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1  **$K_d$  distributions in freshwater systems as a function of material type, mass-volume ratio,**  
2 **dissolved organic carbon and pH**

3

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12

13 **Highlights:**

- 14 • Solid-liquid distribution coefficients of metals and radionuclides in freshwater systems.  
15 • New  $K_d$  database for freshwater systems.  
16 •  $K_d$  distributions as a function of material type, m/V, DOC and pH.  
17 • Reducing the variability of  $K_d$  distributions by several orders of magnitude.

18

19 **Abstract**

20 The contamination of freshwater systems by metals is a worldwide problem due to their  
21 toxicity, abundance and persistence in the environment. One of the main processes affecting  
22 their residence time in freshwater systems is their solid-liquid fractionation, often modeled by  
23 the  $K_d$  approach defined as the concentration ratio between the particulate and dissolved  
24 phases under the assumptions of reversibility, equilibrium and trace conditions. Because  $K_d$  is  
25 an empirical parameter that depends on several environmental factors, its variability can cover  
26 orders of magnitude for a single element. Such variability is unknown for most case studies,  
27 but the modelers need it to evaluate the uncertainty of their calculations. In order to fill this  
28 gap, this paper presents statistical  $K_d$  distributions for *in situ* suspended matters as a function  
29 of suspended load, dissolved organic carbon and pH. They were obtained using a database  
30 containing 8564  $K_d$  values from 50 elements, classified as a function of three exchange  
31 conditions (adsorption, desorption and *in situ*) and two environmental components (suspended  
32 and deposited sediments). These distributions and relations can be used to reduce of several  
33 order of magnitudes the global variability of  $K_d$  values in the case where *in situ* data are not  
34 available.

35

36 **Keywords:** log-normal  $K_d$  distributions; metals; radionuclides; suspended and deposited  
37 sediments; freshwater systems

38

## 39 **1. Introduction**

40 Environmental contaminations by heavy metals and radionuclides have been widely studied  
41 because of their high toxicity and persistence: they are poorly degraded by natural processes  
42 and can be accumulated in different compartments of the environment (Liu et al., 2018; Singh  
43 and Kumar, 2017; Wang et al., 2015). Aquatic systems are particularly impacted because  
44 metals and radionuclides are introduced by numerous pathways (atmospheric deposition,  
45 erosion and weathering of soils, direct releases) and by a large variety of anthropogenic  
46 activities. Furthermore, aquatic systems are used as natural sewers for decades, and they  
47 receive numerous effluents from industries or large cities.

48 Metals in aquatic systems are distributed among dissolved, colloidal and particulate phases,  
49 the last one corresponding to suspended particles or deposited sediments. Even if the surface  
50 freshwaters are characterized by a large variability of environmental conditions (e.g.,  
51 temperature, pH, chemical composition, organic matter content; Veselý et al., 2001), most of  
52 the metals have a high affinity with chemically reactive solid surfaces of particles, and their  
53 behavior is thus directly associated with those of the particles (Calmano and Förstner, 1993;  
54 Miller & Orbock Miller, 2007).

55 The term “suspended sediments” (SS) relates to the particles suspended in the water column  
56 and transported with the water flow. They can be organic or inorganic, and are characterized  
57 by a large range of sizes, mainly from colloid to silt. They are a very important transport  
58 agent for metals because they constitute a main vector to the food chain and regulate the  
59 exchange between the water column and bed sediments through erosion and deposition  
60 processes (Webster et al., 2000; Turner and Millward, 2002). Therefore, suspended sediments  
61 strongly control the reactivity, transport and biological impacts of metals and radionuclides in  
62 freshwater environments.

63 Deposited sediments (DS) contain a more important fraction of sand than suspended  
64 sediments and, generally, lower organic matter contents (due to degradation during early  
65 diagenesis). They also play a role of temporary or permanent reservoirs in metal cycles,  
66 through long-term storage and slow release of accumulated metals as a function of  
67 environmental conditions (Wang et al., 2015; Webster and Ridgway, 1994). Since sediment  
68 hosts an important benthic ecosystem, sediment quality guidelines have been proposed for

69 some metals (Simpson et al., 2013) in order to limit their risk for organisms and to guide the  
70 restoration of contaminated sites (Luoma & Rainbow, 2008).

71 An important indicator of environmental risk linked to potential toxic hazards by metals and  
72 radionuclides is their mobility, which depends first on their partitioning between the dissolved  
73 and particulate forms. This partitioning occurs through complex physical, chemical and  
74 biological processes including sorption, adsorption, desorption, complexation, surface  
75 precipitation and co-precipitation (Bayen, 2012; Bordas and Bourg, 2001; Fan et al., 2017);  
76 however, it is also controlled by environmental conditions and the speciation of the elements  
77 (Eyrolle and Charmasson, 2001; Standring et al., 2002). Consequently, partitioning plays a  
78 critical role in the distribution, transport and behavior of these elements in water systems  
79 (Alkhatib et al., 2016; Benoit and Rozan, 1999), and, thus, on their biogeochemical cycles  
80 (Town and Filella al., 2002).

81 Usually, the simplest and most operational method to assess the partitioning of elements in  
82 the environment is to determine their solid-liquid distribution coefficient  $K_d$ , defined as the  
83 concentration ratio between the particulate phase  $C_s$  (Bq/kg or mg/kg) and the dissolved  
84 phase  $C_L$  (Bq/L or mg/L) under the assumptions of equilibrium, reversibility and trace  
85 conditions:

86

$$87 \quad K_d = \frac{C_s}{C_L} \left[ \frac{\text{L}}{\text{kg}} \right] \quad (1)$$

88

89 In freshwater systems  $K_d$  values typically range from  $10^2$  to  $10^6$  L/kg. Elements characterized  
90 by high  $K_d$  values form stable complexes with the particulate phase, whereas those with low  
91  $K_d$  values tend to remain in the dissolved form, and their concentrations may change rapidly  
92 due to their high mobility (Barreto et al., 2011; Veselý et al., 2001).

93  $K_d$  is an empirical parameter that groups together numerous physicochemical processes such  
94 as hydrogen bonding, electrostatic and van der Waals forces, surface precipitation and  
95 surface co-precipitation (Heling et al., 1999, Durrieu et al., 2006) and many biochemical  
96 processes such as microbial alkylation and volatilization that can change, independently of  
97 solid-liquid exchanges, the solution concentrations of elements such as selenium, arsenic and  
98 mercury (Peitzsch et al., 2010).

99 Also, it can be strongly affected by various environmental factors including:

- 100 - pH (Alkhatib et al., 2016; Gurumurthy et al., 2017; Lu and Allen, 2001; Peng et al., 2003;  
101 Shi et al., 1998; Tessier et al., 1989; Wang et al., 2017; White and Driscoll, 1987; Young and  
102 Harvey, 1992),  
103 - organic matter, generally defined by concentrations of dissolved and particulate organic  
104 carbon (Alkhatib et al., 2016; Zhang et al., 2013; Barreto et al., 2011; Lu and Allen, 2001;  
105 Mason and Sullivan, 1998; Naik and Hammerschmidt, 2011; Shafer et al., 1999),  
106 - salinity or conductivity and temperature (Warren and Zimmerman, 1994; Alkhatib et al.,  
107 2016 and 2016b; Duc et al., 2013),  
108 - mass/volume ratio (Apte et al., 1995; Babiarz et al., 2001; Barreto et al., 2011; Dominik et  
109 al., 2007; Guéguen et al., 2000; Jweda et al., 2008; Maia et al., 2009; Quémerais et al., 1998),  
110 - particles size (Abril and Fraga, 1996; Fan et al., 2014; Fan et al., 2017; He and Walling,  
111 1996; Perriñez, 2004; Sheppard et al., 2011; Yao et al., 2015).

112 In rivers, particle size plays a very important role because it can greatly vary and affect both  
113 the solid-liquid fractionation of pollutants and their transport according to the sedimentary  
114 dynamic of the contaminated particles by erosion, sedimentation and transport (Sigg et al.,  
115 2000). In addition, metal partitioning also depends on the anthropogenic factors associated  
116 with the conditions of metal release such as pollution origin, concentration and flux (Guéguen  
117 and Dominik, 2003), and to the sampling and measuring techniques.

118 The large variability of  $K_d$  coefficients in freshwater systems is well known (Veselý et al.,  
119 2001) but not sufficiently specified. Even if  $K_d$  values have been widely reported in the  
120 literature, there are still significant uncertainties and gaps about the statistical distributions of  
121 freshwater  $K_d$  according to the main environmental co-factors. In order to fill these gaps this  
122 paper presents conditional statistical  $K_d$  distributions for *in situ* suspended matters as a  
123 function of suspended load, dissolve organic carbon and pH. These distributions reduce over  
124 several orders of magnitudes the global variability of  $K_d$  values, and they should be very  
125 helpful to modelers who need to evaluate and reduce the uncertainty of their calculations.  
126 They were obtained after an update of the freshwater  $K_d$  database presented by Boyer et al.  
127 (Boyer et al., 2018), implemented by the Working Group 4 (WG4) of the program Modelling  
128 and Data for Radiological Impact Assessments (MODARIA I), organised by the International  
129 Atomic Energy Agency (IAEA).

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131

132

## 133 2. Material and methods

### 134 2.1. Updated database

135 A previous study (Boyer et al., 2018) has presented a freshwater  $K_d$  database for 52 elements:  
136 Ag, Al, Am, As, B, Ba, Be, Ca, Cd, Ce, Cm, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Hf, Ho, I, K,  
137 La, Li, Mg, Mn, Mo, Na, Ni, Np, Pb, Pm, Po, Pr, Pu, Ra, Rb, Ru, S, Sb, Se, Si, Sn, Sr, Th, Ti,  
138 U, V, Zn, Zr. In the present paper,  $K_d$  values of 22 elements (Ag, Al, As, Ba, Be, Ca, Cd, Ce,  
139 Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Po, Si, Sr, U, Zn) were updated using values reported in  
140 49 recent articles (Table S.1). In particular,  $K_d$  data for Hg, previously unavailable, have been  
141 added.

142 3896 new values were added to the initial 4668 values. Among them, 76.5% correspond to  
143 suspended sediments and 23.5% to deposited sediments. 80.5% have been obtained by *in situ*  
144 measurements, 19.1% through adsorption studies and only about 0.4% by desorption studies.  
145 The highest number of new  $K_d$  values are for the following elements: Hg (547 values vs 0  
146 initially), Cu (458 vs 131), Pb (419 vs 99), Zn (392 vs 81) and Fe (308 vs 88).

147 The freshwater  $K_d$  database has been classified using 50 elements; two material types:  
148 suspended (65.7%) and deposited sediments (34.3%); and three exchange conditions: *in situ*  
149 (64.1%), adsorption (31.6%) and desorption (4.3%). A significant part (63%) of the  $K_d$  values  
150 correspond to stable nuclides (i.e. metals), because studies focusing on  $K_d$  for radionuclides in  
151 freshwaters are limited and mainly related to Am, Be, Cm, Cs, I, Po, Pu, Ra, Ru and Th.  
152 Finally, the most frequently reported  $K_d$  values in freshwaters are those for stable nuclides,  
153 suspended sediments and in the case of *in situ* conditions.

