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1 **Fractionation of inherited and spiked antimony (Sb) in fluvial/estuarine** 2 **bulk sediments: unexpected anomalies in parallel selective extraction** 3 **protocols**

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7

8 **ABSTRACT**

9 Selective extractions are widely used in sediment, soil and sludge samples to assess trace element
10 carrier phases, mobility and potential bioaccessibility. Commonly used selective parallel extractions
11 were applied to natural and isotopically-labelled bulk sediments from the Gironde fluvial-estuarine
12 system and the Rhône River (France) to determine the solid phase fractionation of antimony (Sb), a
13 priority contaminant in EU and US regulations and an important radionuclide in decay series occurring
14 in the environment after nuclear power plant accidents. Antimony fractions obtained from several,
15 parallel selective extraction solutions targeting Fe/Mn oxides (i.e., hydroxylamine-, oxalate- and
16 ascorbate-based, herein assigned as fractions from “F2” solutions) and acid-soluble operationally
17 defined phases (HCl- and HNO₃-based, herein assigned as fractions from “F4” solutions) were
18 compared (i) between each other’s, and (ii) with those of other trace elements (Co, Cu, Ni, Pb, Zn, Th
19 and U) in the same extractions. The solid fractionation of inherited Sb and spiked Sb was studied by
20 applying a complete set of parallel selective extractions to isotopically-labelled sediments of the
21 Gironde Estuary. Results suggest protocol-related and sediment-dependent anomalies in Sb selective
22 extractions, compared to results expected from the operationally-defined extraction scheme and
23 obtained for other trace elements. In fact, Sb fractions extracted with oxalate- and ascorbate-based
24 solutions were greater than acid-soluble fractions (1M HCl and 1M HNO₃) in the Garonne/Gironde
25 fluvial estuarine sediments. A similar anomaly occurred for oxalate-based extractions of Sb in Rhône
26 River sediments. These observations suggest that reducing conditions and the presence of strongly
27 complexing organic ligands in the environment may mobilise respectively 2-fold and ~5-fold more Sb
28 from natural bulk sediment and from sediments spiked with isotopically-labelled Sb than the acid-
29 soluble fraction, usually used to assess the reactive, potentially bioaccessible fractions. The
30 underestimation of the reactive, potentially bioaccessible fractions of Sb may bias the environmental
31 interpretation of Sb solid fractionation and should be taken into account when assessing stable Sb
32 cycles and Sb radionuclide dispersion scenarios in continent-ocean transition systems.

33

34 **Keywords:** suspended particulate matter, isotopically labelled sediments, Gironde Estuary, Rhône
35 River

36 1. INTRODUCTION

37 Solid phases (e.g., suspended matter, sediments, and soils) play a fundamental role in the
38 biogeochemical cycles of potentially toxic trace elements (metals and metalloids). Suspended particle
39 dynamics control the transport and/or long-term retention of trace elements along river courses and in
40 coastal/estuarine areas. Sediment quality guidelines and regulations are based on total particulate
41 concentrations but trace element mobility/solubility and bioaccessibility actually depend on particle
42 composition. Accordingly, the association of trace elements to specific geochemical carrier phases
43 may control trace element solid/liquid partitioning and reactivity, affecting the effective exposure of
44 biota to certain contaminants. Solid carrier phases include carbonates, sulphides, organic matter, iron
45 and manganese oxides, and clays, among other fractions (Jenne 1968). All these fractions interact
46 differently with trace elements depending on environmental conditions (Kersten and Förstner 1987).
47 Reliable assessment of particle trace element contamination requires evaluating correctly the
48 mobility/solubility and bioavailability of particulate trace elements under different physico-chemical
49 conditions.

50 Different methods, often referred to as “selective extraction techniques”, “speciation schemes” or
51 “fractionation analysis” according to IUPAC (Gleyzes et al. 2002), have been developed to study trace
52 element solid fractionation. The Fe oxide/hydroxide fraction is often targeted given: (i) its relevant
53 sorption role for many target elements, determining their reactivity/mobility (Jenne 1968), and (ii) the
54 diverse response of Fe minerals (amorphous vs crystalline) to reagents/extraction conditions.
55 Amorphous Fe minerals include ferrihydrite ($\text{Fe}(\text{OH})_3$) and lepidocrocite ($\alpha\text{-FeOOH}$), whereas
56 crystalline structures occur in goethite ($\alpha\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and magnetite (Fe_3O_4).

57 Environmental studies addressing the association of trace elements to the Fe oxide fraction use
58 classical schemes such as those defined by Tessier et al. (1979) and by the Community Bureau of
59 Reference (BCR; Ure et al. 1993). These schemes rely on hydroxylamine acid solutions which
60 dissolve Fe oxides of variable degrees of crystallinity according to the extraction conditions. These
61 extractions can be complemented with further extractions using stronger reagents like dithionite or
62 oxalate and ascorbate solutions, which may even completely dissolve crystalline Fe fractions (Leuz
63 2006; Henkel et al. 2016). Kostka and Luther (1994) defined the “reactive/mobile Fe oxide fraction”
64 extracted by an ascorbate solution at pH 8 as an adequate extraction for amorphous Fe oxides with
65 environmental applications. This fraction includes Fe oxides that readily react with sulphides, to form
66 iron sulphides and pyrite, as well as with organic acids. Thus, it is expected to reliably represent
67 environmental processes such as Fe mineral reconversions in early diagenesis (Froelich et al. 1979).
68 However, this extraction procedure using an ascorbate solution at pH 8 is not a widespread method
69 (e.g., Reyes and Torrent 1997) and the response of redox-sensitive species to such extraction under
70 reducing conditions is unknown. In fact, the indiscriminate application of these methods targeting

71 Fe/Mn oxides to extract trace elements other than the originally designated ones seems unwise because
72 extraction conditions can also affect the element speciation/behaviour during the extraction (Müller et
73 al. 2007). For example, the incomplete dissolution of crystalline Fe oxides during hydroxylamine
74 extractions can cause sorption of As onto goethite, underestimating the extraction of As species in
75 contrast to oxalate solutions (pH ~ 3; i.e., “anion-adapted” protocol; Wenzel et al. 2001). This could
76 also be the case for other redox-sensitive elements such as Sb, for which little is known about its
77 behaviour during selective extractions. The understanding of Sb behaviour during these extractions is
78 of relevant importance given that Sb is classified as a pollutant of priority interest for the European
79 Community (Directive 2006/11/EC), the German Research Council (DFG 2012) and the U.S.
80 Environmental Protection Agency (USEPA 2013).

81 In addition, the potentially bioaccessible fraction can be assessed from extractions using diluted
82 acid solutions as they are considered to mimic the acid conditions present in the digestive system of
83 the organisms. Some Australian and New Zealand sediment quality guidelines (ANZECC and
84 ARMCANZ, 2000) include 1M HCl extraction protocols to verify whether sediment samples
85 overpassing total metal guideline concentrations truly imply a relevant bioaccessible fraction or not.
86 These HCl solutions are also commonly applied to marine and estuarine sediments (e.g., Snape et al.
87 2004). Furthermore, the International Standard Organization recently updated an HNO₃-based protocol
88 (ISO 17586:2016) to extract potential environmentally available trace element contaminants in soils
89 concerning “metals, including metalloids, and organic contaminants, including organometallic
90 compounds” (as defined in the previous ISO 17402:2008). However, no fundamental studies have
91 been performed in order to define a unique extraction protocol based on either acid-based method.

