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# Particle-water interactions of bismuth under simulated estuarine conditions

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1 **Particle-water interactions of bismuth under**  
2 **simulated estuarine conditions**

3

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13

## 14 **Abstract**

15 Although the production and usage of bismuth (Bi) have been increasing, very little is known about  
16 the environmental behaviour of this heavy metal. In the present study, the particle-water  
17 interactions of Bi are examined under controlled conditions in which the metal is added as a tracer  
18 to estuarine sediment suspended in different, environmentally-relevant aqueous solutions.  
19 Adsorption isotherms were always linear over the Bi concentration range employed (up to 2000  $\mu\text{g L}^{-1}$ )  
20 and sediment-water distribution coefficients derived from isotherm gradients,  $K_D$  ( $\text{L kg}^{-1}$ ), displayed  
21 an inverse dependence on pH in river water (and ranging from  $K_D = 106,000 \text{ L kg}^{-1}$  at pH 5.0 to  $K_D =$   
22  $17,700 \text{ L kg}^{-1}$  at pH 9.0) that were consistent with the adsorption of hydroxo-complexes to the  
23 sediment surface. Higher adsorption in ultra-pure water of the same pH as river water and an order  
24 of magnitude increase in adsorption in seawater at pH 8.0 ( $K_D = 1,530,000 \text{ L kg}^{-1}$ ) and 0.7 M  $\text{NaNO}_3$  at  
25 pH 6.5 ( $K_D = 4,290,000 \text{ L kg}^{-1}$ ), however, required the presence of additional species or processes that  
26 are likely related to organic complexation of the metal. Thus, experiments conducted in mixtures of  
27 river water and seawater in the absence of sediment suggested that Bi may also be bound to  
28 colloidal organic molecules that undergo flocculation and salting out on estuarine mixing. Compared  
29 with other metals studied under similar conditions, Bi displays a high reactivity towards sediment  
30 particles and is, therefore, predicted to be retained in estuaries to a significant extent from  
31 catchment sources.

32 **Keywords:** bismuth; adsorption; rivers; estuaries; sediment; flocculation

33

## 34 **1. Introduction**

35 Bismuth is the heaviest element in Group 15 of the Periodic Table whose only naturally occurring  
36 isotope ( $^{209}\text{Bi}$ ) is extremely weakly radioactive and decays with a half-life of about  $2 \times 10^{19}$  years  
37 (Beeman et al., 2012). Bismuth is widely distributed in the environment with an average crustal  
38 abundance of 0.2 ppm (Das et al., 2006) but also occurs in bismite ( $\text{Bi}_2\text{O}_3$ ) and bismuthinite ( $\text{Bi}_2\text{S}_3$ )  
39 from which it may be obtained as a by-product of copper and lead ores (Ayres and Hellier, 1998).  
40 Although Bi can exist in a number of oxidation states, the trivalent form is the most stable in the  
41 environment; this contrasts with the Group 15 metalloids, As and Sb, whose most stable state is the  
42 pentavalent (Filella, 2010).

43 Bismuth has no known biological role and is believed to be the least toxic heavy metal to humans,  
44 although some toxicity is exhibited towards certain bacteria and macroalgae (Kearns and Turner,  
45 2016). Its antibacterial properties have been exploited in pharmaceutical products treating bacterial

46 infections as well as medications treating ulcers and gastrointestinal disorders (Tremaine, 2000;  
47 Kotani et al., 2005). Bismuth and its compounds are also used in cosmetics, paints, fusible alloys,  
48 catalysts and semiconductors (Ayres and Hellier, 1998), and recently Bi has gained popularity as a  
49 non-toxic replacement for lead in upland and waterfowl hunting shot (Fahay et al., 2008).

50 Despite these applications and a sharp increase in the recent global production of Bi to over 13,000  
51 tonnes in 2015 (Kelly and Matos, 2017), there exists very little information on the environmental  
52 behaviour of the metal. Filella (2010) suggests that this is due to low concentrations in the  
53 environment, often attributed to the insolubility of its compounds, and low toxicity to humans. Her  
54 review of concentrations of Bi in natural waters revealed a wide dispersion of values (but usually < 1  
55  $\mu\text{g L}^{-1}$ ), which can be partly accounted for by external contamination during sampling and analysis  
56 and by lack of information provided on whether or how samples were filtered. Moreover, an  
57 examination of stability constants used in aqueous speciation calculations were found to be  
58 indirectly sourced from a limited number of old references, one of which when translated from  
59 Russian was found to contain an important error that was subsequently reproduced in the key  
60 reference work of Ahrens (1968). Filella (2010) also suggests that no studies of Bi adsorption to  
61 heterogeneous solids had been undertaken and that the metal had been overlooked in sorption  
62 constant estimations derived from free energy regressions. To our knowledge, the only adsorption  
63 experiments conducted with Bi are reported by Ulrich and Dedueidre (1993). Here, the interactions  
64 of  $^{210}\text{Bi}$  (as a radiotracer) with montmorillonite clay were examined under varying conditions of pH  
65 and ionic strength. Distribution coefficients derived from adsorbed to aqueous concentration ratios  
66 and ranging from  $10^4$  to  $10^7 \text{ L kg}^{-1}$  were later employed by Serne (2007) in order to evaluate the fate,  
67 transport and risk of Bi in agricultural soils and river bank sediments.