154 Table S.1 presents for each element: (i) the type of nuclide (stable or unstable), (ii) the  
155 material (suspended or deposited sediment), (iii) the environment (name of river or lake,  
156 country), (iv) the source of data values (measurements carried out *in situ* or in a laboratory)  
157 and (v) the co-factors associated to the  $K_d$  value (including: m/V ratio, pH, DOC, POC, TOC).

158

### 159 2.2. Statistical analysis

160 The database has been treated with two kinds of statistical analysis. The first one concerns the  
161 update of the  $K_d$  distributions previously published as a function of material type and  
162 exchange conditions (Boyer et al., 2018). These distributions were assumed to be log-normal,  
163 and they were determined by fitting a log-normal distribution to the empirical distribution for  
164 each element that had more than ten  $K_d$  values. Each fit consisted in determining the  
165 geometric mean (GM) and the geometric standard deviation (GSD) and its correctness was  
166 checked with the Kolmogorov-Smirnov test.

167 The second statistical analysis aimed to determine conditional statistical distributions of  $K_d$  as  
168 a function of three selected co-factors: mass/volume ratio, dissolved organic carbon  
169 concentration and pH. For each co-factor, the evolutions of the conditional distributions were  
170 calculated by arranging the  $K_d$  data in increasing order of the co-factor and by using a sliding  
171 window method based on two steps. For a window size defined by a given number of  $K_d$  data,  
172 the first step is to determine the  $GM(K_d)$  and  $GSD(K_d)$  of each window, separated from its  
173 previous one by shifting one datum to the right (Fig. S.1). The co-factor value associated with  
174 each window is the mean value of its co-factor range.

175 The second step consists of determining the most appropriate window size, defined as the  
176 number of  $K_d$  data for which  $GM(K_d)$  and  $GSD(K_d)$  must be calculated. For each  $K_d$  dataset,  
177 step 1 is applied at different window sizes ranging from 10 to 50 data with an increasing step  
178 equal to 5. The best window size is determined by applying step 1 to each case and by  
179 considering the size which gives the best correlation between each window's  $GM(K_d)$  and the  
180 mean tendency of the raw data. Once the best window size has been selected, a least squares  
181 method is used to define the functions describing the evolutions of the  $GM(K_d)$  and  $GSD(K_d)$   
182 in function of the means co-factor. These relations have been recognized as statistically  
183 significant if  $p$ -values were lower than 0.05.

184 The window sliding method was implemented by using MATLAB and Statistics Toolbox  
185 Release 2014a The MathWorks, Inc., Natick, Massachusetts, United States.

186

### 187 **3. Results and discussion**

188 Table S.2 presents the updated version of the freshwater  $K_d$  database for 50 elements. For  
189 each element the geometric mean, the geometric standard deviation, the minimum and  
190 maximum values, the 5th and 95th percentiles, the number of previous and new data, and  
191 finally the type of nuclide (stable or unstable) is given for the different combinations of  
192 sediment type (SS and DS) and experimental conditions (*in situ*, adsorption and desorption).

193

#### 194 **3.1. Evolution of freshwater $K_d$ distributions after updating**

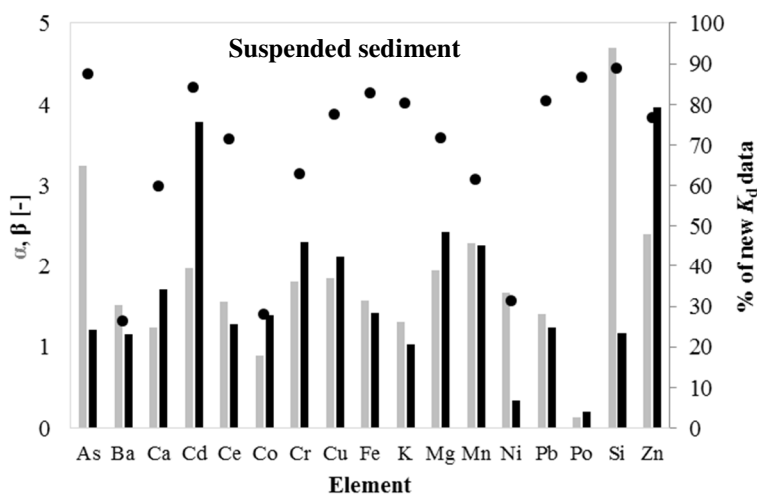
195 Since the database has been updated with a significant number of new  $K_d$  data, the resulting  
196  $K_d$  distributions should be first compared to the previous ones (Boyer et al., 2018) to assess  
197 the robustness and representativeness of the datasets. For this purpose, parameters  $\alpha$  and  $\beta$  are  
198 calculated:

199 
$$\alpha = \frac{GM(K_d)}{GM(K_d)^*} \quad (2)$$

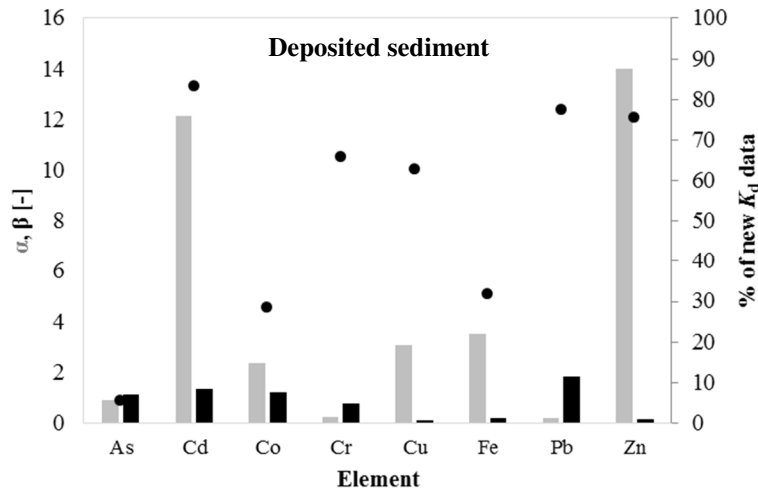
200 
$$\beta = \frac{GSD(K_d)}{GSD(K_d)^*} \quad (3)$$

201  
 202 where  $GM(K_d)$  and  $GSD(K_d)$  relate to the updated database and  $GM(K_d)^*$  and  $GSD(K_d)^*$  to the  
 203 previous one.

204 As the updated database concerns mainly  $K_d$  values for *in situ* conditions, the values obtained  
 205 for  $\alpha$  and  $\beta$  for SS and DS are plotted in Fig. 1, together with the percentage of new  $K_d$  data.  $\alpha$   
 206 values for SS vary from 0.1 to 4.7. This tight range indicates that the  $GM(K_d)$  distributions  
 207 remain close to those of the previous version (Boyer et al., 2018), although a significant  
 208 quantity of new data has been added. For DS  $\alpha$  values range between 0.2 and 3.5, except for  
 209 Cd (12.2) and Zn (14.0). The two high values are due to the large number of new  $K_d$  values,  
 210 which represent 83% and 76% of the new dataset for Cd and Zn.  $\beta$  values vary from 0.2 to 3.8  
 211 for SS, and from 0.1 to 1.8 for DS. The higher  $\beta$  values are all associated to elements  
 212 characterized by a significant amount of new data.

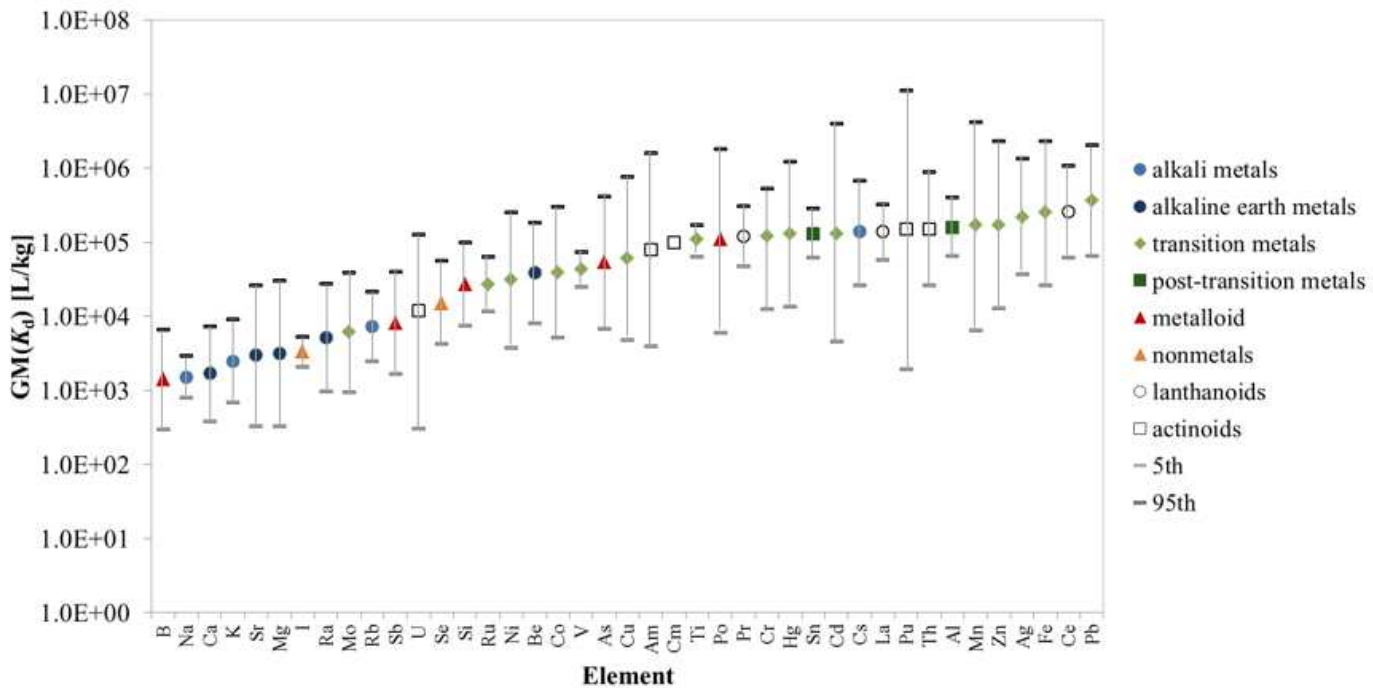






213 Fig. 1.  $\alpha$  ■ ,  $\beta$  ■ and % of new  $K_d$  data ● for SS and DS under *in situ* conditions.  
 214

215 For suspended sediments and *in situ* conditions the  $GM(K_d)$  values range from  $1.20 \cdot 10^3$  L/kg  
 216 to  $3.69 \cdot 10^5$  L/kg, and there is a close relationship between the element  $GM(K_d)$  ranking and  
 217 their geochemical properties regarding the periodic table (Fig. 2).



