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

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Highlights:

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

Abstract

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

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

1. Introduction

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

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

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

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

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

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

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

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

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

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

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

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

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

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

2. Material and methods

2.1. Updated database

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

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

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

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

2.2. Statistical analysis

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

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

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

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

3. Results and discussion

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

3.1. Evolution of freshwater K_d distributions after updating

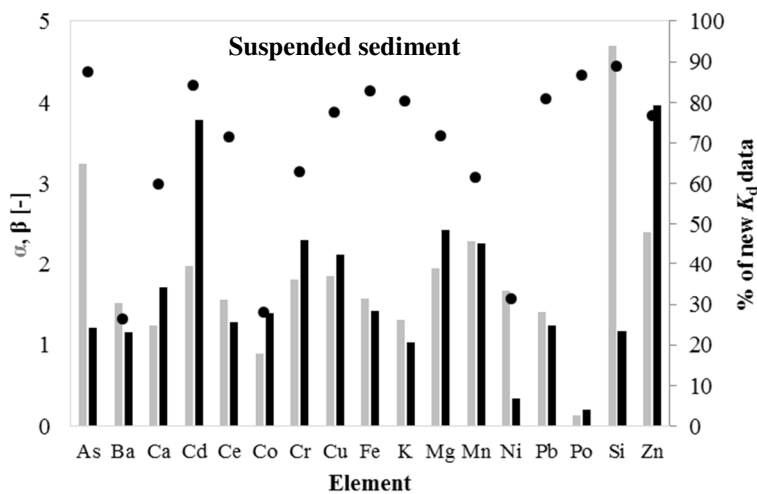
Since the database has been updated with a significant number of new K_d data, the resulting K_d distributions should be first compared to the previous ones (Boyer et al., 2018) to assess the robustness and representativeness of the datasets. For this purpose, parameters α and β are calculated:

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

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

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

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



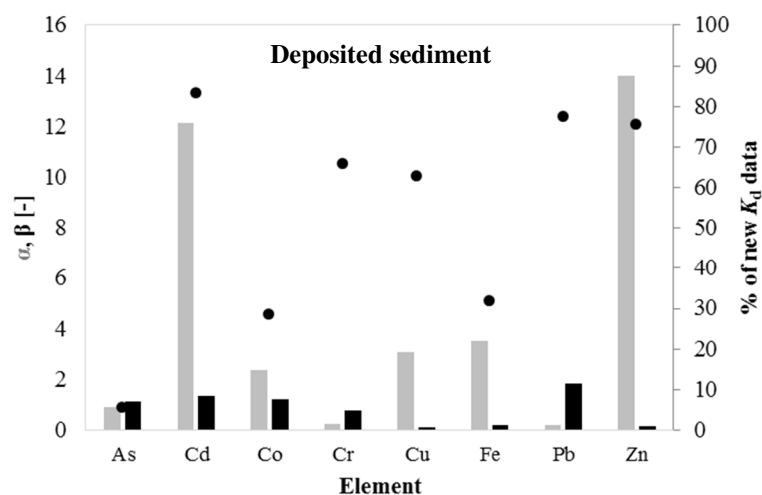


Fig. 1. α \blacksquare , β \blacksquare and % of new K_d data \bullet for SS and DS under *in situ* conditions.

