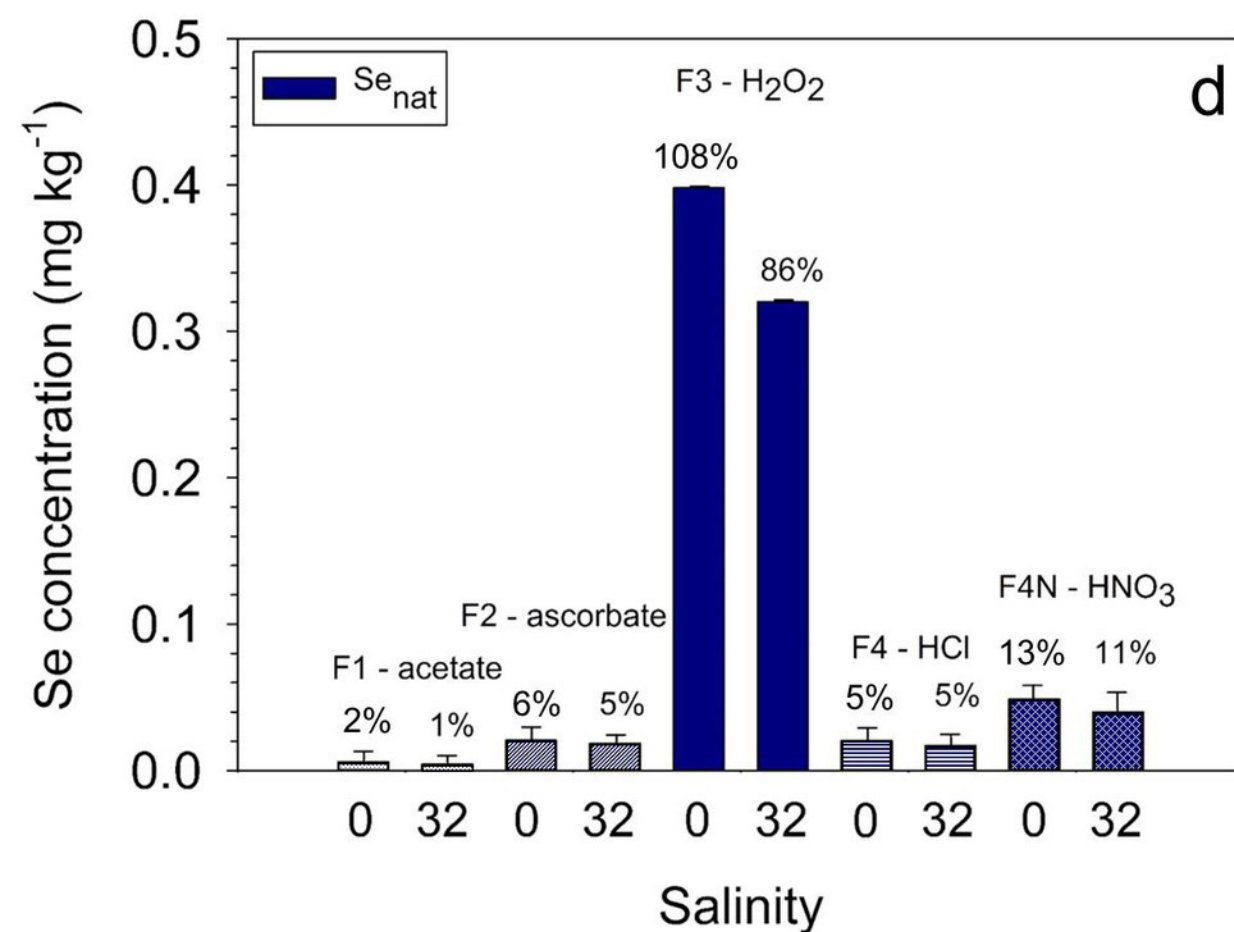
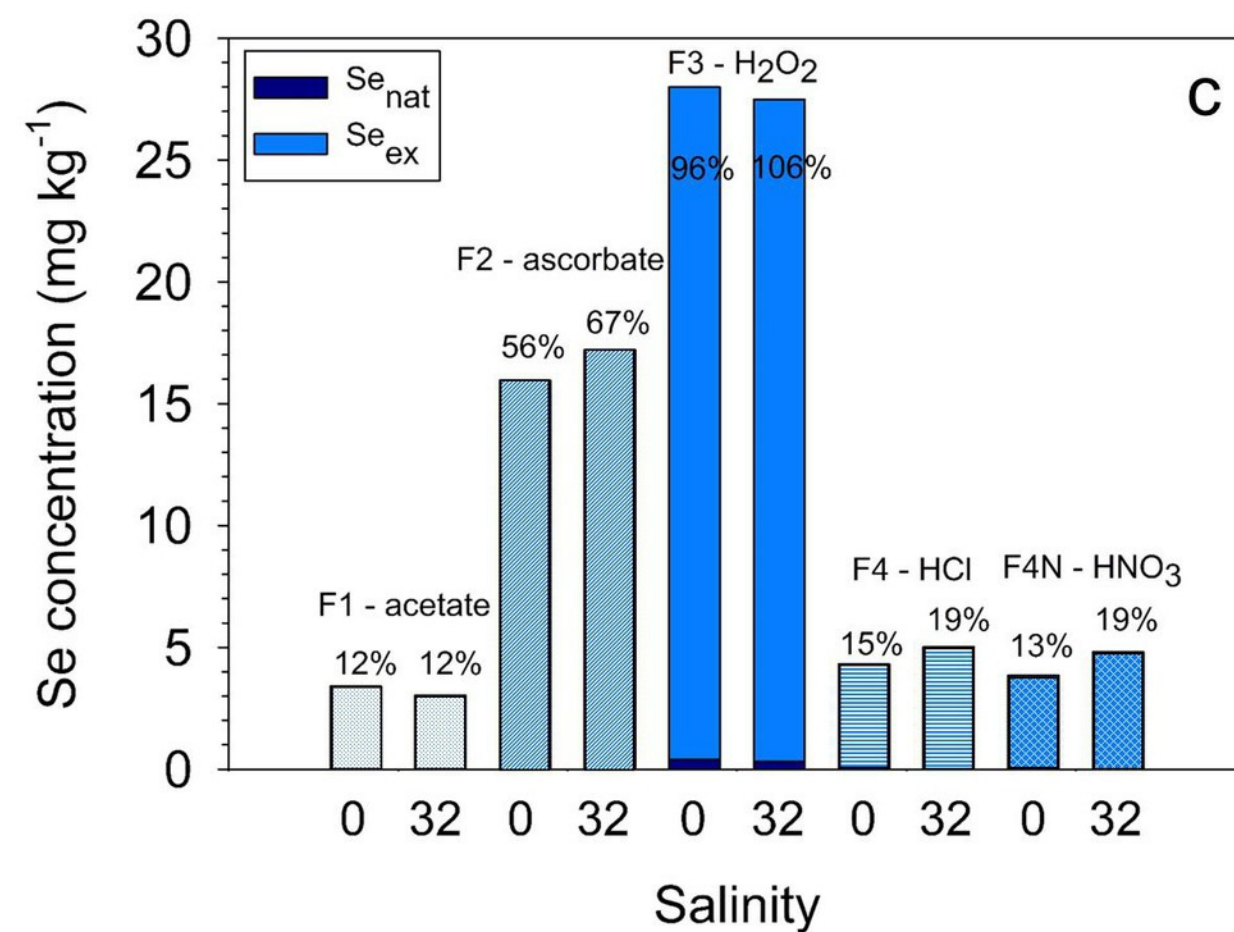
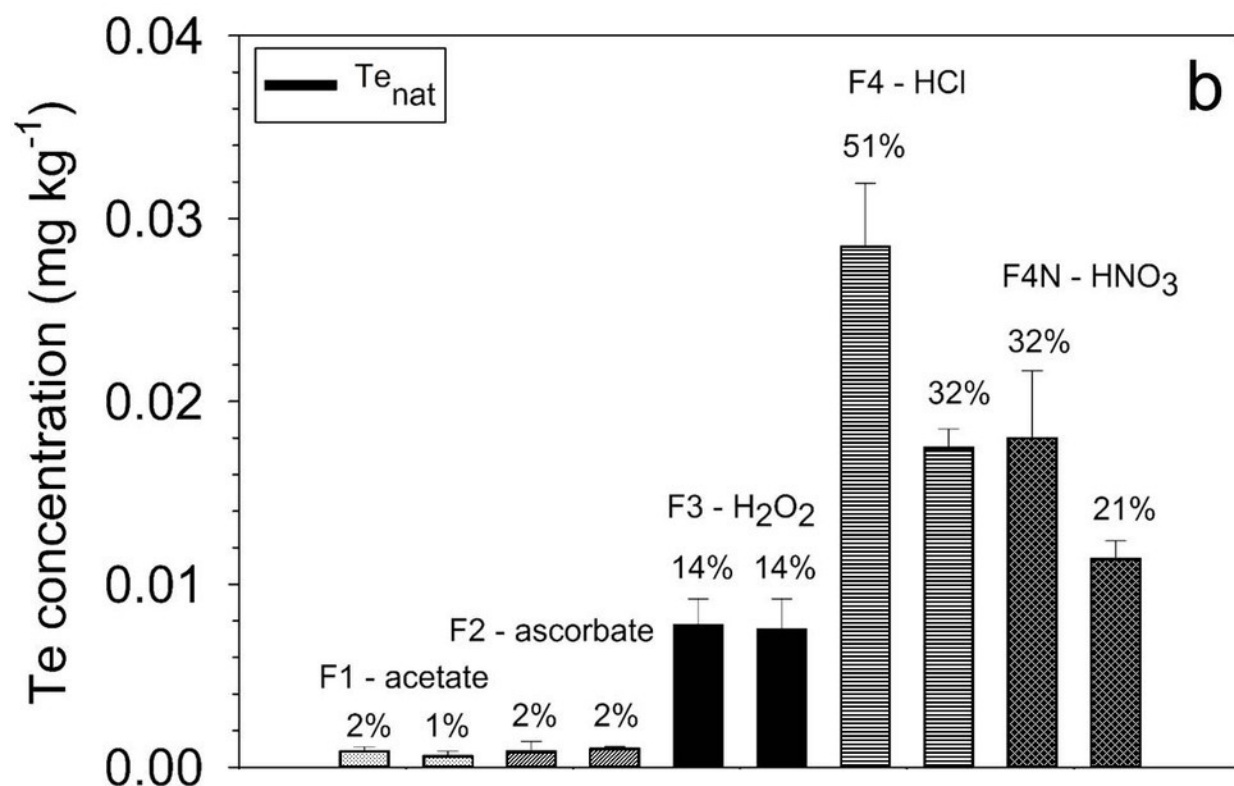
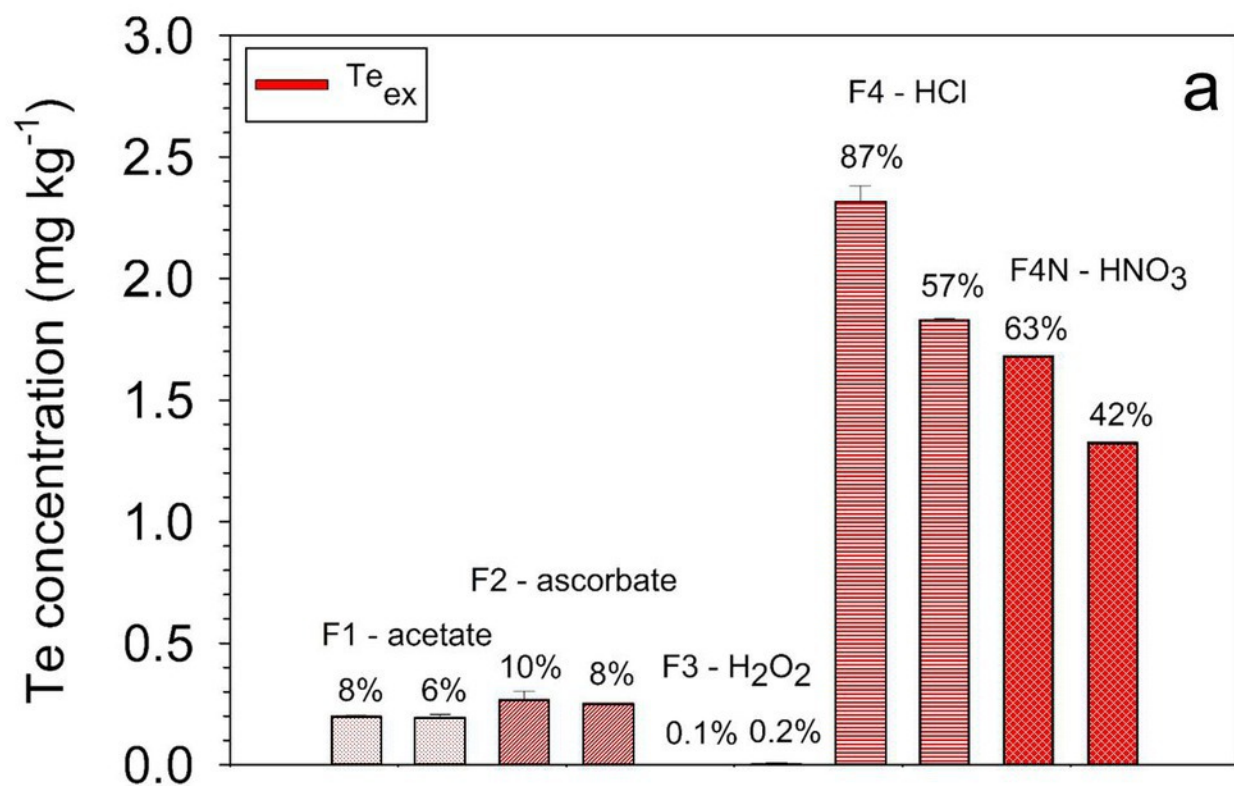
**Figure 1. Sorption of tellurium in natural SPM.** (a) Te sorption kinetics (N=3) in freshwater (empty symbols) and seawater (filled symbols) matrices for 100 mg L<sup>-1</sup> (triangles) and 1000 mg L<sup>-1</sup> (circles) SPM content. Adsorption percentages are calculated as the difference between initial spiking concentration and Te<sub>d</sub> at each sampling time. Tellurium isotherms (N=2, after 48h equilibration) for (b) freshwater sorption in 100 mg L<sup>-1</sup> and (c) 1000 mg L<sup>-1</sup> SPM content, are also shown. Curves and equations correspond to respective fitting regressions. Error bars correspond to standard deviations (SD).