218 Fig. 2. Classification of elements in the increasing order of  $GM(K_d)$  values for SS and *in situ*  
 219 conditions. The 5<sup>th</sup> and 95<sup>th</sup> of their distributions are represented by the little dashes.  
 220  
 221

222 The alkali and alkali earth metals, which are known to preferentially form outer sphere  
 223 complex in water and to be less adsorbed by solid surfaces, have  $GM(K_d)$  lower than  $10^4$  L/kg,  
 224 except Be and Cs. For both of these two elements, the higher values may be due to the fact  
 225 that their  $K_d$  data are mainly or entirely based on radionuclides and not stable elements. It may

226 be surprising that  $GM(K_d)$  of K is an order of magnitude lower than  $GM(K_d)$  of Cs, so these  
227 two elements are known to have similar behavior. These differences maybe due to the  
228 environmental concentrations, K being a major element whereas Cs is only found as trace  
229 concentrations.

230 The  $GM(K_d)$  of transition metals, actinoids or lanthanids, range from  $2 \cdot 10^4$  to  $3.7 \cdot 10^6$  L/kg,  
231 except Mo. Metalloids (B, Si, Sb, Po, As) present very different  $GM(K_d)$  covering two orders  
232 of magnitude, a trend probably due to their complex behavior regarding their high  
233 electronegativity and their capacities to form oxyanions.

234 The  $GM(K_d)$  values for deposited sediments are usually 2 orders of magnitude lower than for  
235 suspended sediments, and range from  $2.56 \cdot 10^1$  L/kg to  $1.93 \cdot 10^6$  L/kg according to the order:

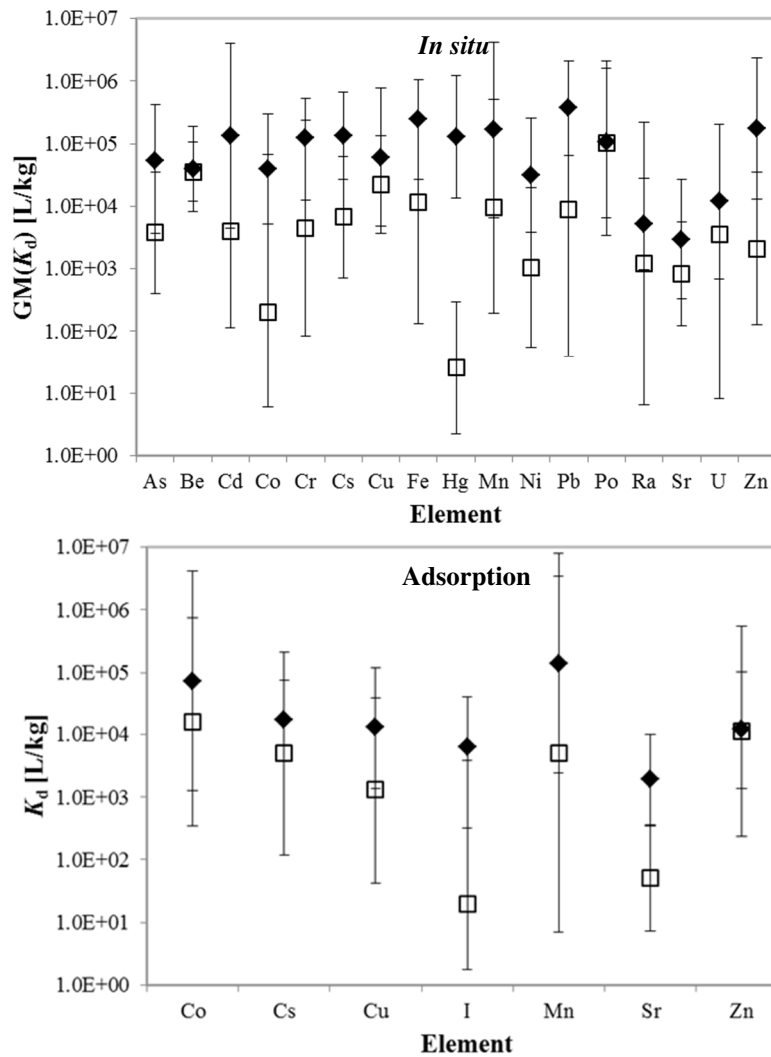
236

237 Hg < Mo < Mg ~ Ca < Co < Ag < Th < Ba ~ Sr < Ni < Ra < Zn < U < As < Cd < Cr < Cs <  
238 Se < Li < Pb < Mn < Fe < Sb < Cu < Be < V < Ti < Po < Pu < Eu < Ho < Gd < Er < Dy < La  
239 < Hf

240

241 The highest  $GM(K_d)$  values are for the lanthanoids, and the lowest are for Hg, Mo and Mg.  
242 The low  $GM(K_d)$  value for Hg agrees with results from Gormley-Gallagher et al. (2015) who  
243 demonstrated that  $K_d$  for Hg in sediments from Scottish Lochs was lower than those of Pb, Ni,  
244 Co, Cu, Cd, Cr, and Mn. The other maxima and minima values are all in agreement with the  
245 previous version of the database (Boyer et al., 2018).

246 Another way to assess the effect of this updating is to compare the impact of the material type  
247 and exchange conditions on  $K_d$  distributions between the two versions of the database, that is  
248 to say to compare the  $GM(K_d)$  obtained for SS and DS for *in situ* and adsorption conditions.  
249 Whatever the condition,  $GM(K_d(SS))$  is higher than  $GM(K_d(DS))$  as underlined before, except  
250 for Be and Po (Fig. 3).



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Fig. 3.  $K_d$  distributions for SS  $\blacklozenge$  and DS  $\square$  under *in situ* and adsorption conditions. (The points correspond to  $GM(K_d)$  and the upper and lower limits to the 5<sup>th</sup> and the 95<sup>th</sup> percentiles)

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### 3.2. $K_d$ distributions between stable and unstable nuclides for SS in *in situ* conditions

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The first objective of this work and of the MODARIA group was to implement a  $K_d$  database for radionuclides. However,  $K_d$  values published for radionuclides are available for few

268 elements only, and it was decided to mix  $K_d$  from stable and unstable nuclides in the dataset in  
269 order to define more general trends (Table S.2). This choice induced the agglomeration of  
270 data corresponding to elements present on exchangeable and non-exchangeable of the solid  
271 phase.

272 The exchangeable group is in dynamic equilibrium and it corresponds to the fractions sorbed  
273 on the surface of the particles by mechanisms dependent on the outer sphere complex (e.g.,  
274 hydrogen links, electrostatic, and van der Waals forces). The non-exchangeable group  
275 concerns the fractions sorbed by mechanisms of surface precipitation, co-precipitation and  
276 inner sphere complex which involve strong and very slowly reversible chemical links (Heling  
277 et al., 1999), plus the fractions present in the crystalline structure of the minerals. It has to be  
278 pointed out that the  $K_d$  coefficient is based on the equilibrium concept, implying that it is only  
279 representative of the exchangeable fraction, while analytical measurements of concentrations  
280 generally involve both the exchangeable and non-exchangeable fractions, thus leading to  
281 overestimation of  $K_d$  values. For artificial radionuclides which are expected to be only on the  
282 exchangeable fraction, the use of data from stable nuclides may thus lead to an overestimation  
283 of their  $K_d$ .

284 To assess this possible effect three categories of  $K_d$  datasets were distinguished: (i) only  
285 unstable nuclides (Am, Be, Cm, I, Po, Pu, Ra, Ru and Th), (ii) mix of stable and unstable  
286 nuclides (Ba, Co, Cs, Mn, Pb, Sb, Sr and U; Fig. S.2) and (iii) only stable nuclides.

287 The representativeness of the  $K_d$  datasets for *in situ* conditions must be considered as a  
288 function of their contents for both stable and unstable nuclides. This was done for Ba, Co, Cs,  
289 Mn and Pb for which more than 10 values were reported for each type of nuclide. All these  
290 elements, except Mn, present similar values of  $K_d$  for stable and unstable nuclides (Fig. S.3).  
291 Such a comparison cannot be made for DS because only Pb has more than 10 values.

