

2020-07

Particle-water interactions of bismuth under simulated estuarine conditions

Knight, LJ

<http://hdl.handle.net/10026.1/15559>

10.1016/j.chemosphere.2020.126400

Chemosphere

Elsevier BV

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

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

3

4 Lydia J. Knight, Andrew Turner*

5 *¹School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake*
6 *Circus, Plymouth PL4 8AA, UK*

7

8

9 *aturner@plymouth.ac.uk

10

11 **Accepted in Chemosphere 29th February 2020**

12 **doi.org/10.1016/j.chemosphere.2020.126400**

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 (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 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}Bi) is extremely weakly radioactive and decays with a half-life of about 2×10^{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 (Bi_2O_3) and bismuthinite (Bi_2S_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}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 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°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 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 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⁻¹ working solution of Bi was prepared in a 50 mL volumetric flask by
113 diluting 500 µL of 10,000 mg L⁻¹ Bi standard (VWR ARISTAR) in filtered river water. Meanwhile, a
114 slurry stock of ~ 4 g dry sediment L⁻¹ 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⁻¹. Bismuth was pipetted to the centrifuge tubes
118 from the working standard to produce a concentration series ranging from 10 to 2000 µg L⁻¹, 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 HNO₃.

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 HNO₃ 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 NaNO₃ (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⁻¹) 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% HNO₃
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⁻¹ prepared in either 2% HNO₃ 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 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 use 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 ± 9.1 , $41,700 \pm 97.1$ and 332 ± 2.54 , respectively,
164 while concentrations of Bi and the other group VA elements, As and Sb, were 0.23 ± 0.09 , 2.49 ± 0.86
165 and 3.12 ± 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.

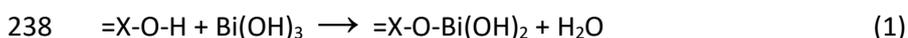
209

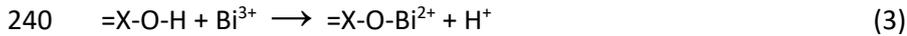
210 **4. Discussion**

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 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 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

299 **Acknowledgements**

300 Alex Taylor and Rob Clough (UoP) are acknowledged for technical support throughout. The study
301 was partly funded by a Plymouth Marine Institute HEIF Grant.

302

303 **References**

304 Ahrens, L.H., 1968. Bismuth. In: Handbook of Geochemistry, Volume II-5, ed. K.H. Wedepohl,
305 Springer, Berlin.

306 Ayres, D.C., Hellier, D.G., 1998. Dictionary of Environmentally Important Chemicals. Blackie
307 Academic and Professional, London, 332pp.

308 Beeman, J.W., Biassoni, M., Brofferio, C., Bucci, C., Capelli, S., Cardani, L., Carrettoni, M., Clemenza,
309 M. and others, 2012. First measurements of the partial widths of Bi-209 decay to the ground and to
310 the first excited states. Physical Review Letters, 108 no. 062501 DOI:
311 10.1103/PhysRevLett.108.062501

312 Bertine, K.K., Koide, M., Goldberg, E.D., 1996. Comparative marine chemistries of some trivalent
313 metals – bismuth, rhodium and rare earth elements. Marine Chemistry 53, 89-100.

314 Byrne, R., 2002. Inorganic speciation of dissolved elements in seawater: the influence of metals
315 speciation in water. Marine Chemistry, 25, 163 – 181.

316 Das, A.K., Chakraborty, R., Cervera, M.L., de la Guardia, M., 2006. Analytical techniques for the
317 determination of bismuth in solid environmental samples. Trends in Analytical Chemistry 25, 599-
318 608.

319 Fahey, N.S.C., Karagatzides, J.D., Jayasinghe, R., Tsuji, L.J.S., 2008. Wetland soil and vegetation
320 bismuth content following experimental deposition of bismuth pellets. Journal of Environmental
321 Monitoring 10, 951-954.

322 Filella, M., 2010. How Reliable Are Environmental Data on 'Orphan' Elements? The Case of Bismuth
323 Concentrations in Surface Waters. Journal of Environmental Monitoring 12, 90–109.