68 Because of the dearth of information on the behaviour of Bi in the natural environment, the present  
69 study set out to systematically examine the adsorption of the metal to estuarine sediment under  
70 different conditions of pH, ionic composition and salinity. The study employs protocols that we have  
71 adopted before and relies on the addition of the metal as a tracer to aqueous suspensions and at  
72 concentrations that are detectable by quadrupole ICP-MS (Turner, 2007; Turner et al., 2010). The  
73 sorption constants derived will enable the transport and fate of Bi to be evaluated and modelled  
74 more accurately in rivers and estuaries, and will improve our more general understanding of the  
75 behaviour of Bi in the aquatic environment.

76

## 77 **2. Methods**

78 *2.1. Sampling*

79 River water used in the experiments was collected on a weekly basis between May and July 2019 in a  
80 5-L high density polyethylene carboy from the Erme near Ivybridge, southwest England (50.388313, -  
81 3.9215163). Here, the bed profile is of low permeability, being comprised of large granite boulders  
82 derived from the protected moorland of central southern Dartmoor (a National Park), and average  
83 river flow is  $1.95 \text{ m}^3 \text{ s}^{-1}$  (National Flow River Archive, 2017). About 0.5 kg of surficial, oxic sediment  
84 from the protected saltmarshes of the upper Erme estuary (50.332221, -3.9337894) was sampled  
85 using a tapered plastic spatula and stored in a zip-locked polyethylene bag. Seawater was available  
86 on tap in the laboratory having been previously collected in bulk from the English Channel.

87

88 *2.2. Sample processing and characterisation*

89 River water and seawater were vacuum-filtered through  $0.45 \mu\text{m}$  cellulose acetate filters into a  
90 series of acid-cleaned 1-L polyethylene bottles and used within 24 hours. Estuarine sediment was  
91 sieved through a  $63 \mu\text{m}$  nylon mesh with the aid of filtered river water and transferred to a series of  
92 50 mL Fisherbrand screw-capped polypropylene centrifuge tubes. The contents of each tube were  
93 centrifuged for 20 minutes at 3500 rpm before supernatants were poured off and remaining  
94 sediment frozen until required.

95 The pH and conductivity (hence salinity) of aqueous samples were determined using colour-fixed  
96 indicator sticks or a Jenway 3305 probe and a YSI 85 conductivity meter, respectively. The presence  
97 of Bi was checked by inductively coupled plasma-mass spectrometry (ICP-MS; see below) after 10 mL  
98 of filtered river water had been spiked with  $100 \mu\text{L}$  of concentrated HCl (VWR ARISTAR) and 2 mL of  
99 filtered seawater had been diluted to 10 mL with 1M HCl. A subsample of fractionated sediment was  
100 thawed out and homogenised using a plastic spatula before  $\sim 1 \text{ g}$  aliquots were used to determine  
101 moisture content on drying at  $105 \text{ }^\circ\text{C}$  for 24 hours, loss on ignition after combustion at  $550^\circ\text{C}$  for 4  
102 hours, and mean particle diameter using a Malvern Instruments Hydro 2000G Mastersizer. In  
103 triplicate, 0.5 g of dried sediment and 0.25 g of a certified reference sample (SS-2 Contaminated Soil,  
104 140-025-002) were digested in 10 mL of boiling aqua regia (VWR ARISTAR HCl and  $\text{HNO}_3$ ) in 50 mL  
105 Pyrex beakers covered with watch glasses; controls were performed likewise but in the absence of  
106 solids. The cooled digests were filtered through Whatman  $85 \text{ g m}^{-2}$  acid-resistant circles and diluted  
107 to 50 mL with Millipore Milli-Q water (MQW). Concentrations of Bi and a suite of other elements  
108 were determined in the diluted digests by ICP-MS (see below).

109

### 110 2.3. Adsorption experiments

111 The general approach for the adsorption isotherm experiments was adapted from Turner et al.  
112 (2010) as follows. A 100 mg L<sup>-1</sup> working solution of Bi was prepared in a 50 mL volumetric flask by  
113 diluting 500 µL of 10,000 mg L<sup>-1</sup> Bi standard (VWR ARISTAR) in filtered river water. Meanwhile, a  
114 slurry stock of ~ 4 g dry sediment L<sup>-1</sup> was prepared by adding 0.5 ± 0.05 g of thawed sediment to 50  
115 mL of filtered river water in a volumetric flask. To a series of screw-capped 50 mL polypropylene  
116 centrifuge tubes, 1 mL of slurry stock was diluted in 40 mL of river or sea water to give a particulate  
117 concentration on a dry weight basis of ~ 100 mg L<sup>-1</sup>. Bismuth was pipetted to the centrifuge tubes  
118 from the working standard to produce a concentration series ranging from 10 to 2000 µg L<sup>-1</sup>, with  
119 two concentrations in each isotherm performed in triplicate. The centrifuge tubes were  
120 subsequently agitated at room temperature (~ 20 °C) and in the dark in the horizontal position on a  
121 lateral shaker for 16-18 h at 100 rpm. Following incubation, particulate and aqueous phases were  
122 separated by vacuum-filtration through 0.45 µm cellulose acetate membranes. Ten mL filtrate  
123 aliquots were transferred to 30 mL Thermo Scientific polystyrene Sterilin tubes and acidified with  
124 100 µl of concentrated HCl. Filters were transferred to Sterilin tubes and Bi was extracted for 18 h in  
125 10 mL of 1M HCl and 10 mL of 1M HNO<sub>3</sub>.