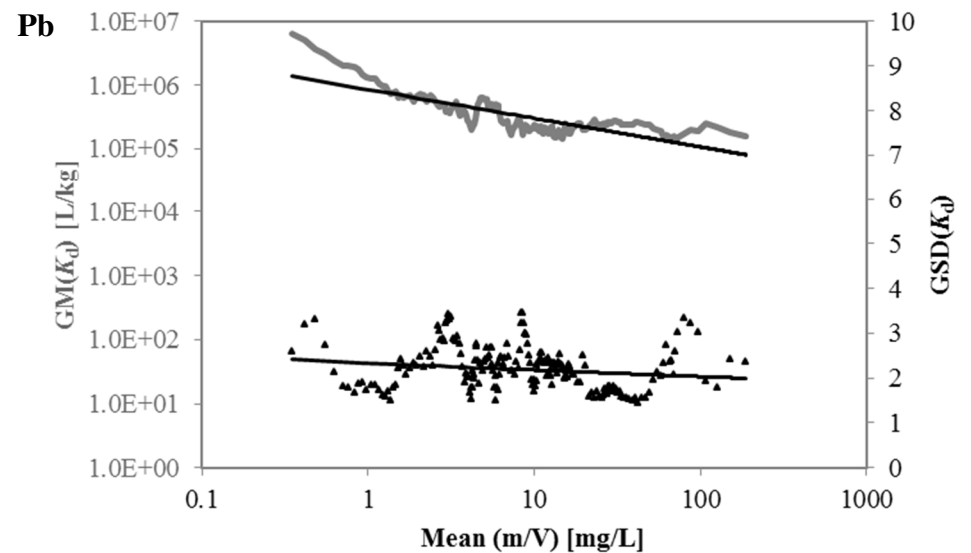
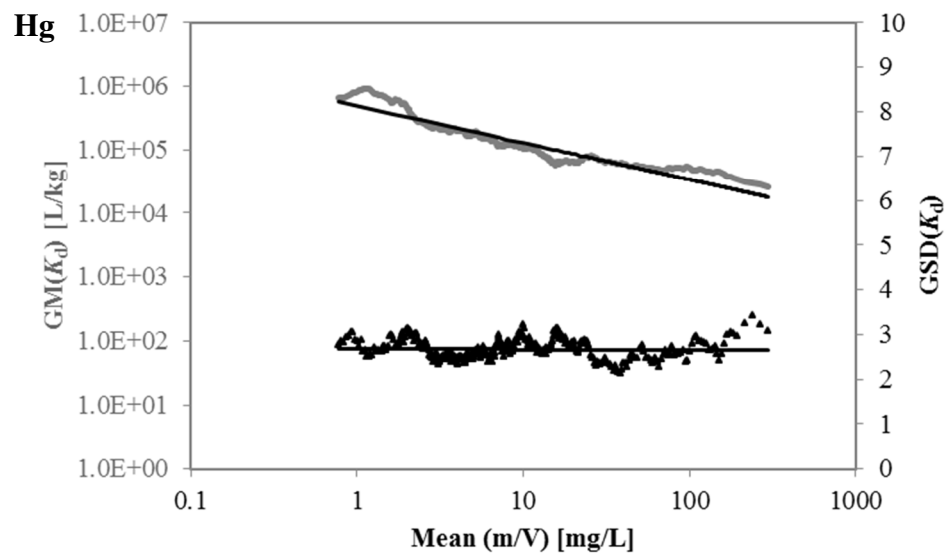
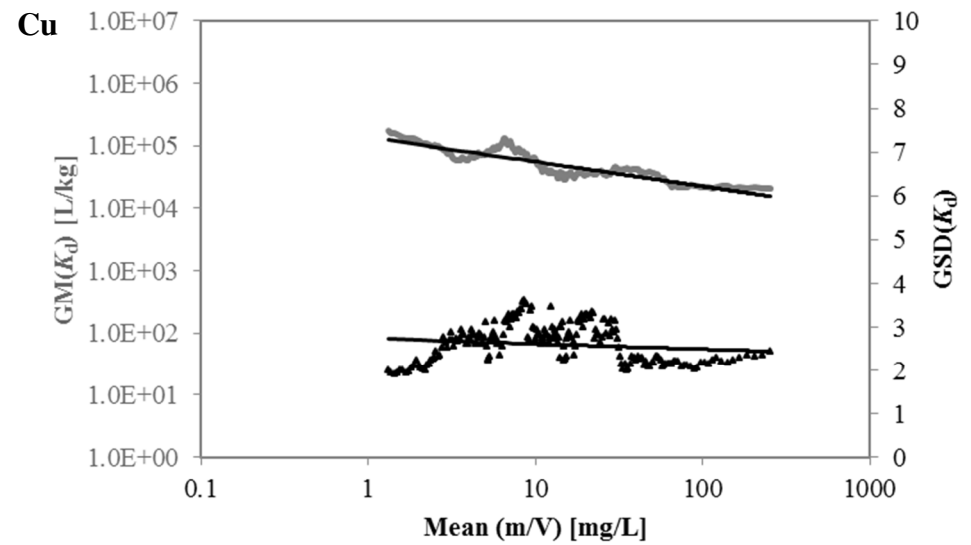
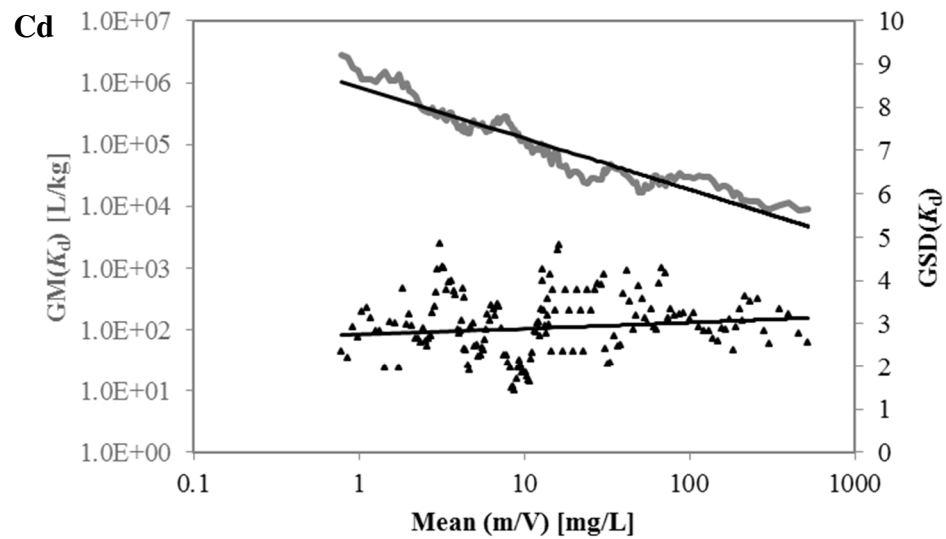
292 For these elements and for *in situ* suspended matters, the origin of the element, which could  
293 be natural (i.e. within the crystal structure of the minerals and/or adsorbed onto the surface) or  
294 anthropic (i.e. rather associated to surface adsorption), does not greatly influence the  $GM(K_d)$ .  
295 This result can be linked to the properties of *in situ* suspended matters which are, in the  
296 majority of cases, associated to low suspended loads (some mg/L to 100 mg/L) and  
297 consequently to very fine particles (some  $\mu\text{m}$  to 100  $\mu\text{m}$ ). At this scale of size, the influence  
298 of the non-exchangeable fractions of atoms on the  $K_d$  values is low because the fraction of  
299 particles which is not in contact with water is limited and most atoms can be exchanged with  
300 the dissolved phase (Abril and Fraga, 1996). This point is discussed in the next section  
301 according to the evolution of  $K_d$  values when the particle size increases.

### 302 **3.3. $K_d$ distributions for SS in *in situ* conditions as a function of m/V**

303 Despite the important role generally attributed to particle size on the distribution coefficient  
304 (Abril and Fraga, 1996; He and Walling, 1996; Perriñez, 2004), very few papers reported  
305 information for this parameter together. In order to fill this gap, Boyer et al. (2018) proposed  
306 to analyze  $K_d$  distributions for SS under *in situ* conditions as a function of the mass/volume  
307 ratio m/V. In rivers, this ratio corresponds to the suspended load which is related to the mean  
308 particle size of suspended sediments because both tends to increase with water flow.

309 Nineteen elements can be used to test this relation, and the evolutions of  $GM(K_d)$  and  
310  $GSD(K_d)$  can be represented by the following equations  $GM(K_d) = a \cdot (m/V)^b$  and  
311  $GSD(K_d) = c \cdot (m/V)^d$ . Parameters  $a$  ( $L/kg$ )<sup>b+1</sup> and  $c$  ( $L/kg$ ) are scaling factors with values  
312 corresponding to  $GM(K_d)$  and  $GSD(K_d)$  when  $SS = 1$  mg/L. The exponents,  $b$  (-) and  $d$  (-),  
313 describe the extent of the deviation of the adsorption process from linearity (He and Walling,  
314 1995). Table 1 summarizes these relationships with their determination coefficient  $R^2$  and  $p$ -  
315 values, and Figure 4 reports the trend for Cd, Cu, Hg and Pb as examples.

316 All the relationships between  $GM(K_d)$  and m/V are statistically significant ( $p$ -value  $\ll 0.05$ )  
317 and negative. This trend could be explained by two major mechanisms: First, the increase of  
318 the particles size induces a decrease of the specific surface of SS (Benoit and Rozan, 1999),  
319 and thus of the number of sites available for adsorption. If the concentration of atoms within  
320 the crystal structure is not negligible, the non-exchangeable fraction of the elements increases  
321 with the particles size and, at the limit, the apparent  $K_d$  of highly soluble natural nuclides  
322 increases as the particles radius increases (Abril and Fraga, 1996). Second, the “colloidal  
323 pumping effect”, a well-known process associated by numerous authors (e.g. Benoit, 1995;  
324 Cobelo-García et al., 2004; Gormley-Gallagher et al., 2015; Veselý et al., 2001, Wen et al.,  
325 1997), leads to an increasing concentration of colloidal particles with the suspended load, that  
326 may favor an “apparent” increase in dissolved concentrations. According to this hypothesis,  
327 an increase in the dissolved phase is due to a higher amount of colloids (very reactive for  
328 metals) that are not retained by the filters generally used to separate the particulate phase.  
329 This analysis is limited to SS for *in situ* conditions because both increase of particle size and  
330 colloidal pumping effect are not reproduced by laboratory experiments (Boyer et al., 2018).



331

Fig. 4.  $K_d$  log-normal distribution (GM( $K_d$ ) — and GSD( $K_d$ )▲) as a function of m/V for SS under *in situ* conditions.

332  
333

Table 1. Relationships between GM( $K_d$ ) and GSD( $K_d$ ) and m/V for SS under *in situ* conditions.