324 Kabata-Pendias, A., Mukherjee, A., 2007. Trace Elements from Soil to Humans, 1st ed. Springer
325 Science and Business Media, Berlin.

326 Kearns, J., Turner, A., 2016. An Evaluation of the Toxicity and Bioaccumulation of Bismuth in the
327 Coastal Environment using Three Species of Macroalgae. Environmental Pollution. 208, 435-441.

328 Kelly, T., Matos, G., 2017. U.S. Geological Survey: Historical Statistics for Mineral and Material
329 Commodities in the United States. [Online]. Available at:
330 [https://www.usgs.gov/centers/nmic/historical-statistics-mineral-and-material-commodities-united-](https://www.usgs.gov/centers/nmic/historical-statistics-mineral-and-material-commodities-united-states)
331 [states](https://www.usgs.gov/centers/nmic/historical-statistics-mineral-and-material-commodities-united-states) [Accessed August 2019].

332 Kotani, T., Nagai, D., Asahi, K., Suzuki, H., Yamao, F., Kataoka, N., Yagura, T., 2005. Antibacterial
333 properties of some cyclic organobismuth(III) compounds. *Antimicrobial agents and chemotherapy*
334 49, 2729-2734.

335 Lee, D.S., 1982. Determination of bismuth in environmental samples by flameless atomic absorption
336 spectrometry with hydride generation. *Analytical Chemistry* 54, 1682 - 1686.

337 Lee, D.S., Edmond, J.M., Bruland, K.W., 1985/1986. Bismuth in the Atlantic and North Pacific: a
338 natural analogue to plutonium and lead. *Earth and Planetary Science Letters* 76, 254-262.

339 National River Flow Archive. (2017). Erme at Ermington. [Online]. Available at:
340 <https://nrfa.ceh.ac.uk/data/station/meanflow/46006> [Accessed July 2019].

341 Peng, S.H., Wang, W.X., Chen, J.S., 2003. Partitioning of trace metals in suspended sediments from
342 Huanghe and Chiangjiang Rivers in eastern China. *Water, Air and Soil Pollution* 148, 243-258.

343 Rawling, M.C., Turner, A., Tyler, A.O., 1998. Particle–water interactions of 2,2',5,5'-
344 tetrachlorobiphenyl under simulated estuarine conditions. *Marine Chemistry* 61, 115-126.

345 Serne, R.J., 2007. K_d Values for Agricultural and Surface Soils for Use in Hanford Site Farm,
346 Residential, and River Shoreline Scenarios. Technical Report for Groundwater Protection Project –
347 Characterization of Systems Task. Pacific Northwest National Laboratory, US Department of Energy,
348 Springfield, VA. 87pp.

349 Tremaine, W.J., 2000. Collagenous colitis and lymphocytic colitis. *Journal of Clinical Gastroenterology*
350 30, 245-249.

351 Turner, A., 2007. Particle–water interactions of platinum group elements under estuarine conditions.
352 *Marine Chemistry* 103, 103-111.

353 Turner, A., Millward, G.E., Le Roux, S.M., 2001. Sediment-water partitioning of inorganic mercury in
354 estuaries. *Environmental Science and Technology* 35, 4648-4654.

355 Turner, A., Cabon, A., Glegg, G., Fisher, A., 2010. Sediment–water interactions of thallium under
356 simulated estuarine conditions. *Geochimica et Cosmochimica Acta* 74, 6779 – 6787.

357 Ulrich, H.J., Degueldre, C., 1993. The sorption of ^{210}Pb , ^{210}Bi and ^{210}Po on montmorillonite: A study
358 with emphasis on reversibility aspects and on the effect of the radioactive decay of adsorbed
359 nuclides. *Radiochimica Acta* 62, 81-90.

360 Windom, H.L., Niencheski, L.F., Smith, R.G., 1999. Biogeochemistry of nutrients and trace metals in
361 the estuarine region of the Patos Lagoon (Brazil). *Estuarine, Coastal and Shelf Science* 48, 113-123.