126 This process was repeated using MQW in place of river water, and after adjusting (and, if necessary,  
127 maintaining) the pH of river water to 5 and 9 by dropwise addition of 1M HNO<sub>3</sub> and 1M NaOH,  
128 respectively. Experiments were also repeated in seawater and using solutions of 0.7 M NaCl (Fisher  
129 Scientific Extra Pure) and 0.7 M NaNO<sub>3</sub> (VWR AnalaR) but with 4 mL filtrates diluted to 20 mL in 1M  
130 HCl. Bismuth adsorption was also studied at a single concentration (1000 µg L<sup>-1</sup>) across the estuarine  
131 gradient in 50 mL solutions of salinities 0, 2, 5, 10, 15, 20 and 30 created by mixing filtered river  
132 water and filtered seawater end-members in different proportions. This process was also repeated  
133 in the absence of sediment in order to evaluate the extent of flocculation and filter adsorption of the  
134 metal. To assess the significance of container adsorption, the emptied centrifuge tubes arising from  
135 various experiments and different added Bi concentrations were extracted with 25 mL of 20% HNO<sub>3</sub>  
136 for 16-18 h under lateral agitation at 100 rpm.

### 137 2.4. ICP-MS analysis

138 Acidified and diluted filtrates, filter extracts, centrifuge tube extracts, and sediment digests and  
139 controls (and any dilutions thereof) were analysed in triplicate for Bi (and, for sediment digests, Al,  
140 As, Ca, Fe, Mn and Sb) by ICP-MS using a Thermo Scientific iCAP TQ with a concentric glass nebuliser  
141 and cyclone spray chamber. The instrument was calibrated using blanks and standards of 1, 4, 10,  
142 40, 100 and 400 µg L<sup>-1</sup> prepared in either 2% HNO<sub>3</sub> or diluted and acidified sea water, while internal

143 standardisation was achieved by addition of  $20 \mu\text{g L}^{-1}$  of Ir to all samples and standards. Instrument  
144 drift was monitored with standard checks after every ten samples, with reanalysis performed if  
145 deviation of more than 10% from the expected value occurred. Elemental concentrations returned  
146 for the certified reference soil were within stated tolerance intervals with the exception of Bi (no  
147 natural geosolid appears to be certified with respect to this metal). Under conditions where Bi  
148 adsorption was replicated ( $n = 3$ ), precision, as relative standard deviation, ranged from 5.1 to 28.2%  
149 (median = 12.6%) for the aqueous phase and 2.3 to 46.4% (median 12.5%) for filter extracts.

### 150 **3. Results**

#### 151 *3.1. Sample characteristics*

152 The pH of filtered Erme river water used in the experiments ranged from 6.2 to 6.5, while  
153 conductivity varied from  $63.5$  to  $107 \mu\text{S cm}^{-1}$ , and the pH and salinity of filtered English Channel  
154 seawater were 8.0 and 30.8, respectively. Although dissolved organic matter was not determined in  
155 the aqueous samples, previous measurements of dissolved organic carbon performed in adjacent  
156 rivers draining the same region of Dartmoor and in the local coastal region of the English Channel  
157 indicate typical values of about  $1.7$  and  $1.4 \text{ mg L}^{-1}$ , respectively (Rawling et al., 1998). The mean,  
158 background concentration of Bi in river water was  $0.28 \pm 0.01 \mu\text{g L}^{-1}$  but in seawater the metal was  
159 below the detection limit of  $< 0.05 \mu\text{g L}^{-1}$ .

160 The fractionated estuarine sediment used in the experiments had a median particle size of  $19.3 \mu\text{m}$   
161 and a moisture content of 59.9%, with a combustible mass when dry (i.e. organic content) of 13.3%.  
162 Dry weight concentrations of Al, Ca, Fe and Mn (in  $\mu\text{g g}^{-1}$  and as the mean  $\pm$  one standard deviation  
163 of three determinations) were  $17,500 \pm 185$ ,  $2670 \pm 9.1$ ,  $41,700 \pm 97.1$  and  $332 \pm 2.54$ , respectively,  
164 while concentrations of Bi and the other group VA elements, As and Sb, were  $0.23 \pm 0.09$ ,  $2.49 \pm 0.86$   
165 and  $3.12 \pm 0.35$ , respectively.