Element	GM( $K_d$ )		GSD( $K_d$ )		N*
	Equation	R <sup>2</sup> ( <i>p</i> -value)	Equation	R <sup>2</sup>	
Am	$GM(K_d) = 4.08 \cdot 10^5 \cdot (m/V)^{-0.72}$	0.8898 ( $2.14 \cdot 10^{-16}$ )	$GSD(K_d) = 2.36 \cdot (m/V)^{0.15}$	0.2034	10
As	$GM(K_d) = 1.64 \cdot 10^5 \cdot (m/V)^{-0.66}$	0.8453 ( $6.34 \cdot 10^{-15}$ )	$GSD(K_d) = 3.02 \cdot (m/V)^{0.08}$	0.0319	40
Ba	$GM(K_d) = 2.30 \cdot 10^4 \cdot (m/V)^{-0.45}$	0.9046 ( $7.65 \cdot 10^{-34}$ )	$GSD(K_d) = 1.00 \cdot (m/V)^{0.18}$	0.3269	15
Be	$GM(K_d) = 7.05 \cdot 10^4 \cdot (m/V)^{-0.32}$	0.6518 ( $2.08 \cdot 10^{-7}$ )	$GSD(K_d) = 2.09 \cdot (m/V)^{0.15}$	0.3107	10
Cd	$GM(K_d) = 8.51 \cdot 10^5 \cdot (m/V)^{-0.83}$	0.9082 ( $3.00 \cdot 10^{-94}$ )	$GSD(K_d) = 2.74 \cdot (m/V)^{0.02}$	0.0176	10
Co	$GM(K_d) = 4.74 \cdot 10^4 \cdot (m/V)^{-0.16}$	0.1440 ( $2.07 \cdot 10^{-5}$ )	$GSD(K_d) = 2.24 \cdot (m/V)^{0.04}$	0.0076	10
Cr	$GM(K_d) = 4.30 \cdot 10^5 \cdot (m/V)^{-0.53}$	0.6770 ( $1.53 \cdot 10^{-25}$ )	$GSD(K_d) = 2.07 \cdot (m/V)^{0.02}$	0.0146	10
Cs	$GM(K_d) = 7.95 \cdot 10^5 \cdot (m/V)^{-0.95}$	0.9421 ( $5.93 \cdot 10^{-37}$ )	$GSD(K_d) = 1.74 \cdot (m/V)^{0.21}$	0.4917	40
Cu	$GM(K_d) = 1.38 \cdot 10^5 \cdot (m/V)^{-0.43}$	0.7916 ( $1.71 \cdot 10^{-75}$ )	$GSD(K_d) = 2.73 \cdot (m/V)^{-0.02}$	0.0250	30
Fe	$GM(K_d) = 8.80 \cdot 10^5 \cdot (m/V)^{-0.63}$	0.8693 ( $1.00 \cdot 10^{-57}$ )	$GSD(K_d) = 2.93 \cdot (m/V)^{0.06}$	0.0597	20
Hg	$GM(K_d) = 4.88 \cdot 10^5 \cdot (m/V)^{-0.58}$	0.8874 ( $5.70 \cdot 10^{-160}$ )	$GSD(K_d) = 2.68 \cdot (m/V)^{-0.01}$	0.0021	40
Mg	$GM(K_d) = 1.25 \cdot 10^4 \cdot (m/V)^{-0.67}$	0.7563 ( $7.80 \cdot 10^{-14}$ )	$GSD(K_d) = 4.07 \cdot (m/V)^{-0.01}$	0.6651	20
Mn	$GM(K_d) = 4.65 \cdot 10^5 \cdot (m/V)^{-0.32}$	0.2514 ( $3.74 \cdot 10^{-10}$ )	$GSD(K_d) = 27.43 \cdot (m/V)^{-0.52}$	0.5518	15
Ni	$GM(K_d) = 3.93 \cdot 10^4 \cdot (m/V)^{-0.06}$	0.0081 ( $5.13 \cdot 10^{-3}$ )	$GSD(K_d) = 0.37 \cdot (m/V)^{0.74}$	0.7303	30
Pb	$GM(K_d) = 8.49 \cdot 10^5 \cdot (m/V)^{-0.45}$	0.6561 ( $4.51 \cdot 10^{-47}$ )	$GSD(K_d) = 2.33 \cdot (m/V)^{-0.03}$	0.0320	10
Pu	$GM(K_d) = 9.82 \cdot 10^5 \cdot (m/V)^{-1.25}$	0.9307 ( $1.58 \cdot 10^{-19}$ )	$GSD(K_d) = 3.67 \cdot (m/V)^{0.16}$	0.1482	15
Si	$GM(K_d) = 2.30 \cdot 10^4 \cdot (m/V)^{-0.13}$	0.0471 ( $3.37 \cdot 10^{-4}$ )	$GSD(K_d) = 1.33 \cdot (m/V)^{0.38}$	0.2680	10
Sr	$GM(K_d) = 3.31 \cdot 10^4 \cdot (m/V)^{-0.96}$	0.8730 ( $9.86 \cdot 10^{-13}$ )	$GSD(K_d) = 1.27 \cdot (m/V)^{0.15}$	0.0897	10
Zn	$GM(K_d) = 4.60 \cdot 10^5 \cdot (m/V)^{-0.51}$	0.9781 ( $1.65 \cdot 10^{-66}$ )	$GSD(K_d) = 4.84 \cdot (m/V)^{-0.12}$	0.5019	50

334 N\* - size of window (number of  $K_d$  data)

335

336 The  $K_d$  distributions from Table 1 are all the more impacted by the m/V ratio when the slope  $b$   
 337 is low and the coefficient R<sup>2</sup> is high. According to Fig. 5, the elements most sensitive to m/V  
 338 are thus Pu, Cs and Cd, and the less sensitive are Mn, Co, Si and Ni. This is in agreement with  
 339 Veselý et al. (2001) who observed small changes in  $K_d$  values for Si as a function of m/V, and  
 340 with Pettine et al. (1994) who did not find any effect of m/V on the  $K_d$  values of Mn and Co in  
 341 the Po River in Italy.

342

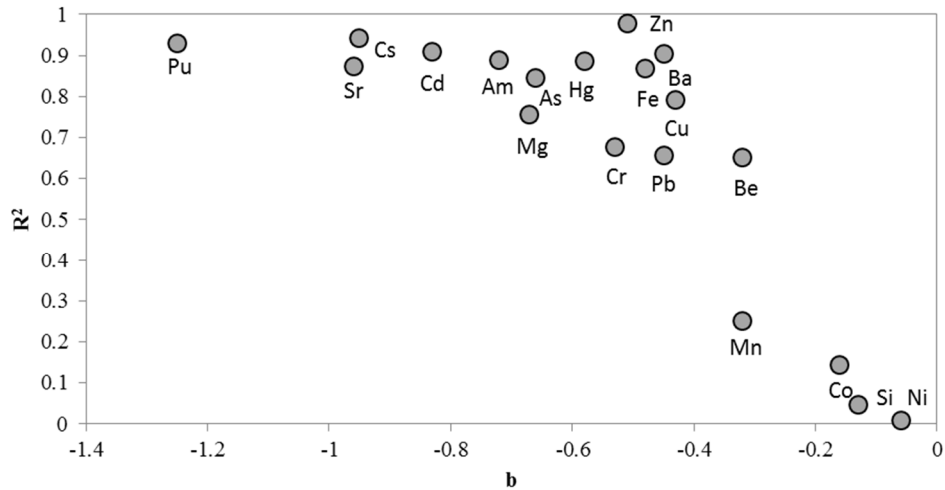


Fig. 5.  $R^2$  as a function of  $b$  for the relation  $GM(K_d) = a \cdot (m/V)^b$ .

343  
344  
345

346 In addition to section 3.2, these results confirm the weak effect on  $K_d$  distributions of atoms  
347 present in the crystal structure because all the  $K_d$  distributions show a decrease ( $b < 0$ ) when  
348 the suspended load and hence the mean particle size increases. The elements which present  
349 the lower decreasing rates are Ni, Si, Co, Mn and Be. However, for Co and Mn, the Fig. S.3  
350 shows that their  $K_d$  distributions as a function of their stable and unstable forms are very  
351 close, suggesting a weak effect of the use of stable forms when assessing  $K_d$  distributions for  
352 SS in *in situ* conditions.

353 The relationships from Table 1 allow to significantly reduce the  $K_d$  variability. For example,  
354 the total  $GSD(K_d)$  of Cu and Ca for SS in *in situ* conditions that initially equal 4.6 and 7.8  
355 respectively (Table S.2) are reduced to 2-3 and 2-4 by considering  $m/V$  (Fig. 4). Thus, the  
356 variability of their distributions decreases of two orders of magnitude. Therefore, suspended  
357 load content is a very important data that should be measured during sampling or evaluated  
358 during modelling.

359

### 360 3.4. $K_d$ distributions for SS in *in situ* conditions as a function of DOC

361 Dissolved and particulate organic matter molecules have very high affinity for numerous  
362 metals in aquatic systems (Kördel et al., 1997). Dissolved organic carbon (DOC) is a mixture  
363 of pedogenic (derived from soil washout) and aquagenic (from material excreted by aquatic  
364 biota) compounds (Town and Fiella, 2002) presenting a high capacity to complex metals and  
365 change their speciation, thus impacting their behavior by affecting their solid-liquid partition.  
366 Metals, for example, can be bounded to dissolved organic ligands and maintained for a longer  
367 time in these dissolved forms (Sauve et al., 2000; Sigg et al., 2000; Aiken et al., 2011; Tanaka



368 et al., 2012). Also, inverse correlations between DOC and  $K_d$  can be expected, at least as a  
369 general approximation.

370 The data from several papers concerning the relationship between  $K_d$  and DOC concentrations  
371 in freshwater systems were compiled to determine this relationship using a statistical  
372 treatment (Babiarz et al., 2001; Barreto et al., 2011; Benoit and Rozan, 1999; Lu and Allehn,  
373 2001; Naik and Hammerschmidt, 2011; Shafer et al., 1999; Veselý et al., 2001). The DOC  
374 concentrations were limited to the range of 2-10 mg/L (Fig. 6), which is representative of  
375 freshwaters but not of poral waters, where DOC can reach 50 mg/L (Sigg et al., 2014).