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

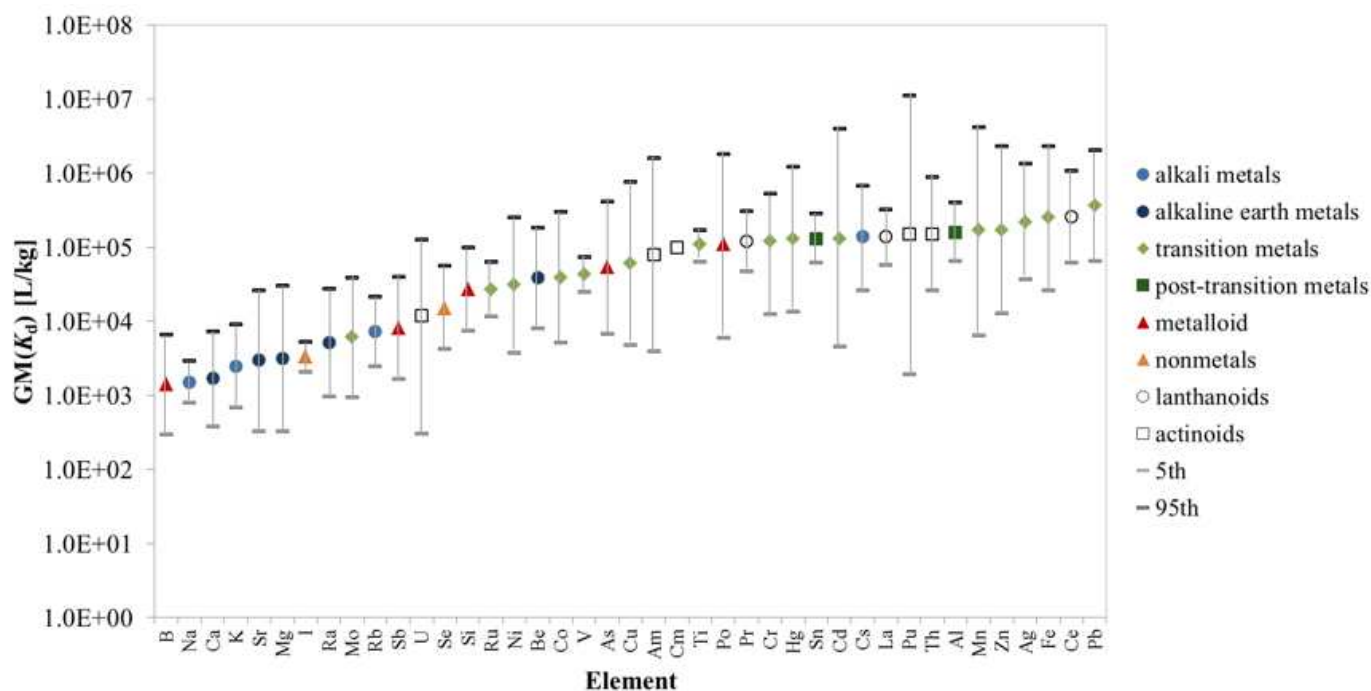


Fig. 2. Classification of elements in the increasing order of $GM(K_d)$ values for SS and *in situ* conditions. The 5th and 95th of their distributions are represented by the little dashes.