92 The aim of this study is to determine the environmentally representative solid phase fractionation
93 of Sb in natural bulk sediments from the Gironde Estuary and the Rhône River, i.e., sediments not
94 associated to highly contaminated areas. Given the unknown response of Sb to selective extracting
95 conditions, this work first compares Sb parallel extractions with different reagents targeting (i) the
96 Fe/Mn oxide fraction (hydroxylamine, oxalate and ascorbate solutions, designated as fractions from
97 “F2” solutions), and (ii) the bioaccessible fraction (1M HCl and 1M HNO₃ solutions, designated as
98 fractions from “F4” solutions). The behaviour of Sb during these extractions is compared with that of
99 “classical” trace (Co, Cu, Ni, Pb, U, Zn) and major elements (Fe and Mn). Finally, the application of a
100 parallel selective extraction scheme (including several fractions, from “F1” to “F4”) to bulk SPM from
101 the Garonne River, previously spiked with isotopically-labelled Sb, aims at evaluating the solid
102 fractionation of both natural/inherited and spiked Sb under contrasting salinity and turbidity
103 conditions. The idea behind this last approach is to examine the solid fractionation of inherited vs
104 spiked Sb to better understand (i) the parallelism between the extractions of both compounds and (ii)
105 the use of studies reporting the natural biogeochemical behaviour of Sb for the development of

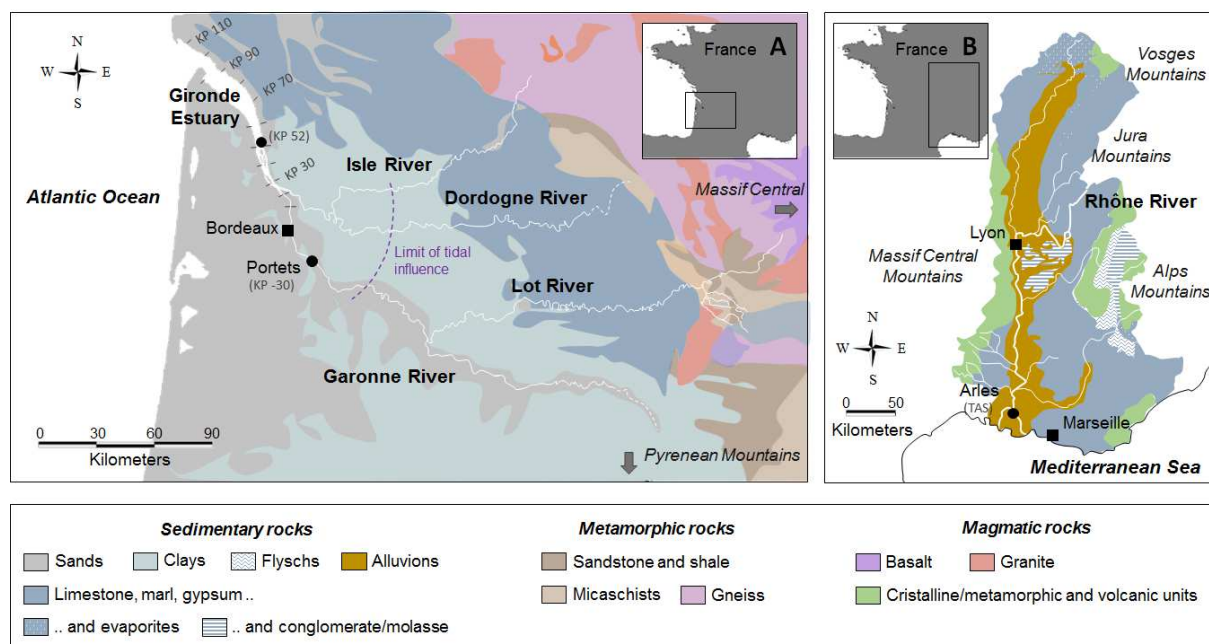
106 environmental dispersion/fate scenarios in case of hypothetical releases of anthropogenic Sb into
107 continent-ocean transition systems.

108

109 2. MATERIAL AND METHODS

110 2.1. Sample collection

111 Sampling sites are located in two areas at the continent-ocean interfaces of the Gironde fluvial-
112 estuarine system (SW France) and the Rhône River (SE France). In total, three oxic sediment samples
113 were collected (Supplementary data, Fig. S1): (i) suspended particulate matter (SPM) at the Kilometric
114 Point 52 (KP52) in the Gironde Estuary (collected on the 11th May 2015), (ii) deposited river bank
115 sediments at Portets (KP-30) along the Garonne River, i.e., the main tributary to the Gironde Estuary
116 (collected on the 17th September 2016), and (iii) SPM collected with a sediment trap (TAS) at the
117 SORA station (Station Observatoire du Rhône à Arles) in the Rhône River (collected between the 2nd
118 May and 4th June 2013). Detailed descriptions of sampling techniques and materials are given in Gil-
119 Diaz et al. (2016) for the Gironde SPM and Masson et al. (2018) for the Rhône. Wet sediments were
120 kept in the fridge and aliquots were freeze-dried (KP52 and TAS) or oven-dried at 70°C (KP-30),
121 homogenised and further divided into subsamples for parallel selective extractions with F2 and F4
122 protocol solutions.



123 **Fig. S1.** Map of the Lot-Garonne-Gironde fluvial-estuarine system (A) and the Rhône River (B). Main
124 cities (squares), sampling sites (circles), rivers and Kilometric Points (KP) are shown. Rock
125 composition along the watershed is denoted by the colour code legend: (A) adapted from BRGM
126 (2014) and (B) simplified from Ollivier et al. (2010).

128

129 **2.2. Preparation of isotopically-labelled (^{123}Sb) sediments**

130 Wet SPM from KP52 was used for batch sorption experiments using isotopically-labelled Sb. For
131 this, a high purity monoisotopic solution of ^{123}Sb (99.43% Oakridge, USA) was spiked to nominal
132 concentrations of $2\ \mu\text{g L}^{-1}$ into aliquots (1L) of three different natural water samples filtered at 0.45
133 μm (Teflon filters, FHLC, Merck Millipore Ltd.). These water samples contained different salinities
134 (S) representing the environmental salinity gradient encountered in the Gironde Estuary. Water
135 samples included natural freshwater (no salinity, $S = 0$) from La Réole (at KP-60, tidal influence limit)
136 and brackish water from the Gironde Estuary ($S = 22$) and a 50/50 mixture of both matrices ($S = 11$).
137 The spiked matrices were left to equilibrate overnight, before being exposed during five days to high
138 concentrations of SPM (nominal $>1000\ \text{mg L}^{-1}$ dry weight, DW) in a tumbling shaker. The sediments
139 were then recovered by centrifugation (10 min at 4000 rpm; Hettich Rotofix 32A centrifuge), oven-
140 dried (50°C stove), grinded in agate mortars and aliquots of each condition prepared for parallel
141 selective extractions comprising several fractions (i.e., from F1 to F4, see section 2.4.).

142

143 **2.3. Parallel selective extractions comparing F2 and F4 solutions**

144 Selective extractions can either be performed sequentially (i.e., subjecting a single and unique
145 sample successively to different reactants) or as single extractions (i.e., applying to several aliquots of
146 the same sample independent extraction reactants), also considered as “single multiple extractions”
147 when the battery of reagents and aliquots are included in the same study. All approaches have
148 advantages and disadvantages (e.g., Gleyzes et al. 2002). The results obtained are method-dependent
149 in all cases. In this study, all the multiple selective extractions applied were single extractions.