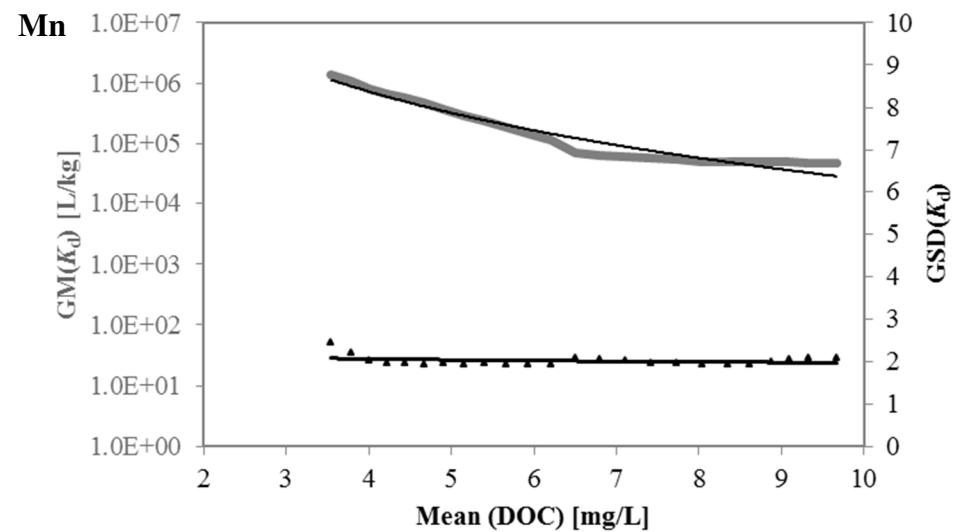
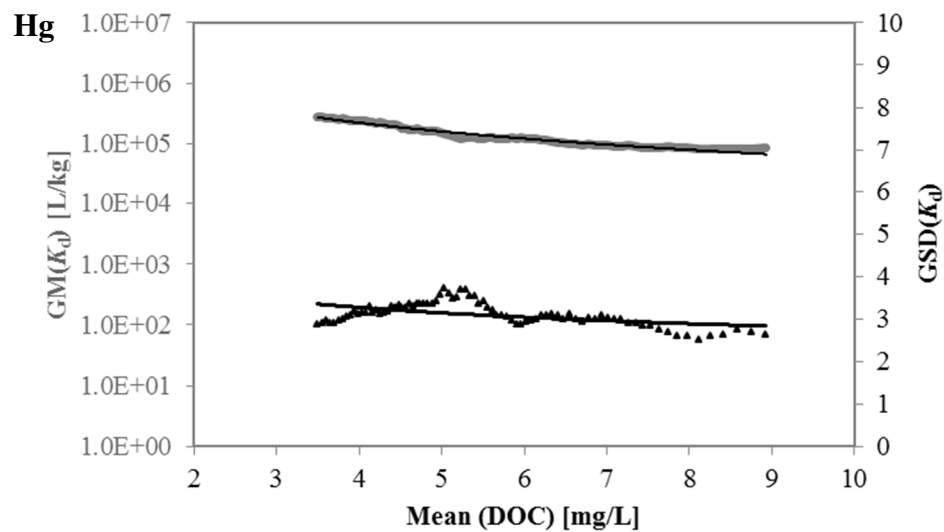
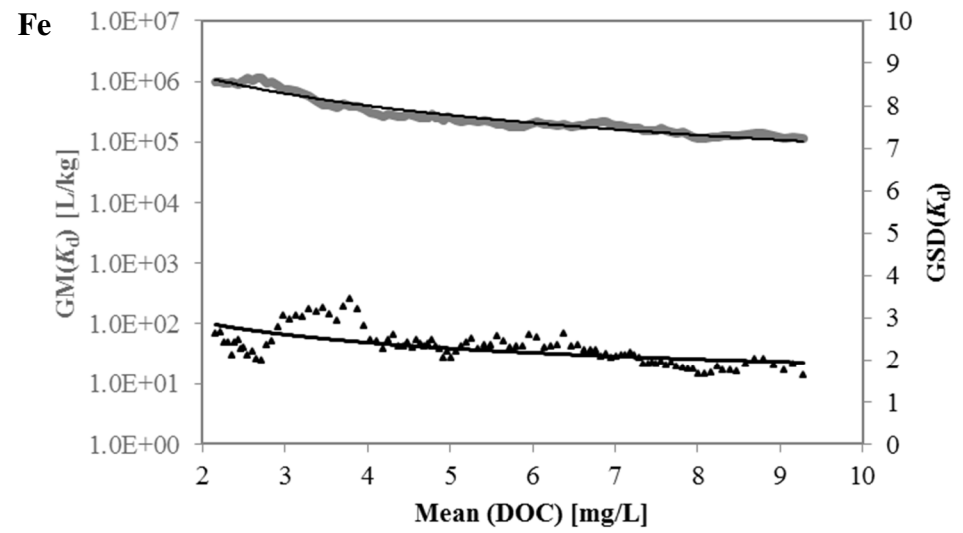
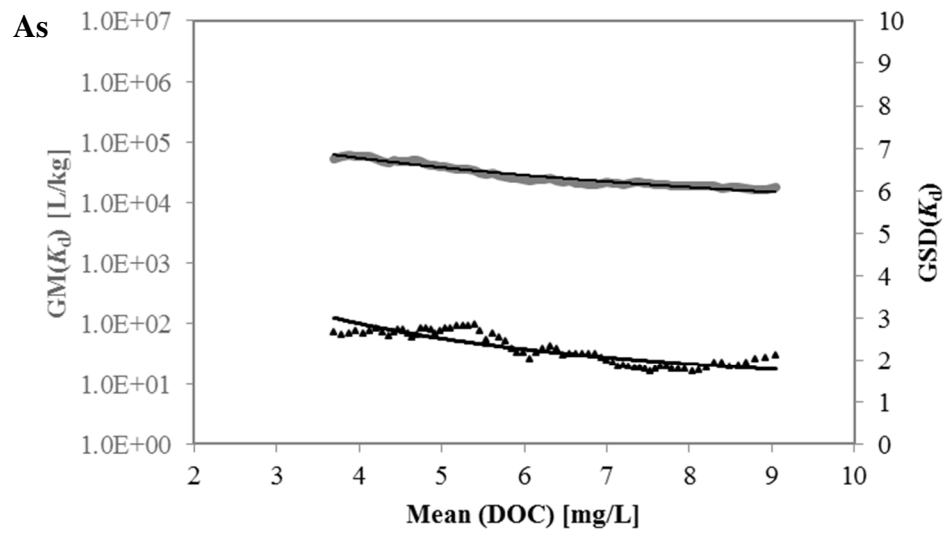


Fig. 6.  $K_d$  log-normal distribution (GM( $K_d$ ))— and GSD( $K_d$ )▲) as a function of DOC for SS under *in situ* conditions.

377 Figure 6 clearly confirms the previous assumption that  $GM(K_d)$  is inversely related to DOC,  
378 most probably as a result of ligand formation between free metal and DOC anionic groups  
379 that maintain metals in the dissolved phase (Naik and Hammerschmidt, 2011).  
380 The relationships for the evolution of  $GM(K_d)$  and  $GSD(K_d)$  as a function of DOC  
381 concentrations (SS and *in situ* conditions only, Table 2) can be fitted according:  $GM(K_d) =$   
382  $a \cdot DOC^b$  and  $GSD(K_d) = c \cdot DOC^d$ . The *p*-values associated with these correlations are well  
383 below 0.05, validating their statistical representativeness.

384

385 Table 2.  $GM(K_d)$  and  $GSD(K_d)$  as a function of DOC for SS under *in situ* conditions.

Element	$GM(K_d)$		$GSD(K_d)$		N*
	Equation	R <sup>2</sup> ( <i>p</i> -value)	Equation	R <sup>2</sup>	
As	$GM(K_d) = 4.96 \cdot 10^5 \cdot (DOC)^{-1.59}$	0.9501 ( $2.70 \cdot 10^{-47}$ )	$GSD(K_d) = 6.48 \cdot (DOC)^{-0.59}$	0.7730	30
Cd	$GM(K_d) = 8.00 \cdot 10^7 \cdot (DOC)^{-3.23}$	0.8760 ( $2.27 \cdot 10^{-5}$ )	$GSD(K_d) = 0.17 \cdot (DOC)^{0.91}$	0.0700	10
Ce	$GM(K_d) = 1.18 \cdot 10^6 \cdot (DOC)^{-0.92}$	0.6947 ( $1.25 \cdot 10^{-17}$ )	$GSD(K_d) = 2.96 \cdot (DOC)^{-0.20}$	0.1544	10
Co	$GM(K_d) = 1.00 \cdot 10^4 \cdot (DOC)^{1.58}$	0.6506 ( $1.74 \cdot 10^{-5}$ )	$GSD(K_d) = 0.0028 \cdot (DOC)^{3.01}$	0.5877	10
Cr	$GM(K_d) = 5.04 \cdot 10^7 \cdot (DOC)^{-3.08}$	0.8450 ( $2.25 \cdot 10^{-10}$ )	$GSD(K_d) = 7470.80 \cdot (DOC)^{-3.93}$	0.7723	25
Cu	$GM(K_d) = 2.68 \cdot 10^7 \cdot (DOC)^{-3.23}$	0.9833 ( $1.50 \cdot 10^{-16}$ )	$GSD(K_d) = 92.63 \cdot (DOC)^{-1.75}$	0.4891	25
Fe	$GM(K_d) = 3.69 \cdot 10^6 \cdot (DOC)^{-1.61}$	0.9426 ( $9.73 \cdot 10^{-66}$ )	$GSD(K_d) = 3.47 \cdot (DOC)^{-0.26}$	0.4183	20
Hg	$GM(K_d) = 1.76 \cdot 10^6 \cdot (DOC)^{-1.49}$	0.9576 ( $1.13 \cdot 10^{-56}$ )	$GSD(K_d) = 4.18 \cdot (DOC)^{-0.18}$	0.2653	50
K	$GM(K_d) = 1.00 \cdot 10^4 \cdot (DOC)^{-0.73}$	0.9706 ( $4.11 \cdot 10^{-46}$ )	$GSD(K_d) = 2.26 \cdot (DOC)^{-0.06}$	0.0678	45
Mg	$GM(K_d) = 2.00 \cdot 10^4 \cdot (DOC)^{-1.15}$	0.9706 ( $1.50 \cdot 10^{-16}$ )	$GSD(K_d) = 3.80 \cdot (DOC)^{-0.32}$	0.5650	25
Mn	$GM(K_d) = 9.27 \cdot 10^7 \cdot (DOC)^{-3.52}$	0.9388 ( $9.10 \cdot 10^{-16}$ )	$GSD(K_d) = 2.20 \cdot (DOC)^{-0.05}$	0.0840	25
Pb	$GM(K_d) = 8.30 \cdot 10^5 \cdot (DOC)^{-0.58}$	0.9490 ( $1.14 \cdot 10^{-32}$ )	$GSD(K_d) = 2.71 \cdot (DOC)^{-0.14}$	0.4264	50
Si	$GM(K_d) = 8.00 \cdot 10^4 \cdot (DOC)^{-0.67}$	0.7290 ( $2.21 \cdot 10^{-20}$ )	$GSD(K_d) = 0.82 \cdot (DOC)^{0.59}$	0.8641	25
Zn	$GM(K_d) = 5.47 \cdot 10^6 \cdot (DOC)^{-1.83}$	0.8989 ( $1.70 \cdot 10^{-21}$ )	$GSD(K_d) = 4.48 \cdot (DOC)^{-0.25}$	0.4539	25

386 N\* - size of window (number of data)

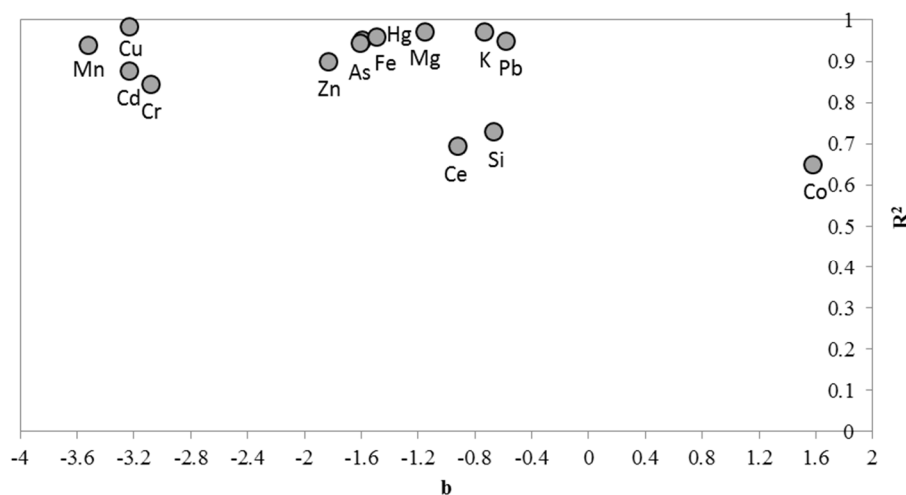


Fig. 7.  $R^2$  as a function of  $b$  for the relationship  $GM(K_d) = a \cdot DOC^b$ .

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389

390 The variation of  $R^2$  as a function of  $b$  (Fig. 7) shows that the most sensitive elements to DOC  
391 concentrations are Mn, Cu, Cd and Cr. This point is well-known for Cu and was demonstrated  
392 by several works (e.g. Lu et al., 2001; Shafer et al., 1999; Shi et al., 1998). Apte et al. (1995)  
393 demonstrated the significance of Cu complexation by DOC by showing that dissolved Cu is  
394 predominantly present in the form of organic complexes in the Fly River and Barreto et al.  
395 (2011) evaluated the formation of DOC and Cd complexes in natural waters. These elements  
396 are thus easily associated to dissolved organic matter and this factor directly controls their  
397 solid-liquid partitioning.