#### 166 *3.2. Container adsorption*

167 Although the aims of the study were to define the adsorption characteristics of Bi to estuarine  
168 sediment, it is useful, more generally, to understand how the metal behaves under controlled and  
169 contained laboratory conditions, and in particular whether there is any loss to non-environmental  
170 phases such as the reactor vessel or filter membrane. Mass balance considerations from the  
171 isotherm experiments revealed average percentages of added Bi that could not be accounted for in  
172 the sediment and aqueous phases ranging from about 26 to 64 (Table 1) but there was no clear  
173 relationship with the pH or ionic strength of the solution or the quantity of Bi added. Subsequent  
174 acid-washing of selected emptied centrifuge tubes revealed that the majority of Bi lost had

175 undergone heterogeneous adsorption to container surfaces, with analysis of filters arising from  
176 experiments conducted in the absence of sediment revealing additional loss of the metal to the  
177 membranes but not quantitatively attaining complete mass balance. Thus, it is critical to measure  
178 the distribution of Bi in all environmental phases considered in laboratory experiments as estimates  
179 relying on difference would lead to significant errors in constants defining adsorption processes.

### 180 *3.2. Adsorption isotherms*

181 Isotherms for Bi adsorption to fractionated estuarine sediment are shown for MQW at pH 6.5 and  
182 river water over a range of pH values in Figure 1. Here, concentrations of Bi extracted from sediment  
183 and normalised to dry mass,  $[Bi]_{ads}$ , are shown as a function of Bi concentrations measured in the  
184 aqueous phase,  $[Bi]_{aq}$ , after a 16-18 h incubation period. Note that in MQW, the full data set is not  
185 shown as the higher concentrations of added Bi were accompanied by significant shifts in aqueous  
186 pH. Isotherms were best defined by a linear model in all cases, with slopes of the relationships used  
187 to derive the sediment-water distribution coefficients,  $K_D$  (in  $L\ kg^{-1}$ ):

$$188\ K_D = [Bi]_{ads} * 10^3 / [Bi]_{aq}$$

189 shown in Table 2. Adsorption of Bi increases with a reduction in pH and from a  $K_D$  of  $17,700\ L\ kg^{-1}$  at  
190 pH 9.0 to a  $K_D$  of  $106,000\ L\ kg^{-1}$  at pH 5.0, but amongst all freshwater media is greatest in MQW ( $K_D =$   
191  $113,000\ L\ kg^{-1}$ ) in which contaminant ions and organic matter are absent.

192 Adsorption isotherms are shown for seawater at pH 8.0 and for aqueous solutions of NaCl and  
193  $NaNO_3$  of equivalent ionic strength (but lower pH) in Figure 2. Note here that aqueous  
194 concentrations, but not particulate concentrations, are considerably lower than those measured in  
195 freshwater above (despite no clear differences in Bi recovery amongst different media reported in  
196 Table 1). Consequently, isotherm slopes and values of  $K_D$  (shown in Table 2) are at least an order of  
197 magnitude higher than those derived in river water and MQW.

### 198 *3.3. Particle-water interactions along the estuarine gradient*

199 Values of  $K_D$ , derived from concentration ratios of Bi extracted from sediment to Bi measured in the  
200 aqueous phase and for an added Bi concentration of  $1000\ \mu g\ L^{-1}$ , are shown after logarithmic  
201 conversion as a function of salinity in Figure 3. Here, the x-axis represents the estuarine gradient, or  
202 the extent of mixing of river water and seawater end members. The logged  $K_D$  data exhibit a  
203 significant and positive linear relationship with salinity defined by a slope of 0.0615 and an intercept  
204 of about 4. In Figure 4, the percentage of Bi added at a concentration of  $1000\ \mu g\ L^{-1}$  that is retained  
205 by filtration but in the absence of estuarine sediment is shown along the estuarine gradient.  
206 Percentages are lowest at the end-members where they may be attributed to filter adsorption and,



207 possibly, precipitation, and are enhanced by end-member mixing, with values exceeding 70% in the  
208 mid-estuarine region.

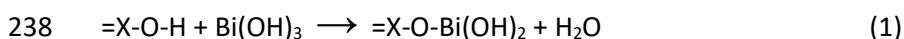
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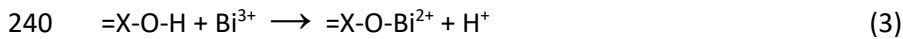
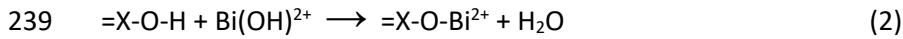
#### 210 **4. Discussion**

211 The findings of the present work indicate substantive loss of Bi to container surfaces, an effect that  
212 has been reported for glass and plastic in previous analytical and experimental studies of the metal  
213 in freshwater and seawater (Lee, 1982; Ulrich and Deguelde, 1993). Clearly, studies involving Bi as a  
214 tracer under contained experimental conditions require careful consideration of reactor adsorption  
215 and the direct analysis of all environmental phases involved. With respect to adsorption studies, it is  
216 critical that both particulate and aqueous Bi are measured and that derivation of concentrations  
217 does not rely on difference. Isotherms reported here and determined directly define the adsorption  
218 of Bi to fractionated estuarine sediment suspended in various environmentally relevant solutions  
219 and appear to be the first documented for this metal using a natural sorbent. That isotherms are  
220 linear suggests binding sites at the particle surface are not limited for Bi, at least over the  
221 concentration range studied, and adsorption constants derived are likely to be applicable at lower,  
222 more environmentally realistic concentrations of the metal.