150 Three types of selective extraction solutions targeting Fe/Mn oxide minerals (“F2” solutions, Table
151 1) were applied to natural sediment aliquots of KP52, KP-30 and TAS in parallel extractions. The first
152 solution contains hydroxylamine (NH_2OH , ACS ThermoFisher® Acros Organics) using acetic acid as
153 complexing agent (HOAc, PlasmaPURE SCP SCIENCE®; Chester and Hughes 1967, Tessier et al.
154 1979). The second extraction follows the known oxyanion-adapted protocol (Wenzel et al. 2001, based
155 on Shuman 1982) consisting of an oxalate buffer extraction with oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$, analytical grade,
156 Fisher Scientific®) and ammonium oxalate as complexing agent ($(\text{NH}_4)_2\text{C}_2\text{O}_4$, R.P. NORMAPUR®).
157 The third extraction uses ascorbic acid as reducing agent ($\text{C}_6\text{H}_8\text{O}_6$, ACS ThermoFisher® Acros
158 Organics), sodium citrate as complexing agent ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, Merck®) and sodium bicarbonate
159 (NaHCO_3 , J.T. Baker) to buffer the pH of the reaction (Kostka and Luther 1994, based on Ferdelman
160 1988). In addition, operationally-defined potentially bioaccessible fractions (“F4” solutions, Table 1)
161 were determined by parallel extractions with either HCl (1M, Suprapur®) or HNO_3 (1M, Suprapur®).

162 All extractions were performed in acid-washed (HNO₃ 10%) PP Falcon 50 mL conical centrifuge
163 tubes (FISHER SCIENTIFIC) previously rinsed with MilliQ water, dried under a laminar flow hood
164 and stored in double-sealed plastic bags pending the experimental use. Natural sediments were
165 extracted with three replicates in each selective extraction, run together with three blanks of each
166 extraction to verify potential reagent contaminations.

167

168 **2.4. Parallel selective extraction scheme (F1 to F4)**

169 Solid fractionation of the isotopically-labelled KP52 was studied with four parallel extractions
170 targeting the following fractions:

- 171 - (F1) easily exchangeable and carbonate fraction, i.e., carbonates, Mn oxyhydroxides, sulphates
172 and organic matter phases (Kersten and Förstner 1987) with an acetate solution (1:20 w/v ratio for
173 1M NaOAc, J.T. Baker) at pH ~ 5 adjusted with 5M HOAc (PlasmaPURE SCP SCIENCE®)
174 during 6h with permanent shaking at 25°C (Tessier et al. 1979),
175
- 176 - (F2) reactive Fe/Mn oxides fraction, extracted with the ascorbate-based solution (Kostka and
177 Luther 1994) as described in section 2.3. and in Table 1,
178
- 179 - (F3) oxidisable fraction, attributed to organic matter and labile/amorphous sulphide phases
180 (Tessier et al. 1979), extracted with H₂O₂ (30%, J.T. Baker) in a tumbling shaker during 5h at
181 85°C, adding NH₄OAc (Merck®) as complexing agent during the last 30min of shaking (Ma and
182 Uren 1995) with a final 1:40 w/v ratio,
183
- 184 - (F4) potentially bioaccessible fraction as assessed through the 1M HCl extraction (as described in
185 section 2.3. and in Table 1).

186 As in the previous experience, these extractions were performed in acid-washed (HNO₃ 10%) PP
187 Falcon 50 mL conical centrifuge tubes (FISHER SCIENTIFIC). Isotopically-labelled sediment was
188 extracted with only one replicate per condition due to mass limitations, run together with three blanks
189 of each extraction.

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Table 1. Reagents and methods used for the extractions of reactive Mn/Fe oxides and potentially bioaccessible (acid-soluble) fractions.

PROTOCOLS	Reducible Fe/Mn oxide fraction (F2 solutions)			Potentially bioaccessible acid-soluble fraction (F4 solutions)	
Reagent	Hydroxylamine + HOAc (HA)	Oxalate buffer (Ox)	Ascorbate solution (Asc)	HCl	HNO ₃
Solid/liquid ratio (w/v)	1:100 (50 mg in 5 mL)	1:100 (400 mg in 40mL)	1:50 (200 mg in 12.5 mL)	1:50 (200 mg in 12.5 mL)	1:50 (200 mg in 12.5 mL)
Solutions	1M NH ₂ OH.HCl 25% v/v HOAc ^a	0.2M (NH ₄) ₂ C ₂ O ₄ 0.2M C ₂ H ₂ O ₄ pH < 3 ^b	12.5 g Na ₃ C ₆ H ₅ O ₇ 12.5 g NaHCO ₃ Deaerating with N ₂ 5 g C ₆ H ₈ O ₆ pH = 8 ^c	1M HCl	1M HNO ₃
Extracting conditions	48 h shaking at 25°C	4 h shaking in the dark at 25°C	24 h shaking at 25°C	24h shaking at 25°C	24h shaking at 25°C
Target phases	Mn oxides and amorphous Fe oxides (e.g., ferrihydrite, lepidocrocite), including highly reactive Fe phases like carbonate Fe (e.g., siderite FeCO ₃) due to HOAc ^d and potentially short-range ordered to highly crystalline phases according to the sediment characteristics ^e	All Mn oxides (e.g., associated to organic matter) and short-range ordered ^f to highly crystalline Fe oxides like magnetite ^{d,g} especially in presence of Fe(II)-bearing minerals ^h	Amorphous Mn and Fe oxides ^e . Citrate solution in excess avoids precipitation of Fe(II) oxy(hydr)oxides ⁱ	Amorphous and crystalline (incompletely) Fe/Mn oxyhydroxides, Fe(II)-bearing minerals, organic matter, carbonates, amorphous sulphides and hydrous aluminosilicates ^{e,j} (except goethite and hematite ^k) 1M HCl has sufficient buffering capacity to dissolve carbonates and has a limited impact on the residual clays or sulphides ^l Conc. HNO ₃ favours pyrite (FeS ₂) dissolution ^l	

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^a Chester and Hughes 1967; ^b Shuman 1982; ^c Kostka and Luther 1994; ^d Poulton and Canfield 2005; ^e Tack et al. 1996; ^f Miller et al. 1986; ^g Suda et al. 2013; ^h Stumm and Sulzberger 1992; ⁱ Henkel et al. 2016; ^j Huerta-Díaz and Morse 1990; ^k Raiswell et al. 1994; ^l Billings and Ragland 1968

197 **2.5. Total element digestion**

198 Total element concentrations were quantified from tri-acid total digestions as described in Schäfer
199 et al. (2002). Briefly, 30 mg of dried and homogenised sediments were digested on a heating plate (2 h
200 at 110 °C) with 1.5 mL HCl (10 M Suprapur®, Merck), 750 µL HNO₃ (14 M Suprapur®, Merck) and
201 2.5 mL HF (29 M Suprapur®, Fisher) in closed PP reactors (DigiTUBEs®, SCP SCIENCE). An
202 evaporation step was then followed by re-dissolution of the residues with 250 µL HNO₃ (14 M),
203 finally brought to 10 mL using Milli-Q® water. Parallel total digestions (N=2) of CRMs (stream
204 sediment DC 73307 and DC 70317, and channel sediment BCR 320R) were performed for quality
205 monitoring purposes.

206 The residual fraction was calculated as the difference between the total element concentration (tri-
207 acid digestion) and that obtained in the acid-soluble fraction (1M HCl acid-soluble fraction, F4).

