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1 **Tellurium and selenium sorption kinetics and solid fractionation under** 2 **contrasting estuarine salinity and turbidity conditions**

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11

12 **Abstract**

13 Tellurium (Te) is a Technology Critical Element (TCE) and a relevant product of nuclear fission. It
14 has an unknown environmental biogeochemical cycle, mostly related to current analytical challenges
15 in measuring its ultra-trace dissolved concentrations in complex environmental matrices. It is therefore
16 generally compared to its geochemical pair selenium (Se), which shows a narrow range between diet
17 essentiality and toxicity properties. Batch experiments using isotopically-labelled stable Te and Se
18 were performed with fresh suspended particulate matter (SPM) from the fluvial part of the Gironde
19 Estuary, simulating both estuarine salinity (S=0 vs S=32) and turbidity (100 mg L⁻¹ vs 1000 mg L⁻¹)
20 gradients to understand the importance of the particulate phases in Te reactivity under estuarine
21 conditions and verify the resemblance to Se behaviour. These experiments addressed sorption kinetics,
22 sorption isotherms and fractionation from selective extractions of final equilibrated SPM. Results
23 showed a strong, salinity-independent affinity of Te for the particulate phases (log₁₀ K_d ~ 4.9 L kg⁻¹),
24 following a Langmuir-type isotherm. Contrastingly, Se adsorbs clearly less to estuarine SPM (log₁₀ K_d
25 ~ 2.5 L kg⁻¹), following a Freundlich-type isotherm. Both isotherms and selective extractions
26 highlighted differences between Te and Se sequestration. Selective extractions suggested higher
27 mobility of particulate Se in contrast to Te. Based on these results the paper sets a first dispersion
28 scenario on the environmental fate of radioactive Te and Se after hypothetical nuclear power plant
29 accidental releases in coastal aquatic systems such as the Garonne-Gironde fluvial-estuarine system.

30

31 *Keywords:* technology critical elements, isotherms, selective extractions, distribution coefficient (K_d),
32 Te environmental cycle, radionuclide releases

33

34 **1. Introduction**

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}Pu - and ^{235}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37 compared to ~11% for Cs and ~10% for I radionuclides (unpublished data calculated from Element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}Te half-life of 3.2 days) produced important
45 atmospheric radioactive emissions (^{132}Te : ~1150 PBq at CNPP and ~180 PBq at FDNPP) comparable
46 to ^{137}Cs and ^{131}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}Te activities in the dissolved (0.13 Bq L^{-1}) and particulate (1.18 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}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⁻¹ and 1000 mg L⁻¹ 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 ¹²⁵Te (99.89% purity; Cortecnet, France)
93 and ⁷⁷Se (99.20% purity; Cortecnet, France) in HCl (2% Suprapur®, Merck) and HNO₃ (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 H₂O₂ (30 µL L⁻¹ 30% J.T. Baker
97 ultrapure) in the different water matrices to favour the oxidation state of ¹²⁵Te(VI) and ⁷⁷Se(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⁻¹ of ¹²⁵Te(VI) and 100 µg
103 L⁻¹ of ⁷⁷Se(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 48h ($N=3$). 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}Te
112 and ^{77}Se potential losses onto PP walls over time.

113 Adsorption isotherms were performed for two SPM concentrations (100 mg L^{-1} and 1000 mg L^{-1})
114 with initial concentrations of dissolved ^{125}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}Se of $0.5, 5, 10, 25, 50, 75, 100\text{ }\mu\text{g L}^{-1}$ ($N=2$) and sampled after 48h . 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 (Te_d) and dissolved Se (Se_d) were
119 monitored. Particulate concentrations were only determined for isotherm experiments using freshwater
120 slurries with 1000 mg L^{-1} SPM for mass balance calculations. In all cases, the dissolved phase was
121 separated from the particulate phase by centrifugation (10 min at 4000 rpm ; Hettich Rotofix 32A
122 centrifuge) and filtered ($0.2\text{ }\mu\text{m}$ Minisart® cellulose acetate) into acid-washed PP 15 mL tubes. These
123 were then acidified with HNO_3 ($1/1000\text{ v/v}$; J.T. Baker ultrapure, 14 M) and stored at 4°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 48h in spiked solutions of nominal $10\text{ }\mu\text{g L}^{-1}$ of ^{125}Te and $100\text{ }\mu\text{g L}^{-1}$ of ^{77}Se . All
129 sediments were recovered by centrifugation (Hettich ROTOFIX 32A), oven dried (70°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 (H_2O_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 HNO₃ 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 H₂O₂ (p.a. grade). High Te
142 contamination of ~35 µg L⁻¹ was observed in the extraction blanks of F3 potentially from the H₂O₂
143 solution or the added ammonium acetate. This contamination is suspected to have been adsorbed into
144 other than H₂O₂-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 (HNO₃ 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_p) and particulate
151 Se (Se_p). Mineralisation of sediment for Te analysis was achieved using a tri-acid digestion with
152 HNO₃ + HCl + HF as described elsewhere (e.g., Schäfer et al. 2002). Briefly, samples of 30 mg were
153 digested in closed PP tubes (DigiTUBE[®], SCP Science) on a heating block (2 h at 110 °C) using 750
154 µL HNO₃ (14 M Suprapur[®], Merck), 1.5 mL HCl (10 M Suprapur[®], Merck) and 2.5 mL HF (29 M
155 Suprapur[®], Fisher). After an evaporation step at 120°C, re-dissolution of the samples was performed
156 with 250 µL HNO₃ (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_p (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 HNO₃ (sub-boiled acid-distilled 65%, p.a. grade, VWR
162 Chemicals), 0.5 mL H₂O₂ (30% Rotipuran[®], Carl Roth), 0.25 mL HF (40% Suprapur[®], Merck KGAA
163 Darmstadt) and 0.5 mL ultrapure Milli-Q water were added. The temperature program was: 18°C min⁻¹
164 to 75°C, followed by 7°C min⁻¹ to 110°C, then 8°C min⁻¹ to 150°C and 6°C min⁻¹ 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 HNO₃ (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% HNO₃ (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}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 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 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}Rh as internal standard to correct for matrix effects. Tellurium was measured in oxygen-shift mode
183 using 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 Te_p
187 concentrations ($\sim 0.04 \text{ mg kg}^{-1}$), natural/inherited Te (Te_{nat}) was quantified from ^{126}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}Xe from analytical blanks
190 ($2\% \text{ HNO}_3$). Spiked/experimental ^{125}Te (Te_{ex}) was determined by TQ ICP-MS in mass-shift 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 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 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}Te spike effect). In
196 selective extractions, Te_{nat} concentrations ranged from 5-fold (in F2 extractions) to 200-fold (in F4
197 extractions) above LOD (0.1 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:H₂ 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 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}Se digestions from the 1000 mg L⁻¹ SPM isotherm experiment were quantified by QQQ-
209 ICP-MS (Agilent 8800, Basel, Switzerland) using external calibration with ^{103}Rh as internal standard
210 and oxygen-shift mode collision gas for ^{77}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 (Se_{nat}) and
214 spiked/experimental Se (Se_{ex}) were quantified with the O₂-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}Se , ^{78}Kr , $^{156}\text{Gd}^{++}$ and $^{156}\text{Dy}^{++}$ in ^{78}Se , $^{81}\text{Br}^1\text{H}$ and ^{82}Kr in ^{82}Se) on both inherited
217 (^{78}Se , ^{80}Se , ^{82}Se) and spiked (^{77}Se) isotopes. Particulate Se_{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 Se_{ex} was calculated from the difference between initially spiked
220 and final Se_{d} after 48h.