223 Increasing adsorption of Bi (as  $K_D$ ) with decreasing pH and increasing salinity are not consistent with  
224 the adsorption of metal cations to soils or sediment. Here, adsorption is predicted to increase with  
225 pH as binding sites become progressively deprotonated and to decrease with increasing salinity  
226 because of competitive adsorption with seawater cations and complexation seawater anions (Peng  
227 et al., 2003; Zwolsman et al., 1997). For Bi, therefore, additional or alternative adsorbing species  
228 appear to be significant in sediment-water suspensions under the conditions tested.

229 Unfortunately, the aqueous speciation of Bi is poorly understood, and relevant constants appear to  
230 have been taken, often indirectly or inappropriately, from old sources (Filella, 2010). What is known  
231 is that  $\text{Bi}^{3+}$  is stable under only strongly acidic conditions and with increasing pH there is an increase  
232 in the variety and abundance of hydroxo-complexes. Under near-neutral freshwater conditions  
233 similar to those adopted herein, calculations undertaken by Ulrich and Deguelde (1993) indicate that  
234 99.9% of the metal should exist as  $\text{Bi}(\text{OH})_3$ , with the remainder comprised of  $\text{Bi}(\text{OH})^{2+}$  and a  
235 vanishingly small quantity of free  $\text{Bi}^{3+}$ . The authors suggest that adsorption can be modelled as a  
236 series of quasi-irreversible complexation reactions that, with respect to the sediment surface,  $=\text{X}$ ,  
237 can be written as follows:





241 Presumably, the dependence of Bi adsorption on pH arises from shifts in the aqueous speciation of  
242 the metal and differences in the complexation constants of each reaction. Specifically, higher  
243 adsorption at pH 5 may be attributed to the greater relative abundance of  $Bi^{3+}$  and a relatively high  
244 complexation constant for reaction 3, while lower adsorption at pH 9 may be attributed to the  
245 greater relative abundance of  $Bi(OH)_3$  and a relatively low complexation constant for reaction 1. The  
246 neutral hydroxide is also likely to be subject to non-specific sorption to the hydrophobic container  
247 surfaces and may explain the loss of Bi observed in the experiments.

248 In seawater, the same species, plus  $Bi(OH)_4^-$ , have been proposed (Byrne, 2002). Because of the  
249 higher pH of seawater than MQW or river water, a reduction in adsorption with increasing salinity  
250 would be predicted on the basis of the arguments above. However, an exponential increase in  $K_D$   
251 across the estuarine gradient (Figure 3) requires that additional species or processes are present. It  
252 has been suggested that cationic chloro-complexes or oxychloro-complexes of high reactivity occur  
253 in seawater (Bertine et al., 1996; Kabata-Pendias and Mukherjee, 2007) but similar adsorption of Bi  
254 observed in solutions of NaCl and  $NaNO_3$  shown in Figure 2 imply that the distribution of  $K_D$  across  
255 the estuarine gradient may be related to ionic strength. Significantly, we note a doubling in  
256 adsorption (as  $K_D$ ) of Bi to montmorillonite from ionic strengths of 0.01 M to 0.2 M reported in Ulrich  
257 and Degueldre (1993) although no explanation is proposed by the authors.

258 Although Bi is known to bind with functional groups on the surfaces of macroalgae (Kearns and  
259 Turner, 2016), no information exists in the literature on the complexation of Bi by dissolved organic  
260 ligands in the environment. The results presented here, however, suggest that the metal is able to  
261 interact with dissolved organic matter in different ways. Thus, firstly, higher adsorption in MQW  
262 than in river water at the same pH (Table 1) suggests that natural organic ligands compete with  
263 adsorption sites on the sediment surface for aqueous Bi and act to stabilise a fraction of the metal in  
264 solution. Secondly, the capture of significant quantities of Bi on filters arising from the mixing of end-  
265 members in the absence of sediment (Figure 4) suggests that associations of Bi with macromolecular  
266 organic matter in river water are destabilised by the addition of seawater ions and are subject to  
267 flocculation or coagulation (Zwolsman et al., 1997; Windom et al., 1999). Thirdly, the exponential  
268 increase in  $K_D$  with increasing salinity is consistent with a modified version of the Setschenow  
269 equation and suggests that organic complexes of Bi may be subject to salting out through  
270 electrostriction (Turner et al., 2001).

271 Despite uncertainties in the aqueous speciation of Bi and the mechanisms by which it interacts at  
272 the particle surface, it is clear that the metal has a high affinity for sediment compared with other  
273 metals. Figure 5 compares  $K_D$  values for Bi derived here with those for a variety of metals studied as  
274 tracers (including radiotracers) in suspensions of estuarine sediment from the Plym (adjacent to the  
275 Erme) in Plym river water and English Channel seawater undertaken under otherwise identical  
276 conditions. Thus, in river water  $K_D$  is greatest for Bi but similar in magnitude to values for Cd, Hg and  
277 Zn, while in seawater  $K_D$  is greatest for Bi among the metals by almost an order of magnitude.  
278 Bismuth is, therefore, highly particle active and estuaries are predicted to be important sinks for  
279 river borne sources of the metal. These assertions are consistent with an oceanic input of the metal  
280 that is believed to be dominated by an aeolian, and probably volcanic, pathway (Lee et al.,  
281 1985/1986), and an estimated oceanic residence time of only 20 years (Bertine et al., 1996).