208

209 **2.6. Quantification of Fe, Mn, Sb and other trace elements**

210 All trace elements (Sb, Co, Cu, Ni, Pb, U and Zn) were analysed by ICP-MS (X7 Series,
211 THERMO®) using external calibration. Extracted Fe and Mn contents were analysed by ICP-OES
212 (700 Series, Agilent®) with external calibration only for sediments from the Gironde Estuary. All
213 calibrations were performed with mono-elemental solutions (SPEX CertiPrep®) and analytical
214 performances were quality checked with certified reference waters (CRM: TMRAIN-04, TMRAIN
215 23.4, SLRS-6, SRM 1640a; NIST 1643-f) for ICP-MS and ICP-OES measurements, producing
216 accuracies between 81% and 119% with precisions of 1% to ~20% (details in Supplementary data,
217 Table S1).

218 Given the lack of adapted CRM for multi-element selective extractions, the resulting dissolutions
219 from selective extractions could not be quality checked. Nevertheless, extracted trace element
220 concentrations were generally > 10-fold higher than the respective LODs (for average minimum
221 values see Supplementary data, Table S1), except for some extractions from TAS sediment, probably
222 due to relatively low total concentrations compared to sediments from the Gironde Estuary. Extracted
223 Fe and Mn contents were always 400 to 1000 times higher than LOD (Supplementary data, Table S1).
224 Quality data from sediment CRMs after total extractions showed recoveries of 101% ± 12% for Sb and
225 between 74% and 110% for the rest of the trace elements (for specific element recoveries and LODs
226 see Supplementary data, Table S2).

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231 **Table S1.** Analytical performance of dissolved (all in $\mu\text{g L}^{-1}$ except * in ng L^{-1} ; mean \pm standard deviations, SD) certified reference materials (CRM: rain
 232 water TMRAIN-04, TMRAIN 23.4; river water SLRS-6, NIST 1643-f; spring water SRM 1640a), maximum limits of detection (LOD = $3 \cdot \text{SD}(\text{blanks})$) and
 233 minimum sample fold above LOD (Factor $>\text{LOD}$) for all extractions performed.

Element	TMRAIN-04		TMRAIN 23.4		SLRS-6		SRM 1640a / NIST 1643-f		LOD	Factor >LOD
	Certified	Measured	Certified	Measured	Certified	Measured	Certified	Measured		
Co	0.25 ± 0.06	0.26 ± 0.02	7.08 ± 0.55	6.49 ± 0.14	$53 \pm 12^*$	$56.6 \pm 9.1^*$	25.1 ± 0.2	21.8 ± 0.8	0.05	10
Cu	7.03 ± 0.80	6.81 ± 0.75	8.52 ± 0.83	8.00 ± 0.14	23.9 ± 1.80	23.1 ± 0.9	21.7 ± 0.7	18.7 ± 1.1	0.18	5
Fe	24.7 ± 4.1	25.1 ± 0.7	14.7 ± 2.4	12.8 ± 0.2	84.3 ± 3.6	77.5 ± 1.2	36.8 ± 1.8	35.4 ± 1.6	0.75	400
Mn	6.70 ± 0.66	6.70 ± 0.31	8.78 ± 0.63	8.52 ± 0.19	2.12 ± 0.10	1.93 ± 0.05	40.4 ± 0.4	39.5 ± 1.8	0.39	1000
Ni	0.91 ± 0.12	0.89 ± 0.08	4.96 ± 0.62	5.61 ± 0.22	0.62 ± 0.02	0.67 ± 0.04	59.8 ± 1.4	52.0 ± 2.8	0.29	10
Pb	0.35 ± 0.07	0.34 ± 0.01	2.98 ± 0.27	2.56 ± 0.03	0.17 ± 0.03	0.16 ± 0.02	18.5 ± 0.08	15.8 ± 0.1	24.3^*	10
Sb	0.35 ± 0.07	0.34 ± 0.01	3.26 ± 0.32	2.91 ± 0.03	0.34 ± 0.01	0.31 ± 0.01	55.5 ± 0.4	49.5 ± 0.9	5.13^*	10
U	0.29 ± 0.03	0.24 ± 0.01	5.00 ± 0.39	4.06 ± 0.01	$69.8 \pm 3.4^*$	$57.5 \pm 1.8^*$	-	-	7.23^*	20
Zn	8.47 ± 2.11	10.1 ± 0.1	-	-	1.76 ± 0.12	1.95 ± 0.43	74.4 ± 1.7	83.3 ± 3.4	0.50	10
Replicates	N = 8 (ICP-MS) N = 8 (ICP-OES)		N = 4 (ICP-MS) N = 5 (ICP-OES)		N = 7 (ICP-MS) N = 3 (ICP-OES)		N = 3 (ICP-MS) N = 7 (ICP-OES)		-	-

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244 **Table S2.** Analytical performance of solid certified reference materials (CRM: stream sediment DC 73307 and DC 70317, and channel sediment BCR 320R)
 245 after tri-acid (HNO₃/HCl/HF) total digestions (all in mg kg⁻¹ except * in µg kg⁻¹; mean ± standard deviations, SD), including maximum limits of detection
 246 (LOD = 3·SD(blanks) calculated for a typical mass of 30 mg of solid).

Element	DC 73307		DC 70317		BCR 320R		LOD
	Certified	Measured	Certified	Measured	Certified	Measured	
Co	14.4 ± 1.2	13.3 ± 3.6	9.80 ± 0.70	9.61 ± 0.09	9.70 ± 0.60	8.81 ± 0.26	1.47*
Cu	32.0 ± 2.0	32.2 ± 1.1	247 ± 6	248 ± 3	46.3 ± 2.9	44.3 ± 2.3	4.45*
Ni	32.0 ± 2.0	33.3 ± 8.0	20.8 ± 0.7	20.2 ± 0.4	27.1 ± 2.2	25.0 ± 1.7	0.02
Pb	23.0 ± 3.0	18.7 ± 0.9	127 ± 11	127 ± 2	85.0 ± 5.0	86.9 ± 3.0	1.70*
Sb	0.81 ± 0.15	0.72 ± 0.12	4.44 ± 0.44	4.89 ± 0.10	-	-	0.68*
U	2.60 ± 0.40	2.12 ± 0.60	3.40 ± 0.20	2.83 ± 0.30	1.56 ± 0.20	1.28 ± 0.03	0.39*
Zn	78.0 ± 4.0	76.3 ± 7.3	116 ± 4	122 ± 2	319 ± 20	313 ± 8	0.05
Replicates	N = 7 (ICP-MS)		N = 3 (ICP-MS)		N = 4 (ICP-MS)		-

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252 In all extractions of isotopically-labelled sediments, both inherited (Sb_{nat}) and spiked (Sb_{ex})
253 concentrations were determined by using the following approach:

$$254 \quad {}^{121}Sb = Ab_{121nat} \cdot Sb_{nat} + Ab_{121ex} \cdot Sb_{ex}$$

$$255 \quad {}^{123}Sb = Ab_{123nat} \cdot Sb_{nat} + Ab_{123ex} \cdot Sb_{ex}$$

256

257 when the system of two equations and two unknowns is solved:

258

$$259 \quad Sb_{ex} = \frac{{}^{121}Sb \cdot Ab_{123nat} - {}^{123}Sb \cdot Ab_{121nat}}{Ab_{121ex} \cdot Ab_{123nat} - Ab_{123ex} \cdot Ab_{121nat}}$$

260

$$261 \quad Sb_{nat} = \frac{{}^{121}Sb \cdot Ab_{123ex} - {}^{123}Sb \cdot Ab_{121ex}}{Ab_{123ex} \cdot Ab_{121nat} - Ab_{121ex} \cdot Ab_{123nat}}$$

262

263 where all Sb_{ex} and Sb_{nat} correspond to spike and natural Sb concentrations, respectively, ${}^{121}Sb$ and
264 ${}^{123}Sb$ are the concentrations of the respective isotopes as determined by abundance-weighted external
265 calibration curves, i.e., external calibration curves recalculated to represent independent ${}^{121}Sb$ and
266 ${}^{123}Sb$ concentrations, and Ab corresponds to the natural (nat) or spiked (ex) isotopic abundances:
267 $Ab_{121nat} = 0.573$; $Ab_{123nat} = 0.427$; $Ab_{121ex} = 0.0057$; $Ab_{123ex} = 0.9943$.