221

222 2.5. Distribution coefficient (K_d)

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_d),
225 described in Sung (1995). Briefly, K_d (in L kg⁻¹) is the particulate (mg kg⁻¹) to dissolved (mg L⁻¹)
226 concentration ratio (Equation 1). The relative contribution of the particulate concentration (X_p) of a
227 given element X to the total (dissolved + particulate) concentration of the same element (X_T, Equation
228 2) is expressed as the fraction of X_p (F_p, 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_p is expressed in mg kg⁻¹, X_d in mg L⁻¹, X_T in mg L⁻¹ and SPM in kg L⁻¹. This K_d 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 (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 (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 mg L^{-1} SPM within 3 min. Equilibrium between the dissolved and particulate phases was
269 achieved at $\geq 48\text{h}$ in 100 mg L^{-1} SPM and in <5h for 1000 mg L^{-1} SPM (Figure 1a). Experimental
270 blanks (i.e., no SPM) showed no measurable 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 ± 0.02 L
273 kg^{-1} for 100 mg L^{-1} and 5.31 ± 0.01 L kg^{-1} for 1000 mg L^{-1} , whereas in seawater K_d values were $4.98 \pm$
274 0.02 L kg^{-1} for 100 mg L^{-1} and 4.96 ± 0.09 L kg^{-1} for 1000 mg L^{-1} .

275 Sorption isotherms showed non-linear correlations at low SPM concentrations (100 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 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 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 mg L^{-1}), reaching
288 solid/liquid equilibrium in <24h for 1000 mg L^{-1} with max. 25% sorption. Precise sorption kinetics and
289 equilibrium time for 100 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 ± 0.08 L kg^{-1} for 100 mg L^{-1} and 2.42 ± 0.04 L kg^{-1} for 1000 mg L^{-1}
293 in freshwater, whereas in seawater they were 2.87 ± 0.10 L kg^{-1} for 100 mg L^{-1} and 2.57 ± 0.04 L kg^{-1}
294 for 1000 mg L^{-1} .

295 Sorption isotherms for both SPM conditions (100 mg L^{-1} and 1000 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 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⁻¹ for Te_{nat} whereas 2.68 mg kg⁻¹ in
307 S=0 and 3.20 mg kg⁻¹ in S=32 for respective Te_{ex} concentrations. Total Se_{nat} concentrations ranged
308 between 0.37-0.53 mg kg⁻¹ and average Se_{ex} was 25.7 mg kg⁻¹ in both, freshwater and seawater.

309 The acid-soluble fractions showed the highest Te_{nat} contribution (~50% in F4 and ~30% in F4N,
310 Figure 3a) for freshwater experiments and were 10-20% lower in seawater experiments. Average Te_{nat}
311 contribution was 14% in the H₂O₂ 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_{ex} 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_{ex} in the residual fraction. Up to 10% of Te_{ex} 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-H₂O₂ organic matter and labile/amorphous sulphide
319 phases). In any case, low differences (~5%) were observed between freshwater-adsorbed and
320 seawater-adsorbed Te_{ex} except for acid-soluble fractions where this difference varied from 20 to 30%.