282

## 283 **5. Conclusions**

284 Very limited thermodynamic or empirical information exists relating to the behaviour of Bi in the  
285 aquatic environment. Here, it has been shown that Bi, added as a tracer, has a high affinity for  
286 sediment suspended in natural and synthetic media, with sediment water distribution coefficients of  
287 about  $70,000 \text{ L kg}^{-1}$  in river water at pH 6.5 (and that display an inverse dependency on pH between  
288 5.0 and 9.0) and  $1,500,000 \text{ L kg}^{-1}$  in sea water. Adsorption is attributed to the complexation of  
289 various species (believed to be mainly hydroxides) at the particle surface. Results also indicate that a  
290 significant fraction of added Bi undergoes flocculation when the salinity of river water is increased,  
291 suggesting that Bi has some affinity for organic molecules that are destabilised as the concentration  
292 of aqueous ions is increased. With an increase in the global production and usage of Bi, further  
293 studies that better define its aqueous speciation and environmental fate are called for.

294

## 295 **Declaration of competing interest**

296 The authors declare that they have no known competing financial interests or personal relationships  
297 that could have influenced the findings of the study.

298

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302

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362 Zwolsman, J.J.G., Van Eck, B.T.M., Van der Weijden, C.H., 1997. Geochemistry of dissolved trace  
 363 metals (cadmium, copper, zinc) in the Scheldt estuary, southwestern Netherlands: Impact of  
 364 seasonal variability. *Geochimica et Cosmochimica Acta* 61, 1635-1652.

365 Table 1: Percentage of added Bi (as mean  $\pm$  one standard deviation) that was unaccounted for in the  
 366 isotherm experiments conducted in suspensions of fractionated estuarine sediment suspended in  
 367 different aqueous solutions.

aqueous solution	pH	% unaccounted
MQW	6.5	35.2 $\pm$ 10.7
river water	6.5	48.0 $\pm$ 9.0
	9.0	39.6 $\pm$ 15.0
	5.0	26.2 $\pm$ 7.7
seawater	8.0	33.9 $\pm$ 9.7
	6.5	52.8 $\pm$ 8.8
0.7 M NaNO <sub>3</sub>	6.5	52.8 $\pm$ 8.8
0.7 M NaCl	6.5	63.5 $\pm$ 11.8

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371 Table 2: Sediment-water distribution coefficients defining the slopes of the isotherms in Figures 1  
 372 and 2 along with goodness of fits to the data (note that  $p < 0.01$  in all cases).

aqueous solution	pH	$K_D$ , L kg <sup>-1</sup>	$r^2$
MQW	6.5	113,000	0.992
river water	6.5	68,100	0.968
	9.0	17,700	0.974
	5.0	106,000	0.907
seawater	8.0	1,530,000	0.872
	6.5	4,290,000	0.995
0.7 M NaNO <sub>3</sub>	6.5	4,290,000	0.995
0.7 M NaCl	6.5	3,170,000	0.994

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Figure 1: Isotherms for Bi adsorption to fractionated sediment suspended in different freshwater solutions. Solid lines denote best fits by linear regression analysis whose slopes (as  $K_D$ ) and goodness of fits are shown in Table 2.