268

269 3. RESULTS

270 3.1. Fractionation (F2 and F4 extractions) of Fe, Mn and trace elements in sediments from 271 the Gironde and Rhône River systems

272 Sediments from the Garonne/Gironde fluvial estuarine system (KP52 and KP-30) showed
273 systematically higher Fe, Mn and trace element concentrations in all selective extractions and total
274 digestions compared to the Rhône River sediments (TAS, Fig. 2). This difference in the extraction
275 pattern between watersheds was also observed for Al content and is probably due to differences in
276 mineral composition (e.g., Fig. S1) and/or grain size distribution. Sediments of the Gironde Estuary
277 show characteristic particulate organic carbon (POC) contents ranging from 0.05 to 1.5% (Coyne et
278 al. 2016) and grain sizes of mainly silts and some sands (i.e., grain size diameter ranging from 7 to 480
279 μm ; Coyne et al. 2016) whereas the Rhône River sediments show variable POC contents from 1.5 to
280 3.5% for silts (10-15 μm).

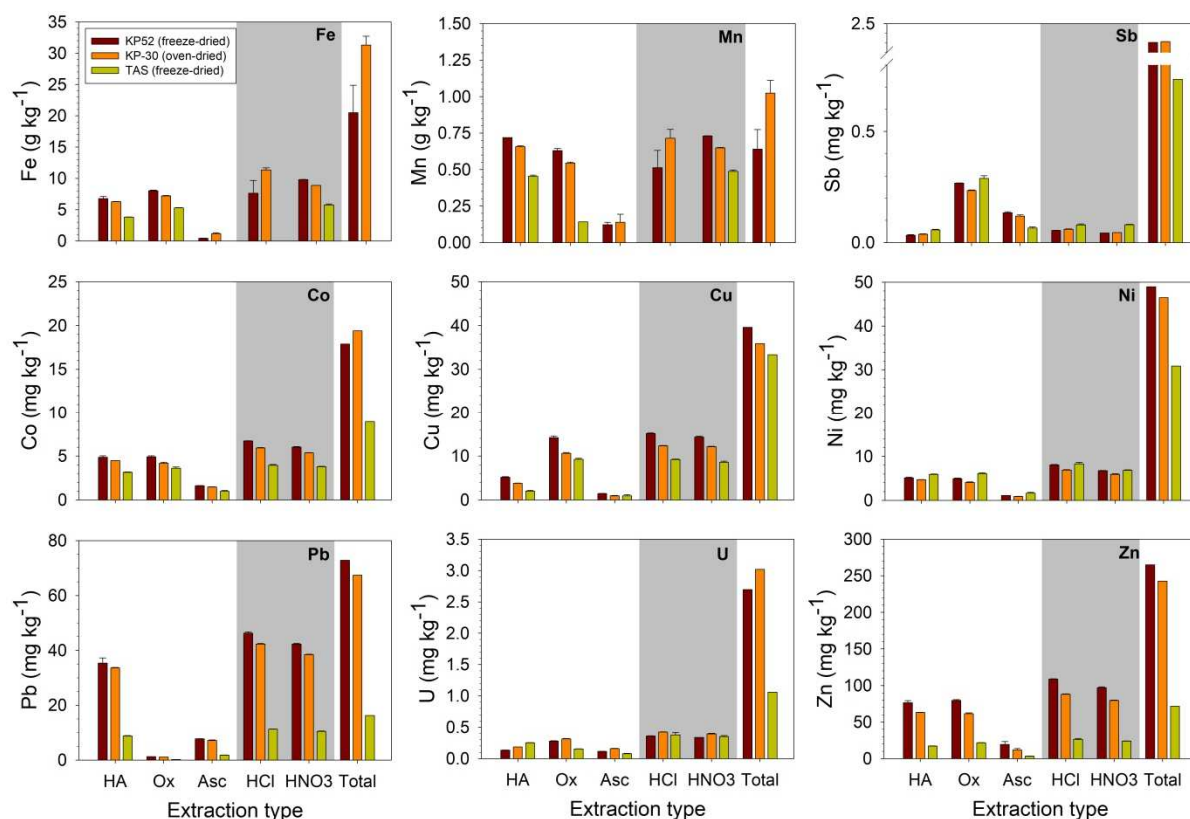
281 Selective extractions targeting Fe/Mn oxides extracted similar amounts of Fe and Mn from Gironde
282 Estuary sediments when using either hydroxylamine or oxalate buffer solutions (Fig. 2). The extracted
283 Fe and Mn fractions were always consistent with, or smaller than, those obtained from the acid
284 extractions (1M HCl and 1M HNO₃, Fig. 2), accounting for ~35% of total Fe content and ~90% of
285 total Mn in the Garonne/Gironde sediments (KP52, KP-30). However, the ascorbate solution always
286 showed lower Fe and Mn extractions, equivalent to ~3% and ~15% of total Fe and Mn concentrations,
287 respectively.

288 Similar to the fractionation pattern of Fe and Mn obtained for F2 and F4 extractions, highest trace
289 element fractions occurred in F4 solutions, with concentrations in hydroxylamine and oxalate
290 solutions similar or slightly lower than those in acid-soluble fractions (Fig. 2). Again, the lowest
291 extraction efficiencies were obtained with the ascorbate solution for all studied trace elements (Co, Cu,
292 Ni, Pb, Zn and U), except Pb in the oxalate extraction (Fig. 2).

293 In contrast, the applied parallel selective extractions showed unexpected results for Sb extractions,
294 with Sb concentrations in the reducible (F2) fractions using oxalate and ascorbate clearly higher than
295 those in the acid-soluble fractions (F4; Fig. 2). In fact, Sb was more efficiently extracted with oxalate
296 (~12% of total Sb in KP52, ~40% in TAS) and ascorbate solutions (~6% of total Sb in KP52, ~10% in
297 TAS) than with hydroxylamine (~1.5% of total Sb in KP52, ~7% in TAS) and 1M acids (~2% of total
298 Sb in KP52, ~10% in TAS). Thus, the detected anomaly is reproducible among sediments, and more
299 pronounced in the Garonne/Gironde fluvial estuarine system than in the Rhône River.