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

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

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

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

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

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

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

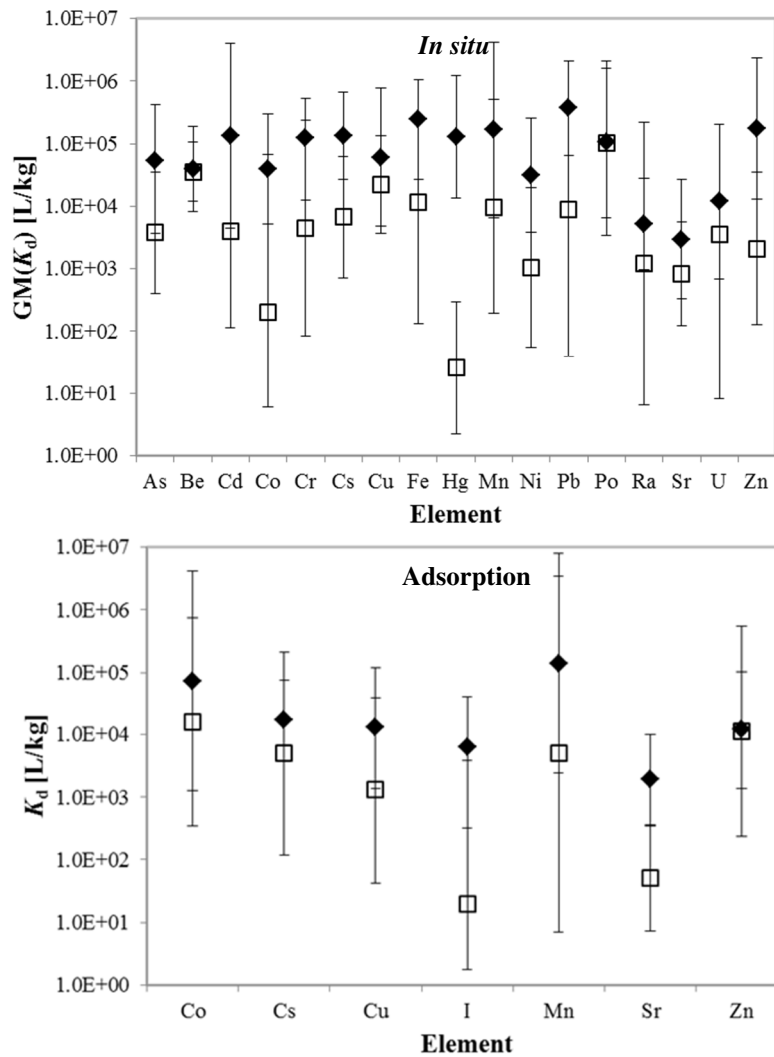


Fig. 3. K_d distributions for SS \blacklozenge and DS \square under *in situ* and adsorption conditions. (The points correspond to $GM(K_d)$ and the upper and lower limits to the 5th and the 95th percentiles)

There is therefore a recurrent difference between the K_d distributions in function of SS and DS, and this is probably associated with the different properties of the particles rather than to the speciation in the dissolved phase. Mean particles size of DS, for example, are generally higher than those of SS and thus tend to have lower metal sorption capacity. DS are also characterized by lower porosity than SS, leading to a lower exchange surface and thus decreasing metal sorption process. It can also be considered that the properties of the organic matter of DS are different from those SS due to the degradation of organic carbon during early diagenesis (Henrichs, 1992; Zhang et al., 2014).