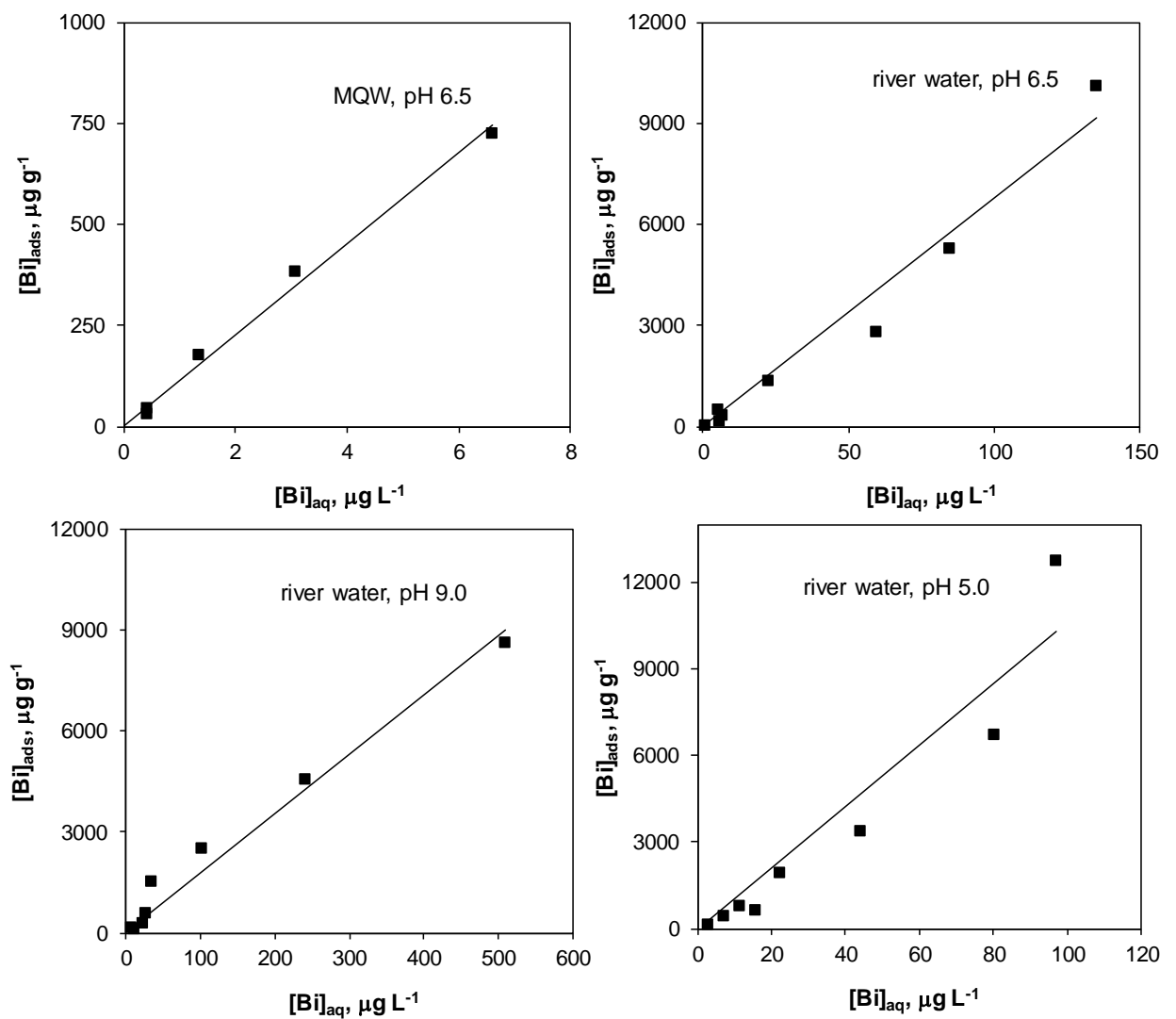
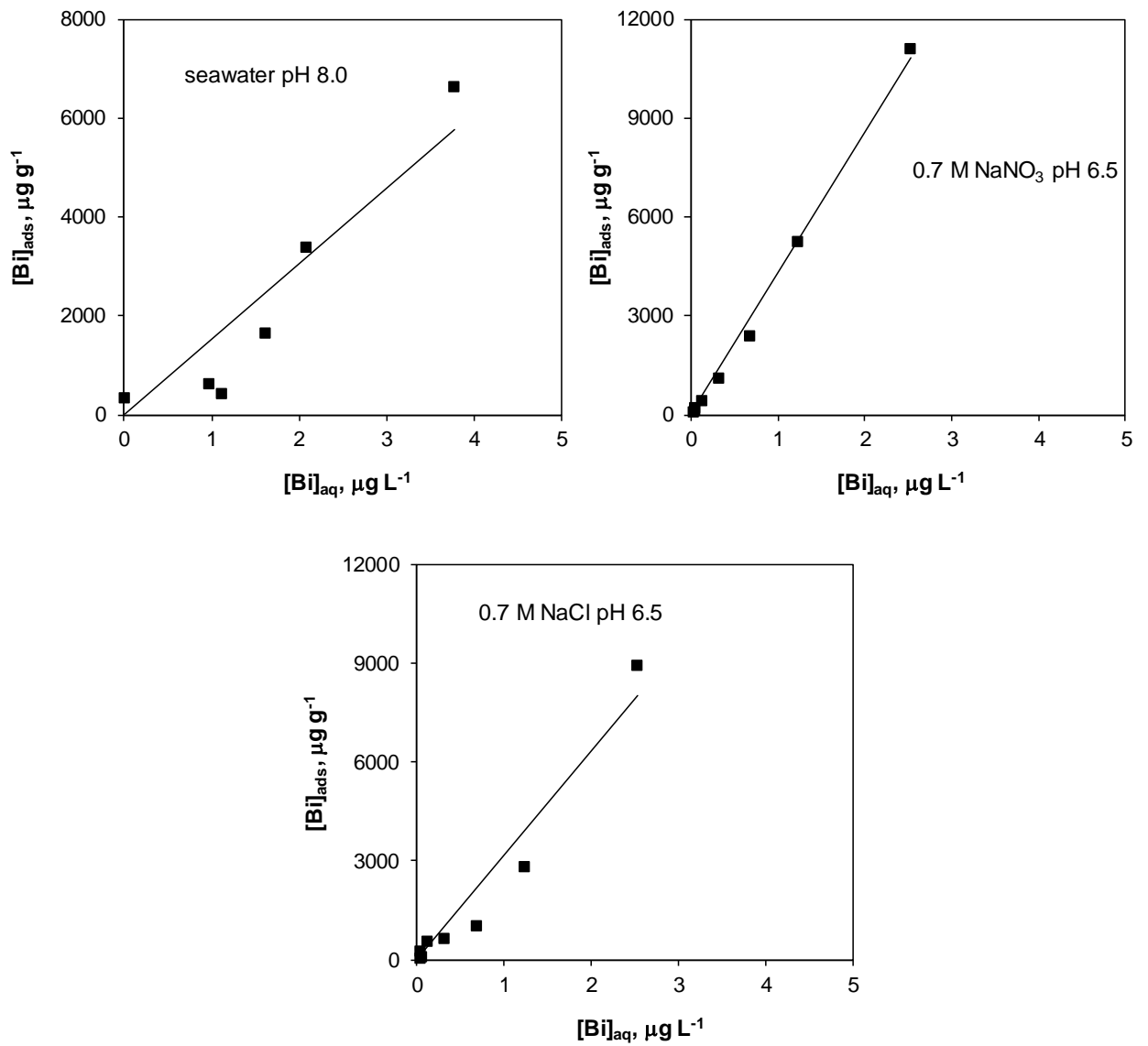


Figure 2: Isotherms for Bi adsorption to fractionated sediment suspended in different saline media. Solid lines denote best fits by linear regression analysis whose slopes (as  $K_b$ ) and goodness of fits are shown in Table 2.