300

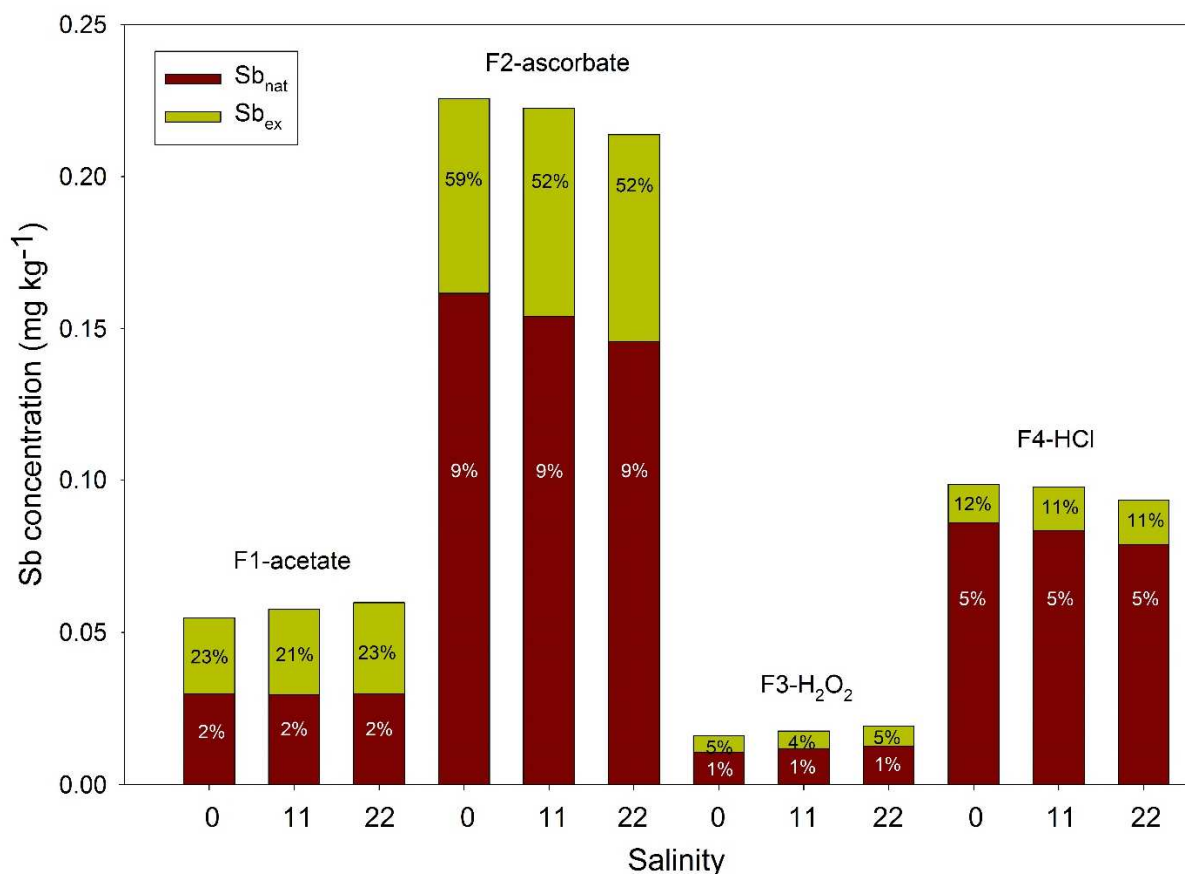
301



302
 303 **Fig. 2.** Selectively extracted and total concentrations (N=3) of Fe, Mn, Co, Cu, Ni, Pb, Sb, U and Zn in
 304 sediments from KP-30 (oven-dried SPM from Portets, Gironde Estuary), KP52 (freeze-dried SPM,
 305 Gironde Estuary) and TAS (freeze-dried SPM from Arles, Rhône River). F2 solutions: HA:
 306 hydroxylamine+HOAc, Ox: oxalate buffer and Asc: ascorbate solution. F4 solutions (in grey area):
 307 1M HCl and 1M HNO₃. Error bars correspond to standard deviations (SD) between replicates.

308
 309 **3.2. Fractionation of natural and spiked Sb adsorbed to SPM in contrasting estuarine**
 310 **conditions**

311 Results from the complete selective extraction scheme (F1 to F4) showed similar fractionation
 312 patterns for spiked Sb (Sb_{ex}) compared to that of inherited/natural Sb (Sb_{nat}), independent from salinity
 313 (Fig. 3). However, the extracted fractions of Sb_{ex} were consistently and clearly higher than those of
 314 Sb_{nat}, with the mobility of Sb_{ex} in the different fractions being between 2-fold (F4) and 10-fold (F1)
 315 greater than that of Sb_{nat}. The highest extracted Sb concentrations occurred in the F2-Asc fraction (i.e.,
 316 reducible Fe/Mn oxides, equivalent to ~55% of total sorbed Sb_{ex} and 10% of total Sb_{nat}), followed by
 317 the F1-acetate fraction (i.e., easily exchangeable and/or carbonate fraction, equivalent to ~22% of total
 318 Sb_{ex} and 2% of total Sb_{nat}). These fractions were higher than the acid-soluble fraction (F4, equivalent to
 319 ~12% of total Sb_{ex} and 5% of total Sb_{nat}). The lowest Sb fractions were obtained within the F3-H₂O₂
 320 fraction (i.e., oxidisable phases, ~5% of total Sb_{ex} and 1% of total Sb_{nat}).



321
 322 **Fig. 3.** Parallel selective extractions of Sb (N = 3) from isotopically-labelled sediments, prepared by 5-
 323 days incubations of SPM = 1000 mg L⁻¹ in three salinity matrices (S=0, S=11 and S=22). Absolute
 324 concentrations (mg kg⁻¹) of Sb_{nat} and Sb_{ex} and fractions (% of total Sb_{nat} and % of total Sb_{ex}) are given.
 325 F1: acetate extracted fraction (“easily exchangeable and/or carbonate fraction”), F2: ascorbate
 326 extracted fraction (“amorphous Fe/Mn oxides and citrate-complexed Sb”), F3: H₂O₂-soluble fraction
 327 (“oxidisable fraction”), F4: 1M HCl-soluble fraction (“potentially bioaccessible”).

328

329 4. DISCUSSION

330 4.1. The F2 fractions obtained from oxalate, hydroxylamine and ascorbate-based reagents

331 The extraction efficiency of the different reagents commonly applied to assess the F2 fraction,
 332 attributed to Fe/Mn oxydes and hydroxides, depends not only on the abundance of Fe and Mn phases
 333 present in the sample but also on their quality in terms of crystallinity degree and the presence of
 334 Fe(II) vs Fe(III) (Stumm and Sulzberger 1992). The results obtained for Fe and Mn in the present
 335 work are widely consistent with a previous comparison of extraction efficiencies of the oxalate- and
 336 ascorbate-based extractions applied to marine sediments (Kostka and Luther 1994). These authors
 337 mentioned that the oxalate extraction might be too strong, due to the presence of Fe(II) minerals
 338 enhancing the oxalate extracting power from other mineral phases such as sulphides, silicates and

339 crystalline Fe oxides (e.g. hematite), which leads to an overestimation of amorphous Fe(III) minerals
340 and underestimating crystalline Fe(III) minerals. To the best of our knowledge, this is the first study
341 directly comparing the parallel extraction efficiencies of oxalate- and ascorbate-based reagents to
342 those of hydroxylamine-based extractions from estuarine and river sediments. The fact that
343 hydroxylamine extracted similar proportions of Fe and Mn as oxalate solutions may suggest that the
344 acid pH of these reagents also contributes to Fe and Mn release from mineral phases other than the
345 targeted amorphous or partially crystalline phases. In fact, the ascorbate solution is the only non-acidic
346 F2 extraction reagent (pH=8). This observation is consistent with Kostka and Luther (1994)
347 highlighting the selectivity and efficiency of the ascorbate solution, dissolving Fe(II) and Fe(III)
348 amorphous (hydr)oxides but not magnetite, or other crystalline Fe phases (at least at pH > 6; Reyes
349 and Torrent 1997), not even other Fe-bearing mineral phases like chlorite (Kostka and Luther 1994).