321 Selective extractions for Se_{nat} showed highest contributions (≥85%) in the F3-H₂O₂ 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_{nat}
324 extractions than 1M HNO₃. Ascorbate solutions extracted concentrations of Se_{nat} similar to that of
325 HCl-extracted aliquots, and the lowest Se_{nat} fractions occurred in acetate extractions (~1%, Figure 3b).
326 Spiked concentrations were also highly extracted in the F3-H₂O₂ fraction, representing 95-105% of
327 total sorbed Se_{ex}. Noteworthy, the second most important fraction was the F2-ascorbate fraction,
328 extracting ~60% of Se_{ex}, presumably from amorphous Mn/Fe oxide mineral phases. This amount of
329 Se_{ex} extracted was higher than that in the acid-soluble fractions F4 and F4N, both extracting ~20% of
330 Se_{ex}. Only 12% of Se_{ex} was leached in the easily exchangeable/carbonate fraction (F1-acetate
331 extraction). Differences between freshwater-adsorbed and seawater-adsorbed Se_{ex} 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 log₁₀ K_d 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⁻¹. These values are up to one order of magnitude greater than those of
340 natural As (3.5 – 4.8 L kg⁻¹) and Sb (3.8 – 4.8 L kg⁻¹; 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⁻¹, 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⁻¹, the reported Cs \log_{10} Kd values range from <4.7 L kg⁻¹ in river systems
350 (Ciffroy et al. 2009) to typical values of \log_{10} Kd 5.1 to 6.8 L kg⁻¹ 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⁻¹ in the seawater, similar decreases
353 to that observed for Sb in the Gironde Estuary (i.e., 0.2 L kg⁻¹; Gil-Díaz et al. 2018). In contrast, the
354 difference in Cs \log_{10} Kd between freshwater and seawater is 1.4 L kg⁻¹ 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⁻¹; Figure 1b) and the high SPM condition (1000 mg
368 L⁻¹; 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⁻¹ 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⁻¹

374 ¹; Sottolichio and Castaing 1999), a hypothetical Te_d concentration of 50 µg L⁻¹ could be retained to
375 ~90% within <3 min. Nearly all Te_d (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⁻³ of ¹³⁷Cs (equivalent to ~20 ng L⁻¹) has been detected in early April in surface
380 waters adjacent to the FDNPP, decreasing to 10 000 Bq m⁻³ (equivalent to ~3 pg L⁻¹) 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 ¹³⁷Cs, nearly all Te_d 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_{nat} in the SPM and ~60% of the experimentally added Te_{ex} 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_{ex} 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_{ex} to both, the bioaccessible (60%) and residual (40%) fractions
398 implies interaction with different mineral surfaces, which would not be consistent with the Te_{ex}
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 HNO₃-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 HNO₃,
403 although previous work has reported similar stability and solubility in both HCl and HNO₃ 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⁻¹, 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}Te to ~ 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}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 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 L kg^{-1} for 100 mg L^{-1} SPM; Benoit et al.
465 2010) and 19 Japanese coastal regions (\log_{10} Kd of 2.6 – 3.9 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 μm ; 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 HNO₃
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⁻¹ and 1000 mg L⁻¹ 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., ⁷⁵Se, ⁷⁹Se and ⁸²Se) 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 10⁵ g y⁻¹ 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 ⁷⁵Se (~119 d half-life), ⁷⁹Se (~10⁵ y
549 half-life) and ⁸²Se (~10¹⁹ 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 hypothetic 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