398 The elements less sensitive to the DOC concentrations are Co and Si. In particular, Co is the  
399 only element for which the slope  $b$  is positive and, for Si, this result is in accordance with the  
400 work of Veselý et al. (2001). At this stage, it can also be noted that the  $K_d$  distributions of Si  
401 and Co are independent of both parameters  $m/V$  and DOC.

402 As for  $m/V$ , taking into account the DOC concentration leads to a significant reduction of the  
403  $GSD(K_d)$  values. For example, the total  $GSD(K_d)$  for Mn shifts from 7.1 (Table S.2) to 2 by  
404 considering DOC concentrations (Fig. 6), which represents a decrease in the variability of  
405 their distributions over more than four orders of magnitude.

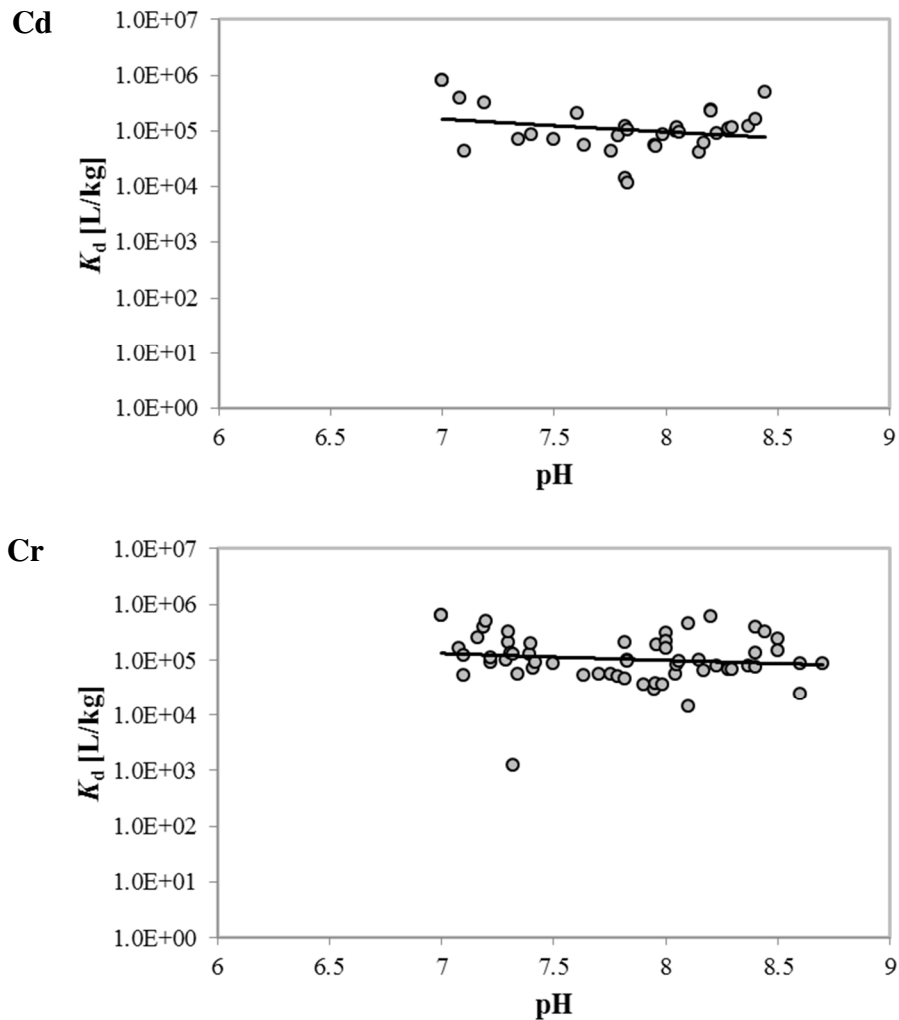
406

### 407 3.5. $K_d$ distributions for *in situ* conditions as a function of pH

408 Obviously pH is a relevant parameter to consider in order to reduce the variability of  $K_d$   
409 distributions, because a large fraction of metals in freshwaters is present as free ions under  
410 acidic conditions, whereas they precipitate with oxy-hydroxyde under alkaline conditions  
411 (Stumm and Morgan, 1995). However, the pH variability in freshwater is limited, and the  $K_d$

412 values compiled in the database for SS and *in situ* conditions correspond to pH ranging  
 413 mainly from 6.6 to 8.4.

414 Moreover, the amount of  $K_d$  data for SS is insufficient to determine the evolutions of  $GM(K_d)$   
 415 and  $GSD(K_d)$  as a function of pH, and only a mean tendency of  $K_d$  can be investigated for *in*  
 416 *situ* conditions.



417 Fig. 8.  $K_d$  of Cd and Cr for SS under *in situ* conditions as a function of pH.

418

419 The pH does not significantly affect the mean tendency of  $K_d$  values in our range of data (6.4-  
 420 9.3). Cd and Cr are given as examples in Fig. 8, but similar results are obtained for the other  
 421 elements, with relation in the form of:  $K_d = a \cdot \text{pH}^b$  (Table 3, SS and *in situ* conditions).

422

423

Table 3. Mean  $K_d$  for SS under *in situ* conditions as a function of pH.

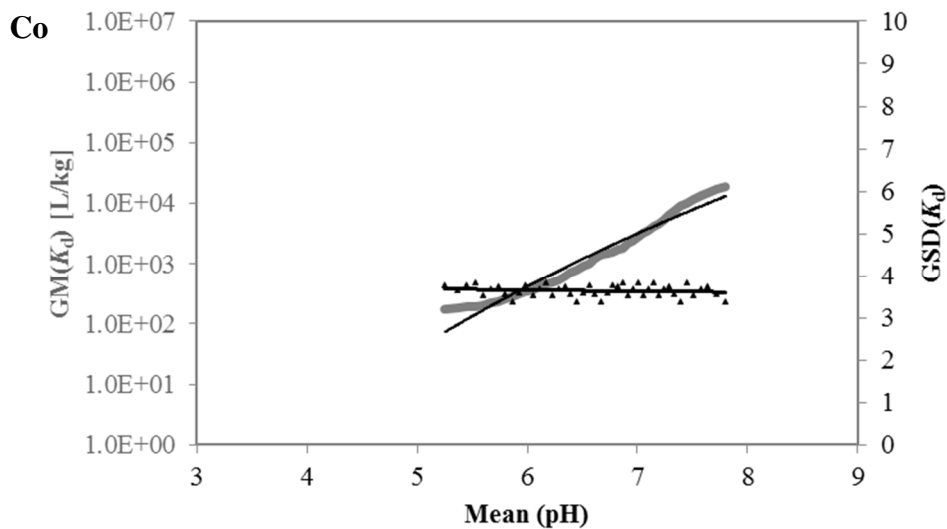
Element	Range of pH	Equation	$R^2$ ( <i>p</i> -value)
Am	6.80-8.90	$K_d = 2.92 \cdot 10^3 \cdot (\text{pH})^{1.66}$	0.0110 ( $2.87 \cdot 10^{-1}$ )

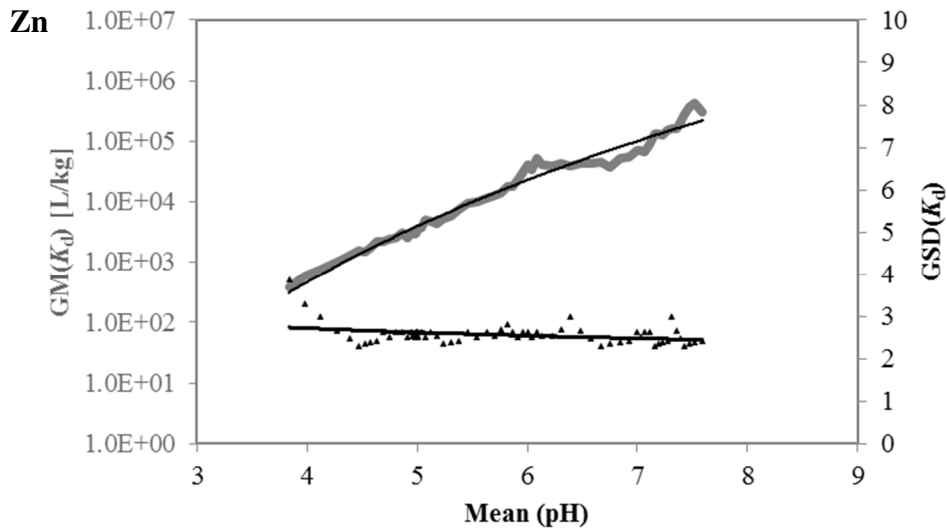
As	7.00-8.44	$K_d = 6.00 \cdot 10^9 \cdot (\text{pH})^{-6.33}$	0.0639 ( $2.44 \cdot 10^{-1}$ )
Cd	7.00-8.44	$K_d = 4.00 \cdot 10^8 \cdot (\text{pH})^{-4.01}$	0.0544 ( $1.91 \cdot 10^{-1}$ )
Co	7.00-8.44	$K_d = 6.00 \cdot 10^{13} \cdot (\text{pH})^{-10.05}$	0.2391 ( $1.83 \cdot 10^{-3}$ )
Cr	7.00-8.60	$K_d = 9.00 \cdot 10^6 \cdot (\text{pH})^{-2.15}$	0.0169 ( $3.27 \cdot 10^{-1}$ )
Cs	6.70-9.30	$K_d = 0.02 \cdot 10^0 \cdot (\text{pH})^{7.33}$	0.2025 ( $1.30 \cdot 10^{-4}$ )
Cu	6.66-8.44	$K_d = 2.00 \cdot 10^{14} \cdot (\text{pH})^{-10.72}$	0.2731 ( $1.12 \cdot 10^{-4}$ )
Fe	6.81-8.44	$K_d = 2.00 \cdot 10^{10} \cdot (\text{pH})^{-5.45}$	0.1297 ( $5.78 \cdot 10^{-3}$ )
Mn	6.81-8.44	$K_d = 2.00 \cdot 10^{19} \cdot (\text{pH})^{-16.35}$	0.0001 ( $9.46 \cdot 10^{-1}$ )
Ni	7.00-8.44	$K_d = 2.00 \cdot 10^{19} \cdot (\text{pH})^{-16.35}$	0.2425 ( $3.80 \cdot 10^{-4}$ )
Pb	5.20-8.44	$K_d = 1.17 \cdot 10^4 \cdot (\text{pH})^{1.46}$	0.0405 ( $1.61 \cdot 10^{-1}$ )
Zn	6.81-8.44	$K_d = 1.00 \cdot 10^{11} \cdot (\text{pH})^{-6.98}$	0.0749 ( $1.06 \cdot 10^{-1}$ )

424

425 These relationships are statistically significant ( $p$ -value < 0.05) for Co, Cs, Cu, Fe and Mn,  
 426 but the determination coefficients ( $R^2$ ) are very low for all elements, varying from 0.0001 to  
 427 0.24.  $K_d$  of As, Co, Cu, Mn and Zn are characterized by a smooth decrease with increasing pH  
 428 ( $b$  values from -6.33 to -16.35).