350 High extraction efficiencies of Mn (~90% Mn extraction out of total Mn) were obtained with the
351 oxalate and hydroxylamine extractions (Fig. 2), showing similar concentrations to those obtained in
352 the acid-soluble fractions (1M HCl and 1M HNO₃). These results are consistent with the acid character
353 of the extractions and the effect of HOAc on carbonates. In fact, Mn is highly present in both oxide
354 and carbonate fractions (Presley et al. 1972). Therefore, the relatively low Mn concentrations obtained
355 from the ascorbate extractions compared to hydroxylamine and oxalate solutions suggest specific
356 solubilisation of poorly crystalline Mn oxides by ascorbate in all sediments.

357 Given the similar values obtained from hydroxylamine and oxalate extractions, the present results
358 suggest that, in parallel extractions, both BCR/Tessier et al. 1979 (cation-adapted) and Wenzel et al.
359 2001 (anion-adapted) protocols are applicable to evaluate Co, Ni, Zn and U fractions bound to
360 amorphous and some crystalline Fe/Mn oxides in sediments from the Garonne/Gironde and Rhône
361 River systems. The lower extraction efficiency of Pb in the oxalate solution may be attributed to Pb-
362 oxalate salt formation (Gleyzes et al. 2002), potentially leading to a 5-fold underestimated Pb fraction
363 in amorphous and partly crystalline oxides, compared to ascorbate extraction. General lower trace
364 element extractions in oven-dried (KP-30) sediments compared to freeze-dried (KP52) sediments are
365 attributed to pre-treatment conditions favouring a transfer of trace elements from the reactive fraction
366 to the residual fraction due to crystallisation of Fe/Mn (hydr)oxides (Gleyzes et al. 2002).

367

368 **4.2. The anomalous fractionation of Sb in F2 and F4 extractions**

369 The operationally defined carrier phases described in classical extraction schemes imply that the
370 acid-soluble fraction (F4; 1M HCl) comprises the fractions extracted by F2 reagents (reduction of
371 amorphous and partly crystalline oxides/hydroxides; Huerta-Díaz and Morse 1990; Snape et al. 2004).
372 The comparison of the results obtained from three different F2 and two different F4 extractions

373 applied to three different sediments confirms this paradigm for Fe and Mn, i.e. the main
374 oxide/hydroxide-forming metals, as well as for a number of trace elements, such as Co, Ni, Zn and U.

375 The observed behaviour of Sb in the same extractions shows that the F4 fraction of Sb cannot
376 entirely comprise the F2 fraction, which can be considered as “anomalous” because it strongly differs
377 from the commonly accepted relative extraction efficiencies of the different reagents. This anomaly is
378 observed in the ascorbate and the oxalate extractions of the Gironde Estuary sediments and the oxalate
379 extraction of the Rhône River sediments, although the latter corresponds to the “anion-adapted” F2
380 protocol proposed for As, the geochemical pair of Sb (Wenzel et al 2001).

381 The encountered inverse relationship between the F2 and F4 fractions of Sb may relate to (i)
382 enhanced Sb solubilisation from non-target carrier phases by oxalate/ascorbate solutions, and/or (ii) Sb
383 losses due to precipitation and/or sorption onto remaining solid phases such as incompletely dissolved
384 mineral phases during F4 acid extractions.

385 Precipitation of Sb in acidic conditions appears unlikely given the low extracted concentrations,
386 probably far from solubility limits (max. $\sim 0.2 \text{ mg kg}^{-1}$ for Sb in KP52, equivalent to $\sim 3 \text{ } \mu\text{g L}^{-1}$ during
387 the extraction). For example, Sb(III) precipitation as Sb_2O_3 at $\text{pH} = 3$ would require relatively high
388 concentrations (e.g., $>63 \text{ } \mu\text{M}$, $\sim 7.6 \text{ mg L}^{-1}$; Leuz 2006). However, given the recommendations to
389 stabilise Sb in highly concentrated standard solutions in dilute HNO_3 by adding HF or organic ligands
390 (e.g., tartrate or citrate/oxalate; www.inorganicventures.com), and the fact that insoluble Sb(V) salts
391 may form in acid conditions (i.e., NaSbO_3 , KSbO_3 or $\text{Mg}^{2+}/\text{Ca}^{2+}$ -related; Blandamer et al. 1974), Sb
392 precipitation cannot be fully excluded.

393 Both HCl and HNO_3 applied separately extract similar Sb concentrations ($\sim 2\%$ of total Sb), despite
394 differences in oxidising power and complexing properties, suggesting that these factors would not
395 influence the supposed precipitation. A combination of hot, concentrated HCl/ HNO_3 (2:1 v/v Aqua
396 Regia at $110 \text{ } ^\circ\text{C}$ during 2 h, N=15) extracted $\sim 18\%$ of total Sb from the same Garonne/Gironde
397 sediments (data not shown), implying that $\sim 80\%$ of total Sb would belong to a residual solid fraction,
398 not extracted by hot Aqua Regia. On the other hand, a total digestion using a mixture of hot
399 HCl/ HNO_3 /HF (section 2.5.) produces full Sb dissolution and recovery in the final solution. As the
400 total digestion protocol includes elimination of both, HF and silicate through volatilisation
401 (evaporation to dryness; Bajo 1978), and subsequent re-dissolution by HNO_3 , neither acid conditions
402 alone nor the absence of HF may explain the low recoveries observed in F4 extractions.

403 The major difference between the hot Aqua Regia extraction and the total digestion was attributed
404 to the presence/absence of silicates after the extraction. The surfaces of such silicates may be modified
405 in acid conditions as applied in the extractions using HCl, HNO_3 and/or Aqua Regia by stripping ions
406 adsorbed. In fact, XRD analyses of the original SPM (KP52, KP-30 and TAS, data not shown) suggest
407 that $\sim 50\%$ of the mineral phases in both SPM types are dominated by phyllosilicates, including illite

408 and muscovite (68% of the clay fraction in KP-30, 83% in TAS), smectite (18% vs <1%, respectively),
409 kaolinite (12% vs 13%, respectively) and chlorite (<2% vs 4%, respectively). Studies on selective
410 extractions of natural sediments also suggest that HCl- and HNO₃-based solutions release major
411 elements (Mg, Fe(II), etc.) from attacked layered/detrital silicates and certain clay minerals (e.g.,
412 Agemian and Chau 1977; Kostka and Luther 1994; Teir et al. 2007). Such activated silicate surfaces
413 would then provide sites for strong Sb sorption under acid conditions. In fact, sorption of Sb(V) to
414 mineral surfaces may be favoured in acid conditions with optimum efficiency at pH 2-4 for activated
415 Alumina (Xu et al. 2001), Kaolinite (Xi et al. 2010) and silicate (Bajo 1978). Accordingly, low Sb
416 recoveries as achieved by the various acid extractions (1M HCl, 1M HNO₃, hot Aqua Regia) were
417 attributed to strong sorption of Sb(V) to activated silicate phases in acid conditions rather than
418 precipitation.