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585

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591

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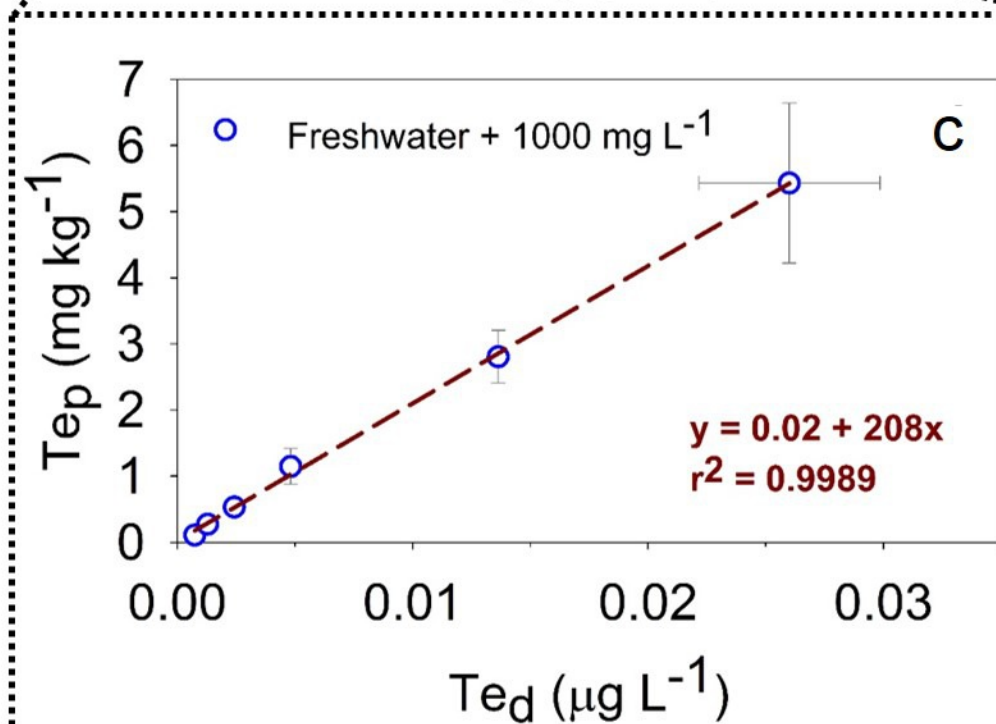
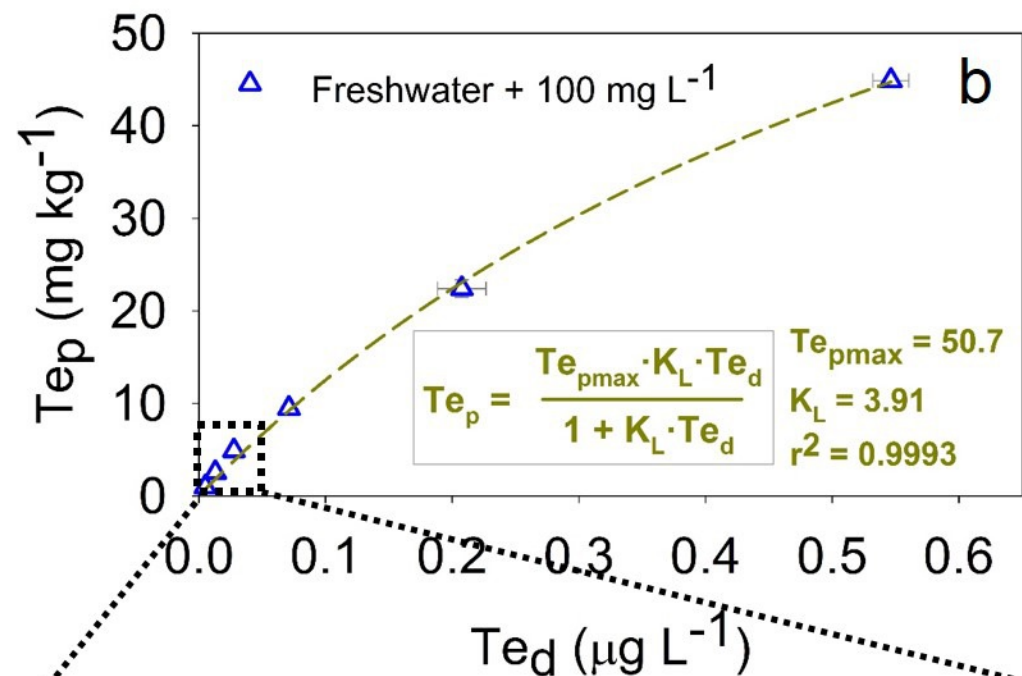
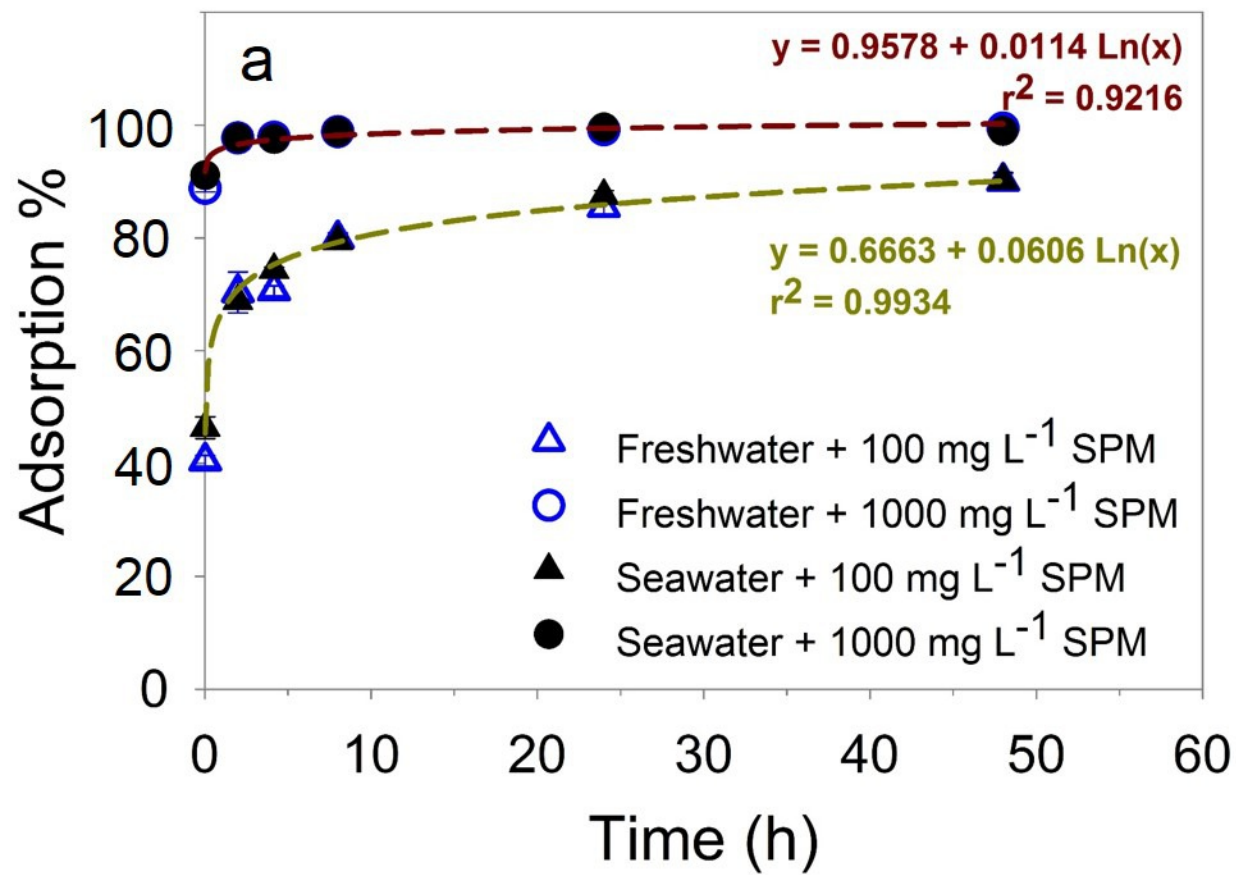
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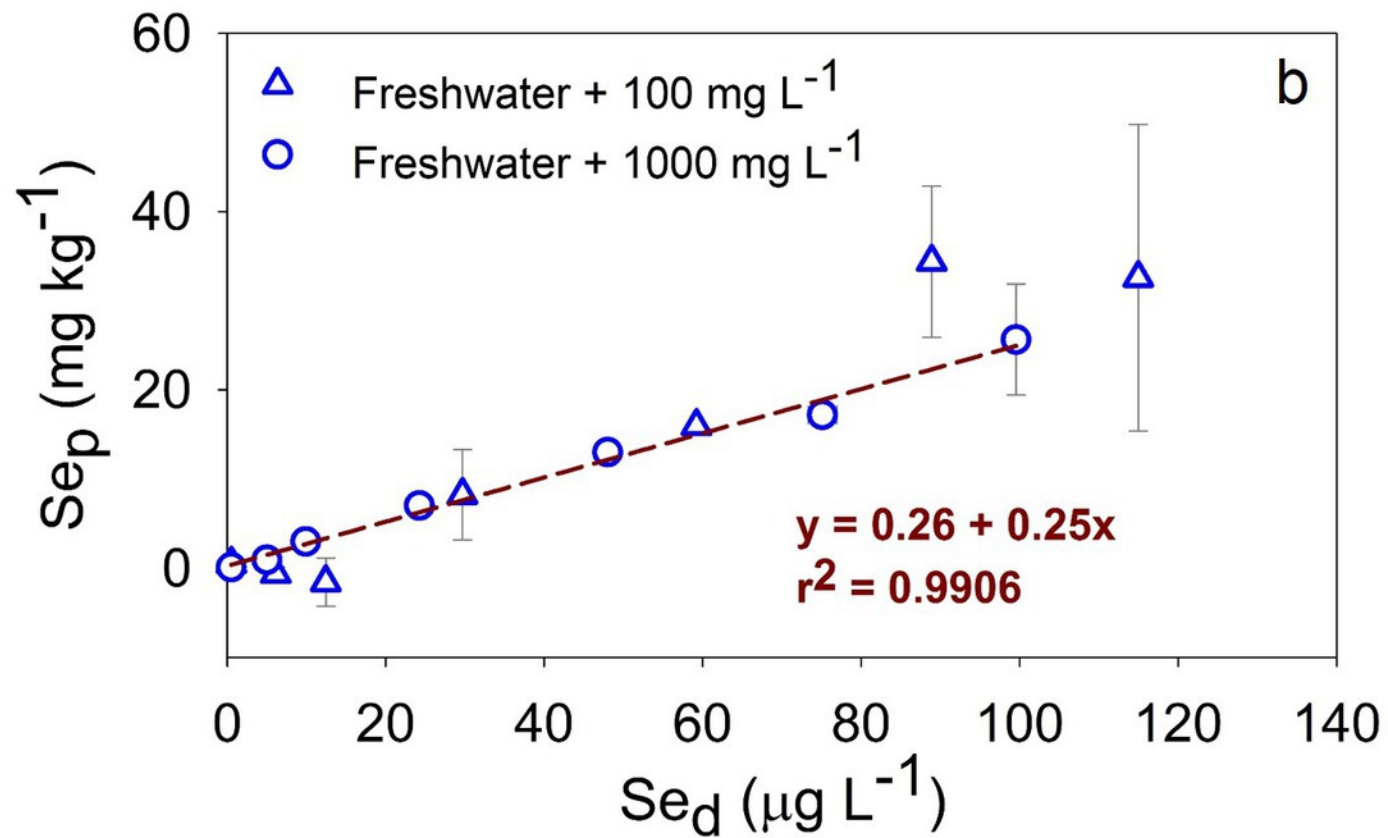
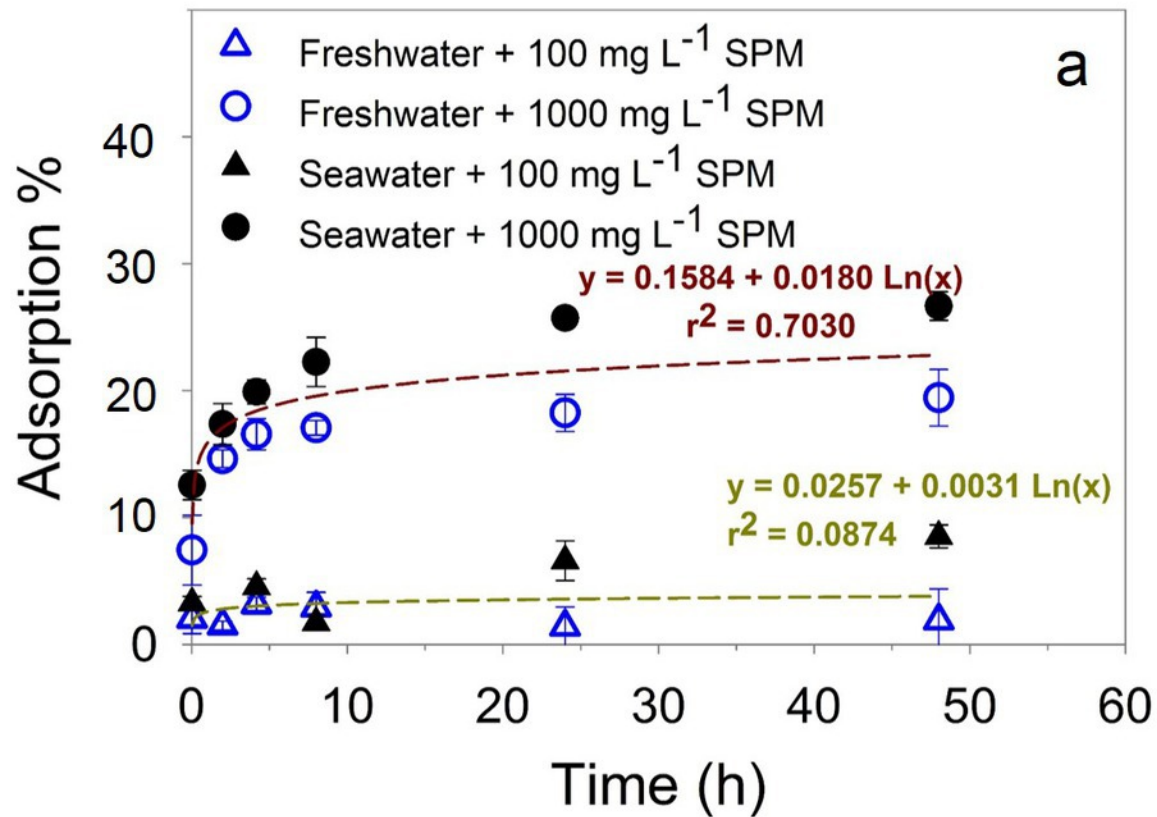
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Figure 1. Sorption of tellurium in natural SPM. (a) Te sorption kinetics (N=3) in freshwater (empty symbols) and seawater (filled symbols) matrices for 100 mg L⁻¹ (triangles) and 1000 mg L⁻¹ (circles) SPM content. Adsorption percentages are calculated as the difference between initial spiking concentration and Te_d at each sampling time. Tellurium isotherms (N=2, after 48h equilibration) for (b) freshwater sorption in 100 mg L⁻¹ and (c) 1000 mg L⁻¹ 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⁻¹ and 1000 mg L⁻¹ SPM content as well as (b) selenium freshwater sorption isotherms (N=2, after 48h equilibration) in 100 mg L⁻¹ (triangles) and 1000 mg L⁻¹ (circles) SPM content. Adsorption percentages are calculated as the difference between initial spiking concentration and Se_d 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_{nat}, N=3), (b) spiked Te (Te_{ex}, N=3), (c) natural Se (Se_{nat}, N=3) and (d) spiked Se (Te_{ex}, 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 (H₂O₂ extraction) and F4 – reactive and potentially bioaccessible fraction (HCl 1 M extraction as F4 and HNO₃ 1M extraction as F4N). Percentages represent the extracted concentration in each fraction compared to total particulate concentration. Error bars correspond to standard deviations (SD).