**Figure 2. Sorption of selenium in natural SPM.** (a) Se sorption kinetics (N=3) in freshwater (empty symbols) and seawater (filled symbols) matrices for 100 mg L<sup>-1</sup> and 1000 mg L<sup>-1</sup> SPM content as well as (b) selenium freshwater sorption isotherms (N=2, after 48h equilibration) in 100 mg L<sup>-1</sup> (triangles) and 1000 mg L<sup>-1</sup> (circles) SPM content. Adsorption percentages are calculated as the difference between initial spiking concentration and Se<sub>d</sub> at each sampling time. Curves and equations correspond to respective fitting regressions. Error bars correspond to standard deviations (SD).

**Figure 3. Parallel selective extractions of Te and Se.** (a) Distribution of natural Te (Te<sub>nat</sub>, N=3), (b) spiked Te (Te<sub>ex</sub>, N=3), (c) natural Se (Se<sub>nat</sub>, N=3) and (d) spiked Se (Te<sub>ex</sub>, N=1) in selective extractions after sorption in freshwater (S=0) and seawater (S=32) conditions. Targeted parallel operationally-defined solid-phase fractions were: F1 – easily exchangeable and/or carbonate fraction (acetate extraction), F2 – reducible Fe/Mn oxides (ascorbate extraction), F3 – oxidisable fraction (H<sub>2</sub>O<sub>2</sub> extraction) and F4 – reactive and potentially bioaccessible fraction (HCl 1 M extraction as F4 and HNO<sub>3</sub> 1M extraction as F4N). Percentages represent the extracted concentration in each fraction compared to total particulate concentration. Error bars correspond to standard deviations (SD).







**Table 1:** Parallel selective extractions as described in Audry et al. (2006).

| <b>Sediment fraction</b>  | <b>Sample weight (mg)</b> | <b>Reagents</b>  | <b>Procedure</b>                           |
|---|---------------------------|--|--|
| F1 – Acetate extraction<br><br>(easily exchangeable and/or carbonate fraction = carbonates + Mn oxyhydroxydes + sulphates + organic matter)   | 500                       | 10 ml of sodium acetate (NaOAc, 1 M) + pH adjustment with acetic acid (HOAc, 5 M) during extraction                                    | 6 h shaking at 25°C                        |
| F2 – Ascorbate extraction<br><br>(reducible Fe/Mn oxides = Mn oxides and amorphous Fe oxides)   | 200                       | 12.5 ml ascorbate solution (pH = 8)  | 24 h shaking at 25°C                       |
| F3 – H <sub>2</sub> O <sub>2</sub> extraction<br><br>(oxidisable fraction = organic matter and labile/amorphous sulphides)  | 500                       | 2.5 ml H <sub>2</sub> O <sub>2</sub> 30% (at pH 5 with NaOH) + 1.5 ml H <sub>2</sub> O <sub>2</sub> 30% + 2.5 ml ammonium acetate (1M) | 2 h + 3 h at 85°C + 30 min shaking at 25°C |
| F4 – acid soluble HCl extraction<br><br>( <i>and complementary F4N – HNO<sub>3</sub> extraction</i> )<br><br>(reactive and potentially bioaccessible = amorphous and crystalline Fe/Mn oxides + carbonate fractions + amorphous monosulphurs + phyllosilicates) | 200                       | 12.5 ml HCl or HNO <sub>3</sub> (Suprapur®, 1 M)   | 24 h shaking at 25°C                       |