419 The relatively high extraction efficiencies of different F2 extractions may be due to Sb reduction
420 and/or the effect of the complexing agents that were added. Both, reduction and complexation may
421 partly outcompete Sb sorption onto silicate, as suggested by the fact that the ascorbate-extracted Sb
422 fraction (at pH = 8) in Rhône River sediments is similar to the acid-soluble fraction. Hydroxylamine
423 appears to be the weakest reducing/complexing agent for Sb, compared to ascorbate and oxalate.
424 Enhanced Sb solubilisation from non-target carrier phases by oxalate/ascorbate solutions is consistent
425 with observations showing that independent Sb(III) and Sb(V) adsorbed to standard/synthetic goethite
426 were extracted in oxalate buffer solution with 73% extraction of total Sb(III) and 36% of total Sb(V)
427 from an undissolved/unaffected goethite mineral (Leuz 2006). Accordingly, the oxalate-based so-
428 called anion-adapted protocols (Wenzel et al. 2001) would produce higher extractions for Sb in
429 oxalate solutions than the hydroxylamine-based standard BCR procedure and that from Tessier et al.
430 (1979). Leuz (2006) concluded that oxalate buffer solutions are not adequate for Sb selective
431 extractions from amorphous and crystalline operationally defined phases because the oxalate itself
432 directly interacts and desorbs Sb from unreacted mineral phases.

433 White and Rose (1953) observed that both oxalic and citric acids were good complexing agents of
434 Sb for extraction purposes. The presence of citrate as a complexing agent in the ascorbate reagent may
435 enhance its extraction efficiency compared to the inorganic hydroxylamine extraction, implying a
436 citrate-ligand complexing effect on Sb from non-attacked mineral phases. In fact, citrate is used as a
437 complexing agent for Sb speciation in analytical chemistry (e.g., HPLC-ICP-MS and in hydride
438 generation; Potin-Gautier et al. 2005). The citrate-effect would be due to complexation, rather than
439 changes in Sb redox state, as citrate does not induce transformations in Sb(V) and Sb(III) redox
440 species (Mohammad et al. 1990; Potin-Gautier et al. 2005). The use of citrate in selective extractions
441 is pertinent concerning the environmental implications of selective extractions because citrate is
442 present and active in several environmental compartments: involved in cellular metabolic pathways
443 (e.g., in oysters; Ivanina et al. 2011), as part of the estuarine dissolved organic matter from terrestrial

444 plant exudates (Mucha et al. 2010) and in H₂S-producing bacteria in estuarine sediments (Jyothsna et
445 al. 2013).

446 Antimony complexation by citrate and other organic ligands would be more efficient under acidic
447 conditions, as observed for Sb(III) (Stumm and Sulzberger 1992, Filella and May 2005) and for the
448 less studied Sb(V) (e.g., Hansen and Pergantis 2006; Tella and Pokrovski 2012). Even at pH=8
449 (ascorbate extraction) one cannot exclude enhanced citrate-related Sb solubility and (non-specific)
450 mobilisation from other mineral phases. As such, organic complexation may partly explain the
451 differences observed for the three F2 solutions tested. Previous work on Sb fractioning by oxalate
452 and/or ascorbate (F2) and dilute HCl (F4) extractions have not identified such inconsistencies because
453 of limited sensibility in Sb detection (Prieto 1998) and/or because these extractions were performed
454 sequentially (Manaka et al. 2007), which masks selectivity biases. To the best of our knowledge, there
455 is to date no published work on Sb fractionation using parallel F2 and F4 extractions which might
456 provide additional information.

457

458 **4.3. Solid fractionation of natural and anthropogenically added Sb**

459 Sediment contamination by a hypothetical anthropogenic release of dissolved Sb into the Gironde
460 Estuary was mimicked by exposing fresh KP52 SPM (~1g L⁻¹ SPM) to isotopically-labelled ¹²³Sb at
461 three salinity conditions (0, 11 and 22). The amount of isotopically-labelled Sb spiked to the sediments
462 of the Gironde Estuary was ~5% of the total Sb available in the solution, whatever the salinity.
463 Assessment of solid fractionation of both inherited and spiked Sb by a complete parallel selective
464 extraction scheme (F1 to F4) showed that the studied SPM can adsorb anthropogenic Sb in addition to
465 their inherited Sb load.

466 In the present work, the fractionation results obtained from parallel extractions suggest that both,
467 inherited and spiked (isotopically-labelled) Sb were present in all fractions, including the residual
468 fraction (i.e. not extracted by 1M HCl), representing 90% of the spiked Sb. This result was rather
469 surprising, as one would expect the spiked Sb to adsorb onto reactive carrier phases and not to the so-
470 called residual fraction. This observation and previously reported incomplete recoveries of spiked Sb
471 (Brannon and Patrick 1985) support the above hypothesis of strong Sb sorption on silicate surfaces
472 (section 4.2.), resulting in incomplete recovery by conventional protocols targeting the acid-soluble
473 fractions and even the oxalate-extracted F2 fraction. The inherited Sb in SPM from the Gironde
474 Estuary was mostly (~95%) in the residual fraction, which is consistent with the majority of published
475 Sb fractionation results (Filella 2011). However, given the above considerations, one cannot exclude
476 that the acid-soluble fraction may strongly underestimate the potentially reactive Sb in natural
477 sediments. These findings imply that the existing estimates of the potentially bioaccessible Sb
478 fractions in sediments may be widely biased and that there is a need for a deeper understanding of the

479 (i) interactions between Sb and the respective potential carrier phases, and (ii) efficiencies of selective
480 extraction techniques in view of future ecological risk assessment of Sb contamination by both, stable
481 isotopes and Sb radionuclides.

482 The applied extractions also showed that the ascorbate-extracted and the acid-soluble fractions are
483 the most important reactive fractions for inherited Sb. However, the isotopically-labelled Sb had the
484 highest recoveries in the ascorbate-extracted (F2: ~52%) and acetate-extracted (F1: ~21%) fractions
485 (Fig. 3). This observation suggests that anthropogenic Sb readily adsorbs to the most reactive carrier
486 phases and that anthropogenic Sb is potentially more mobile than inherited Sb in reducing
487 environments (such as systems presenting early diagenetic processes) and/or in the presence of organic
488 complexes.

489

490 **5. CONCLUSIONS**

491 Selective extraction F2 protocols using strong organic ligands (i.e. citrate and oxalate) tend to
492 overestimate the fraction of Sb associated to the target operationally defined carrier phases (i.e. non-
493 selective extraction of Sb occurs from undestroyed carrier phases), compared to hydroxylamine. The
494 fractions of both, inherited and spiked Sb extracted by F2 protocols using organic ligands are even
495 greater than the acid-soluble F4 fractions, which is not consistent with the extraction efficiencies for
496 target carrier phases as commonly observed for other trace elements. This anomaly also occurs for the
497 so-called anion-adapted protocol developed for As, the geochemical pair of Sb, and only becomes
498 visible in parallel extraction approaches. Sequential methods are probably subjected to the same
499 artefact, but do not allow identifying it.

500 Low recoveries of both inherited and spiked Sb in the acid-soluble fractions suggest Sb losses,
501 implying the risk of systematic underestimation of the potentially bioaccessible fraction, when
502 applying traditional extraction schemes. This may have consequences on the mobility- and ecological
503 risk assessment of anthropogenically released Sb (stable isotopes and radionuclides) into aquatic
504 environments.

505 Further research on the mechanisms involved in the selective dissolution of Sb is a prerequisite for
506 the development of (i) a specific extraction scheme reliably simulating environmental Sb carrier
507 phases and behaviour, and (ii) future understanding of the consequences of anthropogenic Sb inputs
508 into the environment. The application of commonly accepted extraction schemes to “new” elements,
509 such as emerging trace element contaminants, for which the protocols were not originally developed,
510 adapted and tested, implies the risk of producing biased results and interpretations.

511

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521

522

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