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 ₃	6.5	52.8 \pm 8.8
0.7 M NaCl	6.5	63.5 \pm 11.8

368

369

370

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 ⁻¹	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
0.7 M NaNO ₃	6.5	4,290,000	0.995
0.7 M NaCl	6.5	3,170,000	0.994

373

374

375

376

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.

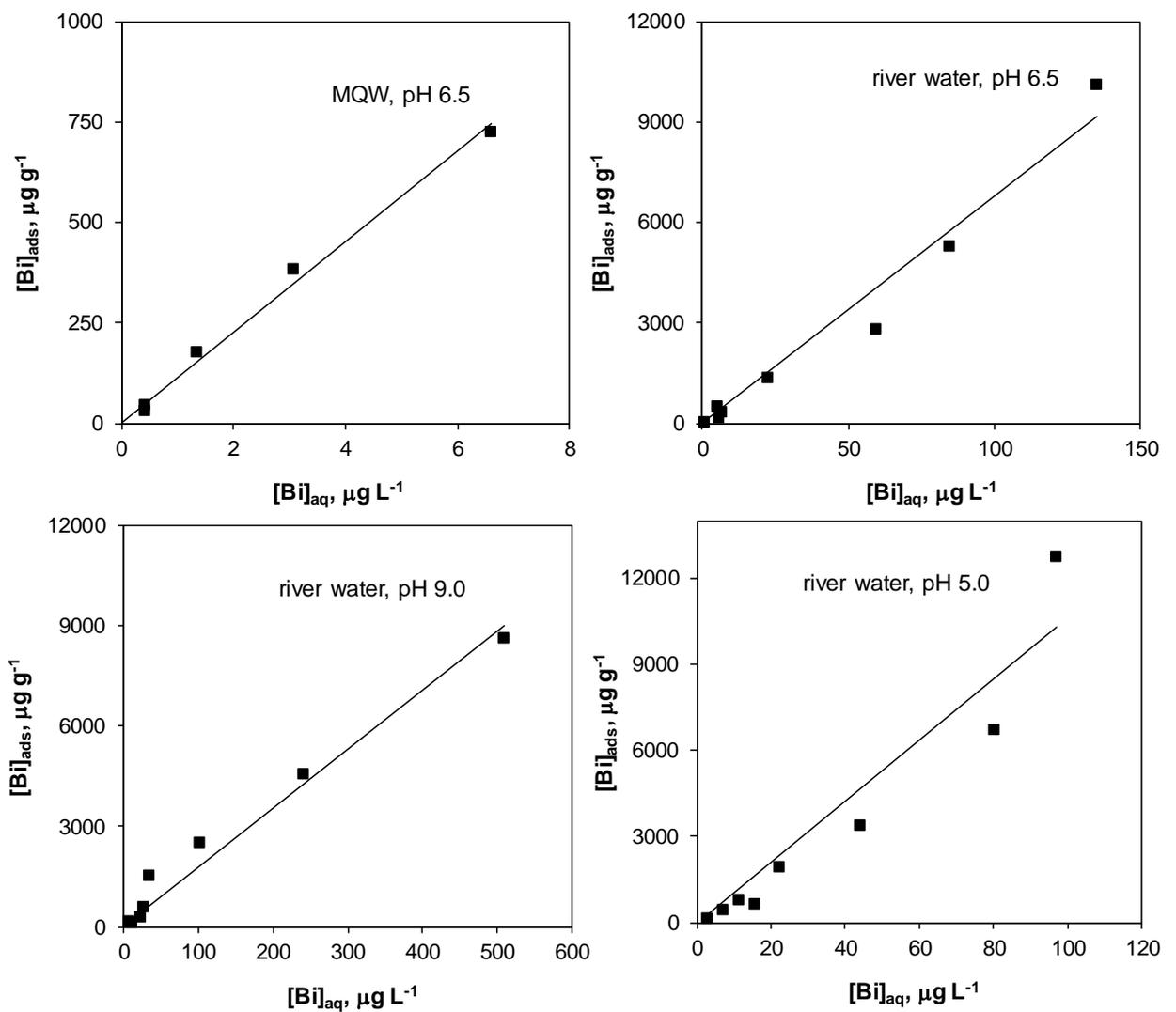
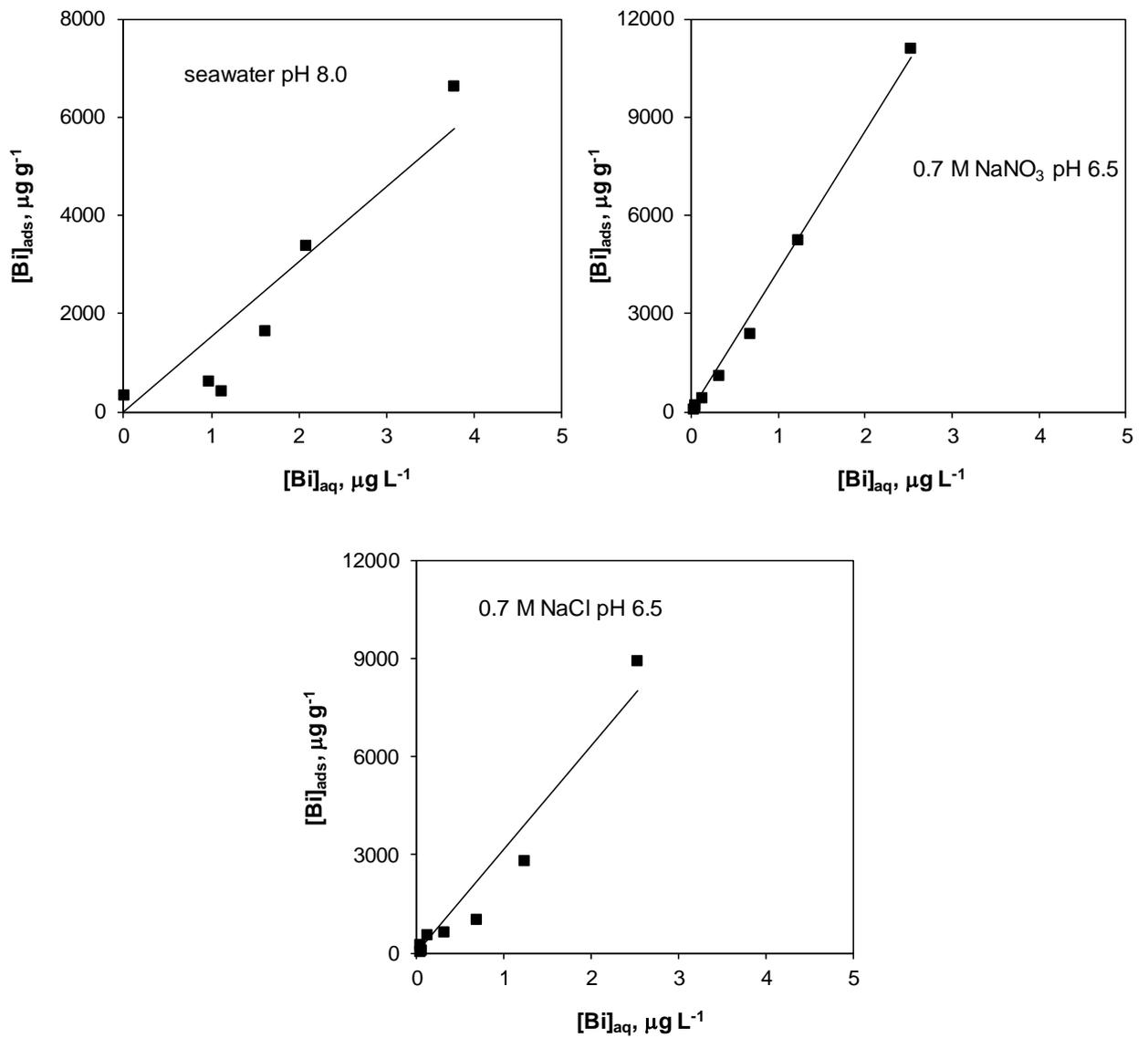


Figure 2: Isotherms for Bi adsorption to fractionated sediment suspended in different saline media. Solid lines denote best fits by linear regression analysis whose slopes (as K_b) and goodness of fits are shown in Table 2.