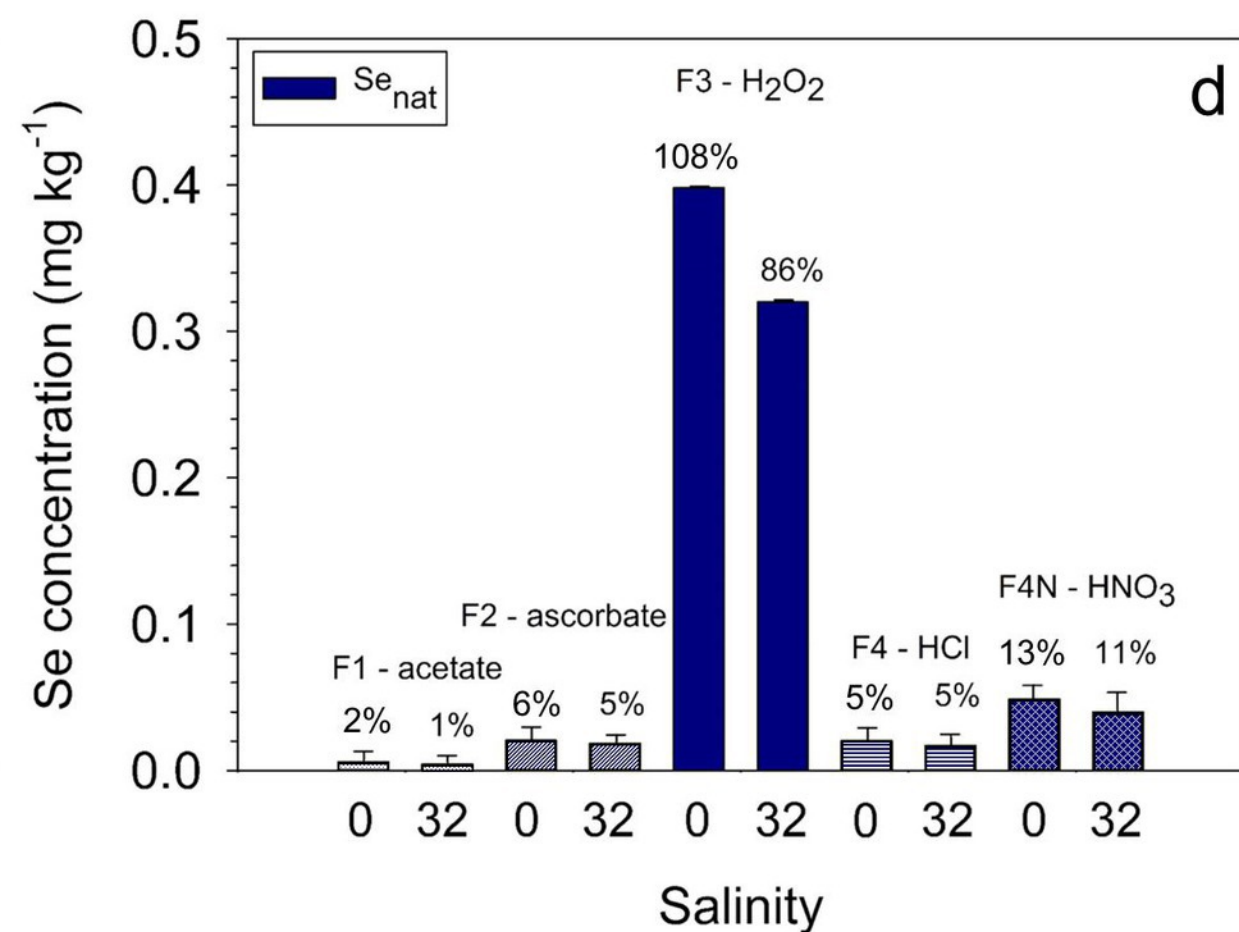
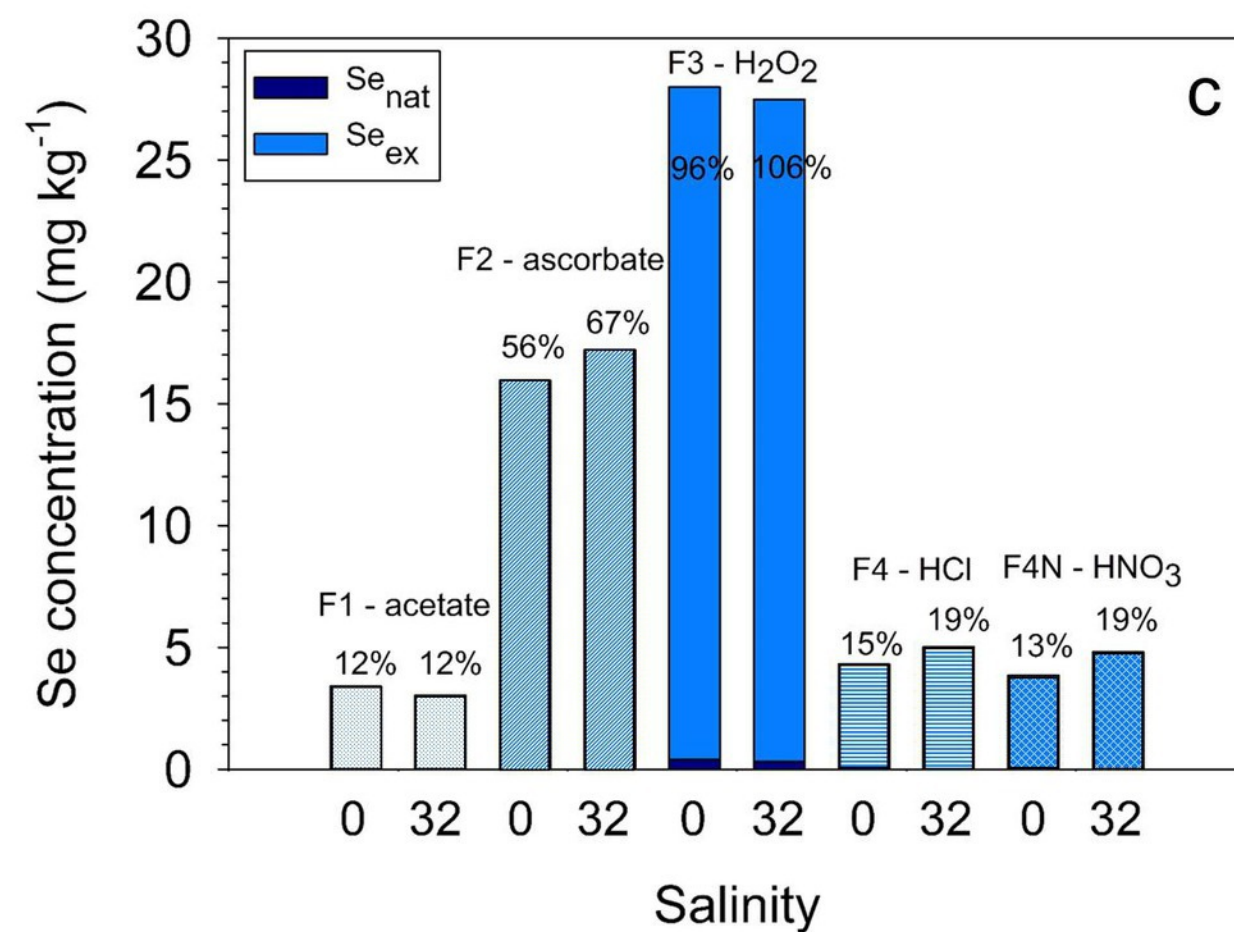
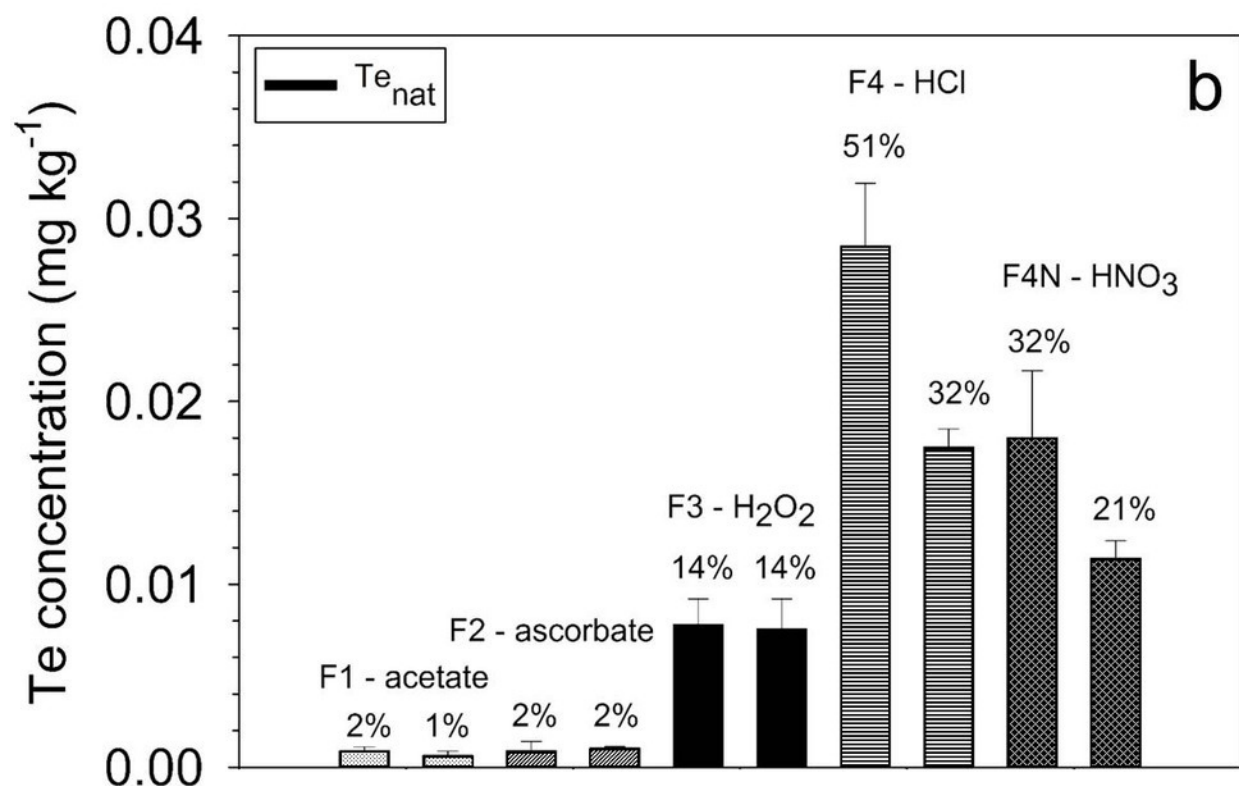
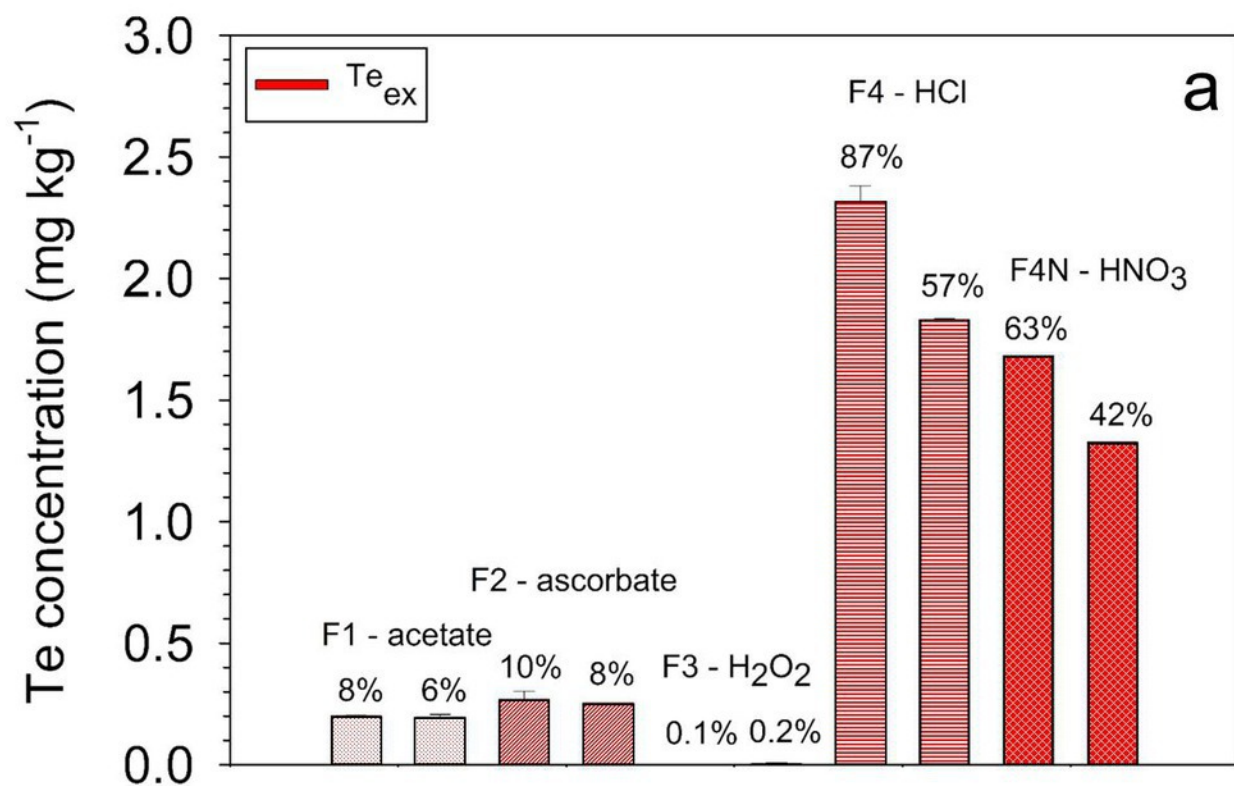


Table 1: Parallel selective extractions as described in Audry et al. (2006).

Sediment fraction	Sample weight (mg)	Reagents	Procedure
F1 – Acetate extraction (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 (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 ₂ O ₂ extraction (oxidisable fraction = organic matter and labile/amorphous sulphides)	500	2.5 ml H ₂ O ₂ 30% (at pH 5 with NaOH) + 1.5 ml H ₂ O ₂ 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 (and complementary F4N – HNO ₃ extraction) (reactive and potentially bioaccessible = amorphous and crystalline Fe/Mn oxides + carbonate fractions + amorphous monosulphurs + phyllosilicates)	200	12.5 ml HCl or HNO ₃ (Suprapur®, 1 M)	24 h shaking at 25°C