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

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

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

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

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

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

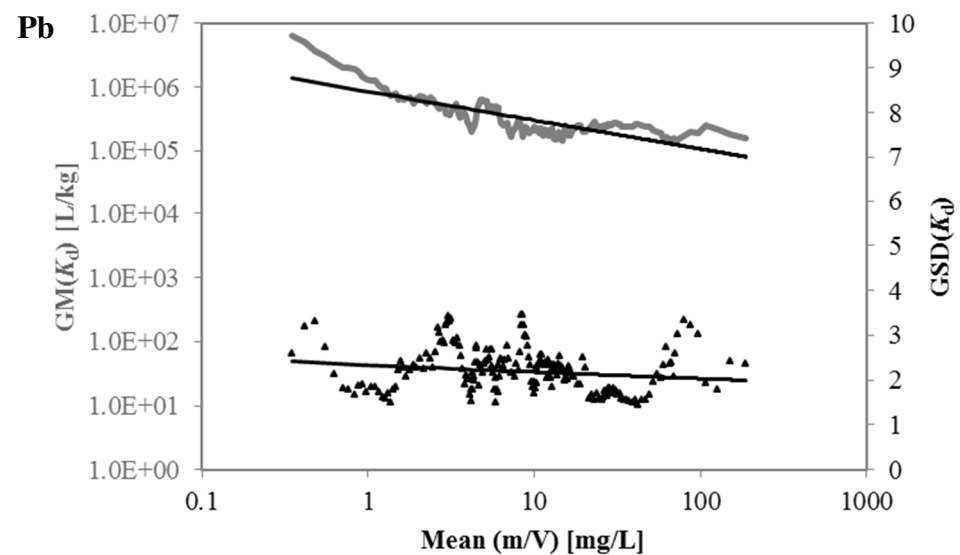
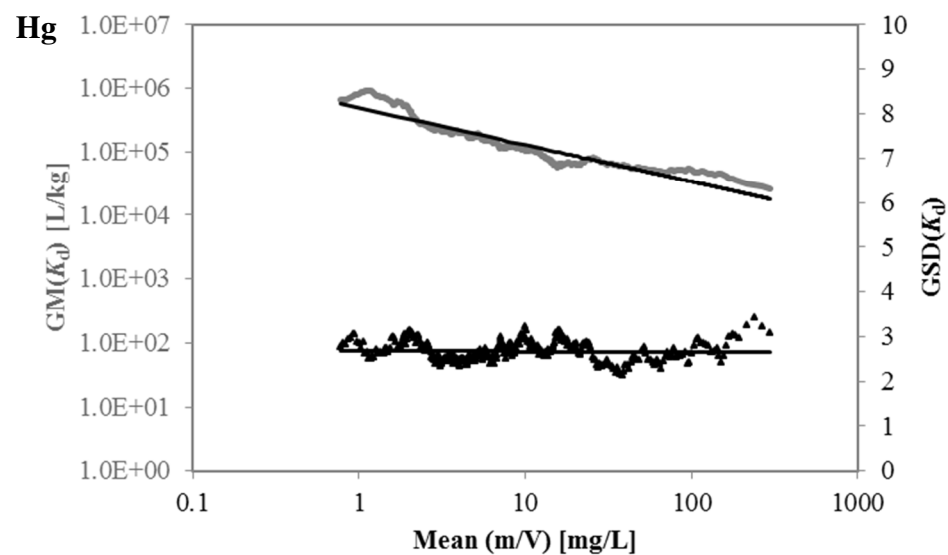
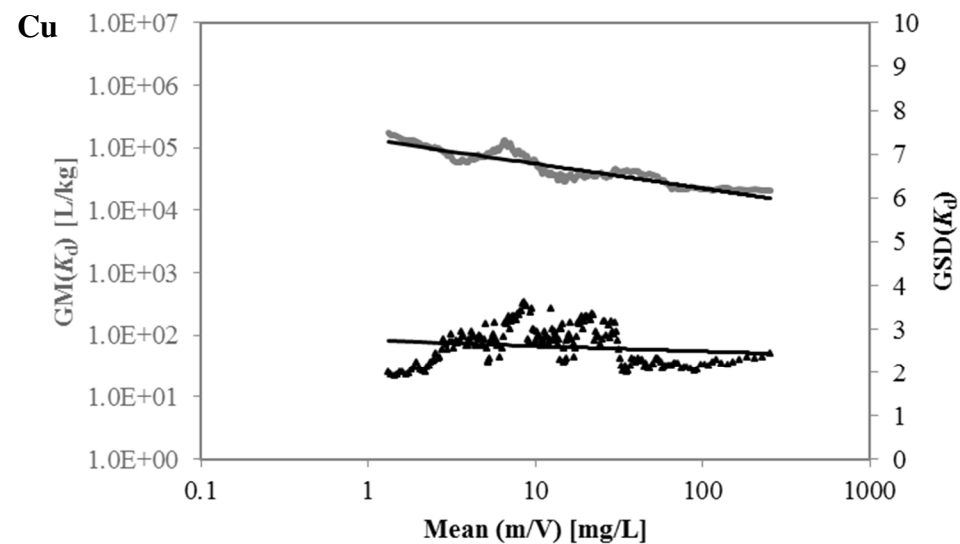
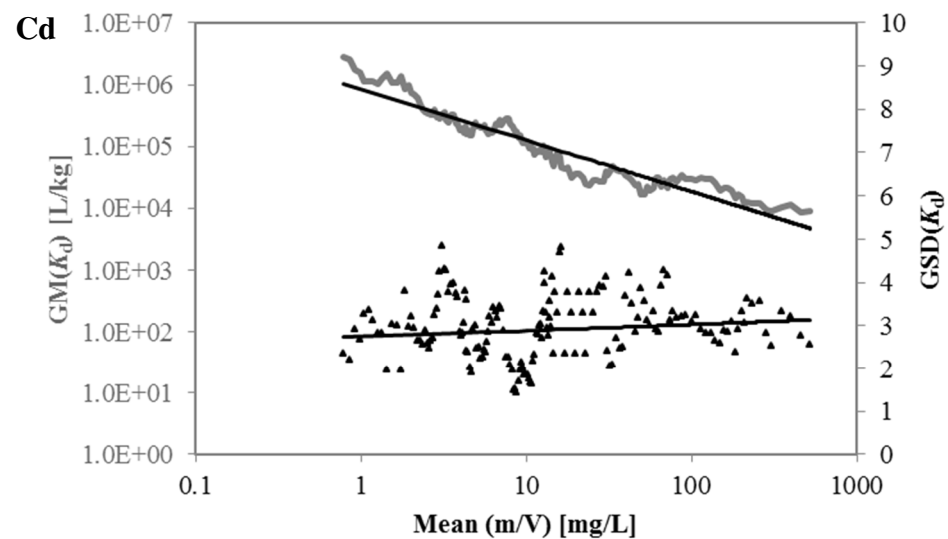
For these elements and for *in situ* suspended matters, the origin of the element, which could be natural (i.e. within the crystal structure of the minerals and/or adsorbed onto the surface) or anthropic (i.e. rather associated to surface adsorption), does not greatly influence the $GM(K_d)$. This result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

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

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

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

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



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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.