429 The compiled  $K_d$  data for DS under *in situ* and adsorption conditions cover a larger range of  
 430 pH values than for SS (Fig. 9 presents Co and Zn as examples in the case of adsorption  
 431 experiments).





432 Fig. 9.  $K_d$  log-normal distributions ( $GM(K_d)$  — and  $GSD(K_d)$ ▲) as a function of pH for DS  
 433 under adsorption conditions.

434

435 Table 4 presents the relationships obtained for the variations of  $GM(K_d)$  and  $GSD(K_d)$  of DS  
 436 as a function of pH. The best correlations were obtained by applying here again the following  
 437 forms:  $GM(K_d) = a \cdot pH^b$  and  $GSD(K_d) = c \cdot pH^d$ . Relations between  $GM(K_d)$  and pH are all  
 438 statistically significant ( $p$ -value  $\ll 0.5$ ), whatever the conditions.

439 For most of the elements, the increase of pH leads to an increase of  $GM(K_d)$ , a trend may be  
 440 related to the change in adsorption capacities of solid surfaces. Under acidic conditions,  
 441 metals form free ionic species, and protons are fixed by the negatively charged surfaces,  
 442 inducing a reduction of their sorption capacities. Adsorption increases with more natural pH  
 443 due to the increase of negative surface charges (Shi et al., 1998) that facilitate the sorption of  
 444 cations (Vesely et al., 2001). Therefore, higher  $K_d$  values are observed when the pH increases.

445

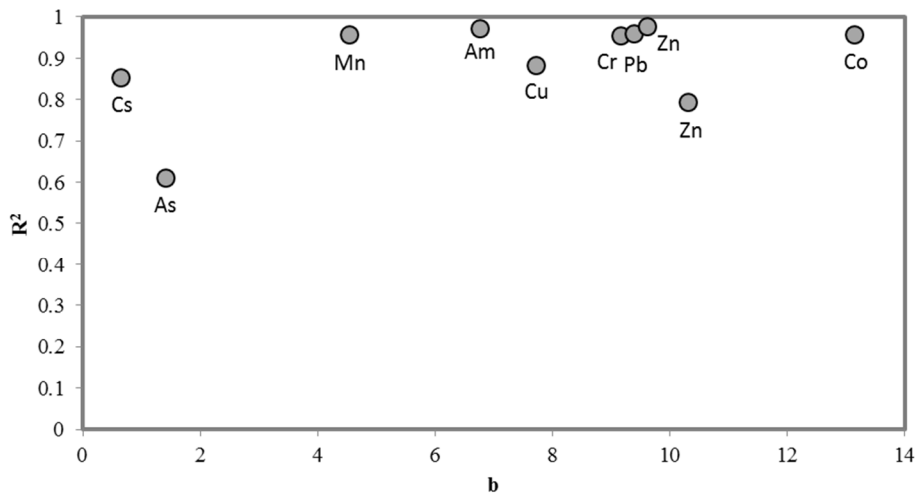
446 Table 4.  $GM(K_d)$  and  $GSD(K_d)$  for DS under *in situ* and adsorption conditions as a function of  
 447 pH.

Element	Process exchange	$GM(K_d)$		$GSD(K_d)$		$N^*$
		Equation	$R^2$ ( $p$ -value)	Equation	$R^2$	
Am	adsorption	$GM(K_d) = 8.25 \cdot 10^{-1} \cdot (pH)^{6.76}$	0.9720 ( $3.92 \cdot 10^{-15}$ )	$GSD(K_d) = 10.87 \cdot (pH)^{-0.88}$	0.5398	10
As	<i>in situ</i>	$GM(K_d) = 5.88 \cdot 10^2 \cdot (pH)^{1.41}$	0.6094 ( $3.77 \cdot 10^{-3}$ )	$GSD(K_d) = 1.60 \cdot (pH)^{0.09}$	0.0453	10
Co	adsorption	$GM(K_d) = 2.00 \cdot 10^{-8} \cdot (pH)^{13.14}$	0.9566 ( $3.11 \cdot 10^{-30}$ )	$GSD(K_d) = 4.00 \cdot (pH)^{-0.05}$	0.0213	40
Cr	<i>in situ</i>	$GM(K_d) = 1.00 \cdot 10^{-3} \cdot (pH)^{9.16}$	0.9532 ( $1.60 \cdot 10^{-7}$ )	$GSD(K_d) = 2.52 \cdot (pH)^{-0.16}$	0.0128	10
Cs	adsorption	$GM(K_d) = 2.12 \cdot 10^3 \cdot (pH)^{0.66}$	0.8535 ( $2.18 \cdot 10^{-20}$ )	$GSD(K_d) = 5.39 \cdot (pH)^{-0.27}$	0.5703	35

Cu	<i>in situ</i>	$GM(K_d) = 2.13 \cdot 10^{-2} \cdot (pH)^{7.72}$	0.8826 ( $9.67 \cdot 10^{-20}$ )	$GSD(K_d) = 1.45 \cdot (pH)^{0.17}$	0.0431	15
Mn	<i>in situ</i>	$GM(K_d) = 7.20 \cdot 10^1 \cdot (pH)^{4.55}$	0.9560 ( $5.45 \cdot 10^{-5}$ )	$GSD(K_d) = 6.75 \cdot (pH)^{0.05}$	0.2242	15
Pb	<i>in situ</i>	$GM(K_d) = 1.20 \cdot 10^{-3} \cdot (pH)^{9.39}$	0.9597 ( $2.68 \cdot 10^{-8}$ )	$GSD(K_d) = 0.94 \cdot (pH)^{0.31}$	0.1490	10
Zn	adsorption	$GM(K_d) = 3.00 \cdot 10^{-4} \cdot (pH)^{10.32}$	0.7922 ( $1.31 \cdot 10^{-53}$ )	$GSD(K_d) = 3.41 \cdot (pH)^{-0.17}$	0.1300	10
	<i>in situ</i>	$GM(K_d) = 8.00 \cdot 10^{-4} \cdot (pH)^{9.61}$	0.9761 ( $4.54 \cdot 10^{-12}$ )	$GSD(K_d) = 4.69 \cdot (pH)^{-0.45}$	0.0409	10

448  $N^*$  - size of window (number of data)

449



450

451

Fig. 10.  $R^2$  as a function of  $b$  for the relation  $GM(K_d) = a \cdot pH^b$ .

452

453 The elements most sensitive to pH are Co, Zn, Pb and Cr (Fig. 10). These results are in  
 454 agreement with previous publications for Pb, Co and Zn (Alkhatib et al., 2016; Alkhatib et al.,  
 455 2016b; Tessier et al., 1989; Vesely et al., 2001; White and Driscoll, 1987), but not for Cr  
 456 (Peng et al., 2003). This difference between the results obtained from a specific study and  
 457 those obtained from a large dataset highlights that these relationships must be applied with  
 458 caution and that the use of local data remains the best choice. Moreover,  $GM(K_d)$  for Cs and  
 459 As are nearly independent of pH.

460 Here again the relationships giving  $GM(K_d)$  as a function of pH permit to reduce significantly  
 461 the variability. For example, total  $GSD(K_d)$  for Co decreases from 9.4 (Table S.2) to 3.5 when  
 462 pH is taken into account (Fig. 9), which represents a decrease in the variability of its  
 463 distribution over five orders of magnitude.

464

#### 465 4. Conclusions

466 A significant amount (3896) of new  $K_d$  data for stable and unstable nuclides (metals and non-  
 467 metals) was uploaded to complete and update the freshwater database of  $K_d$  values presented



468 in Boyer et al. (2018). After this update, the freshwater  $K_d$  database contains 8564  $K_d$  values  
469 for 50 elements: Ag, Al, Am, As, B, Ba, Be, Ca, Cd, Ce, Cm, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe,  
470 Gd, Hf, Hg, Ho, I, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Po, Pr, Pu, Ra, Rb, Ru, S, Sb, Se, Si,  
471 Sn, Sr, Th, Ti, U, V, Zn. For each element, the  $K_d$  values are classified as a function of three  
472 exchange conditions (*in situ*, adsorption, desorption), two environmental components  
473 (suspended and deposited sediments) as well as for stable and unstable nuclides. Moreover,  
474 each  $K_d$  value is associated to several co-factors such as m/V, DOC and pH, when they were  
475 available. The new statistical distributions obtained for the different combinations between  
476 elements, exchange conditions and components do not show significant changes with those of  
477 the previous version of the database that reinforces the robustness of their representativeness.  
478 In the same way, it is again observed, for a large majority of elements, that  $GM(K_d)$  for SS  
479 under *in situ* conditions is two orders of magnitude higher than for DS.  
480 However, the main objective of this paper was to determine conditional statistical  
481 distributions of  $K_d$  as a function of m/V, DOC and pH values. These distributions were  
482 assumed log-normal and obtained by applying a sliding window method which showed that  
483  $GM(K_d)$  and  $GSD(K_d)$  change as power laws of m/V, DOC and pH. Although freshwater  $K_d$   
484 are characterized by high variability, it was shown that for most elements these relationships  
485 between the log-normal  $K_d$  distributions and the key parameters m/V, DOC and pH allowed  
486 reducing, by several orders of magnitudes, the variability of global  $K_d$  distributions for  
487 environmental components and sorption conditions. These relationships are thus very useful  
488 for decreasing the uncertainties in the prediction of the elements mobility in freshwater  
489 systems when the  $K_d$  approach is applied and *in situ* data not available.  
490 The new database of freshwater  $K_d$  compiled for this work contains 8564  $K_d$  values for 50  
491 elements. For each element, the  $K_d$  values were classified as a function of three exchange  
492 conditions (*in situ*, adsorption, desorption), two environmental components (suspended and  
493 deposited sediments) and separated between stable and unstable nuclides. Moreover, each  $K_d$   
494 value was associated to several co-factors such as m/V, DOC and pH when available.  
495 For a large majority of elements,  $GM(K_d)$  for suspended sediments under *in situ* conditions is  
496 two orders of magnitude higher than for deposited sediments. Statistical distributions of  $K_d$   
497 were defined as a function of m/V, DOC and pH values. These distributions were assumed  
498 log-normal and obtained by applying a sliding window method which showed that  $GM(K_d)$   
499 and  $GSD(K_d)$  change as power laws of m/V, DOC and pH. Although freshwater  $K_d$  are  
500 characterized by high variability, it was shown that for most elements these relationships  
501 between the log-normal  $K_d$  distributions and the key parameters m/V, DOC and pH allowed to

502 reduce, by several orders of magnitudes, the variability of global  $K_d$  distributions for  
503 environmental components and sorption conditions. These relationships can be used for  
504 decreasing the uncertainties in the prediction of the elements mobility in freshwater systems  
505 when the  $K_d$  approach is applied and if *in situ* data are not available.

506

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