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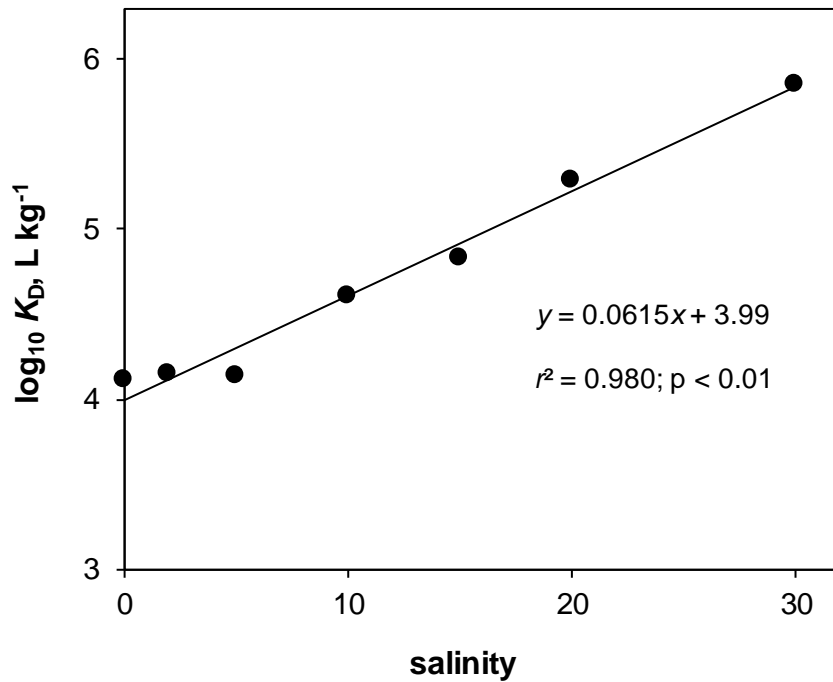
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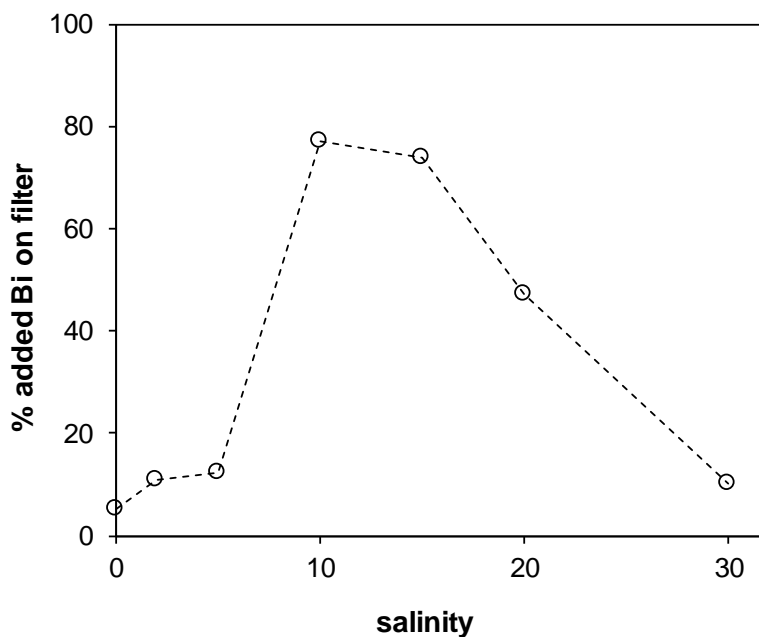
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384 Figure 3: Logged sediment-water distribution coefficients for Bi (added at a concentration of 1000  $\mu\text{g}$   
385  $\text{L}^{-1}$ ) on mixing river water (pH 6.3) and seawater (pH 8.0) and shown as a function of salinity. The  
386 solid line denotes the best fit through the data with the equation, goodness of fit and significance  
387 annotated.



399 Figure 4: The percentage of Bi (added at a concentration of 1000  $\mu\text{g L}^{-1}$ ) retained on filters on mixing  
400 river water (pH 6.3) and seawater (pH 8.0) in the absence of estuarine sediment and shown as a  
401 function of salinity.



410 Figure 5: Logged sediment-water distribution coefficients shown in ascending order for different  
 411 metals studied as tracers in (a) the River Plym (pH 6 to 7) or River Erme (Bi only) and (b) English  
 412 Channel seawater (pH ~8). Data are taken from Table 2 and Turner (2007) and references therein.