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^2 (p -value)	Equation	R^2	
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

N^* - size of window (number of K_d data)

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

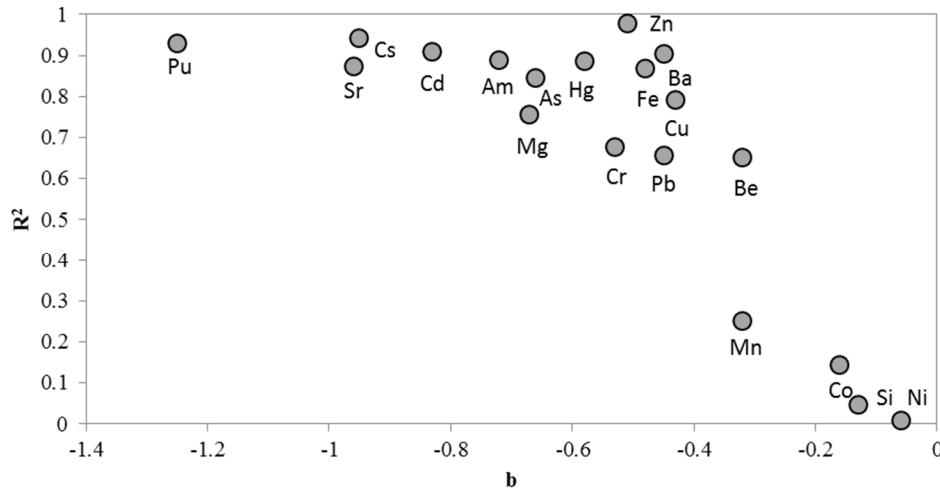


Fig. 5. R^2 as a function of b for the relation $GM(K_d) = a \cdot (m/V)^b$.