377

378

379

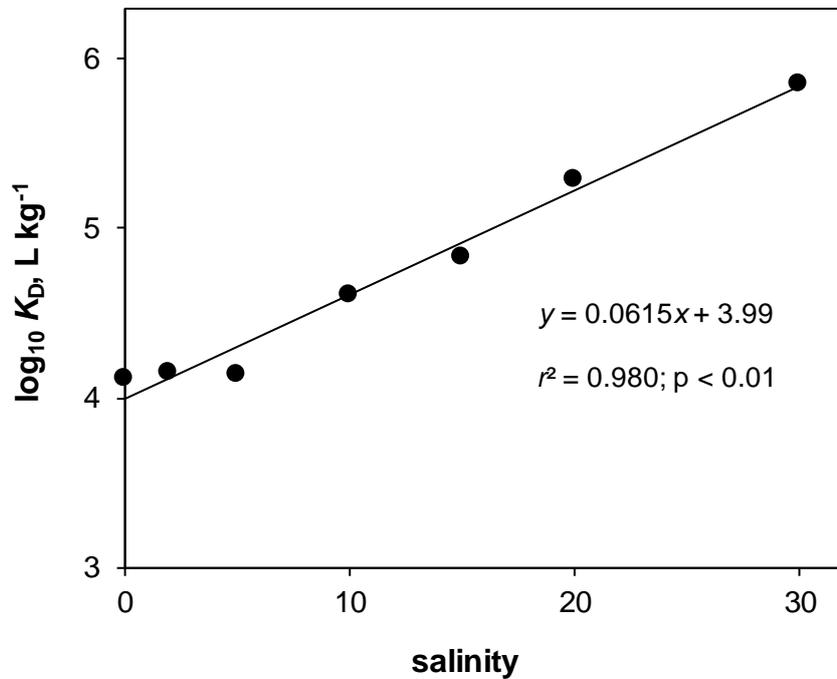
380

381

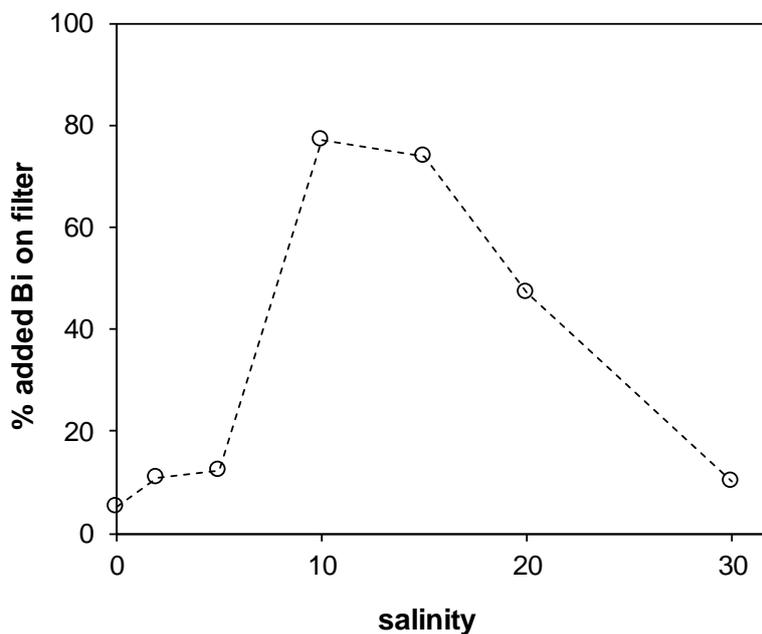
382

383

384 Figure 3: Logged sediment-water distribution coefficients for Bi (added at a concentration of 1000 μg
385 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.