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

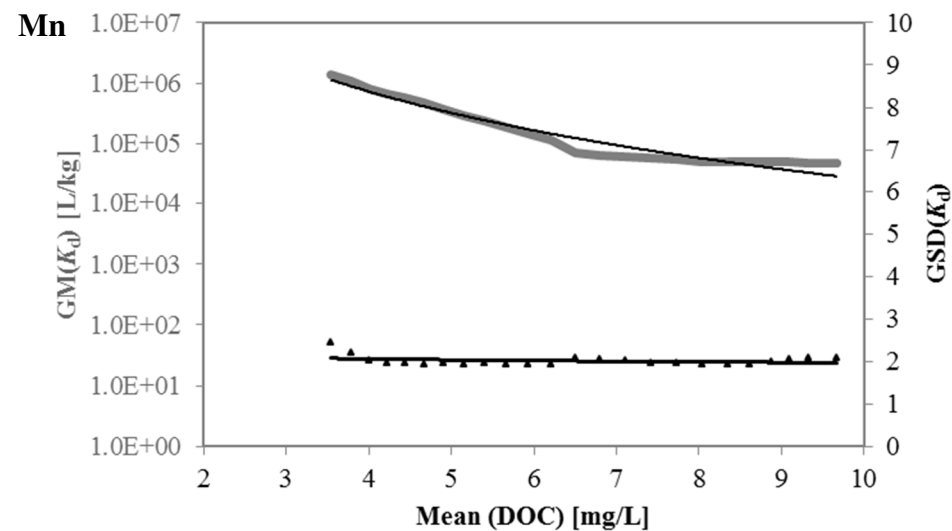
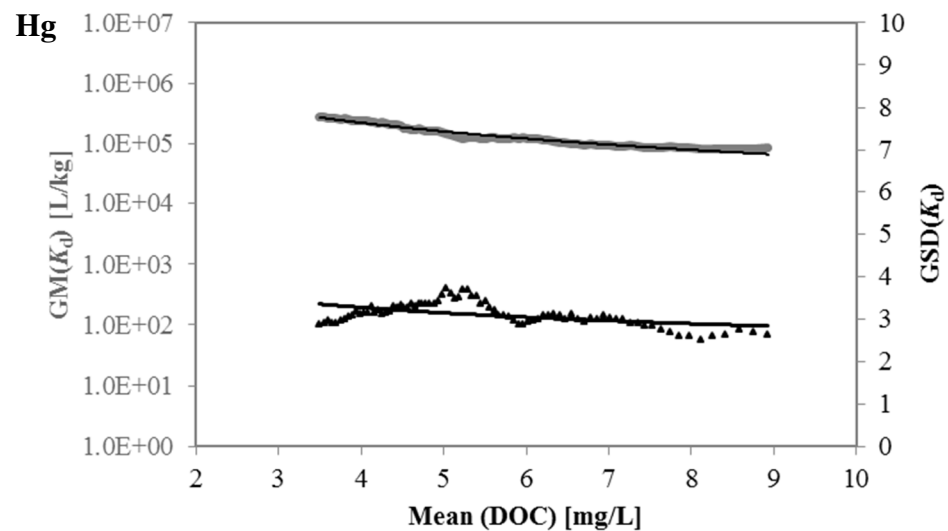
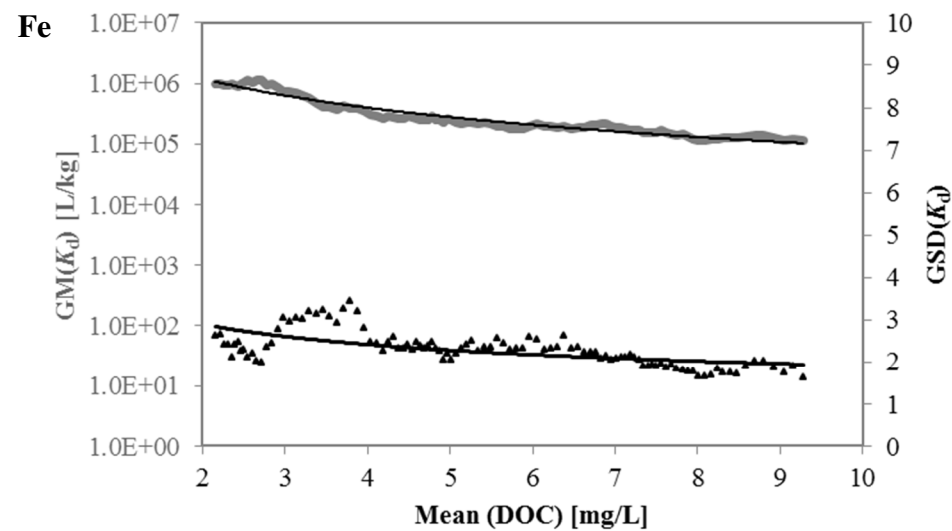
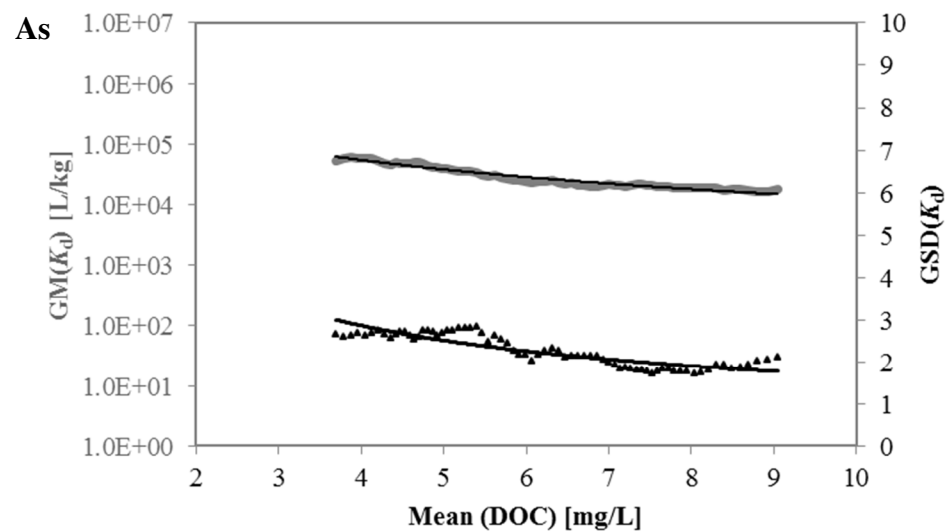
The relationships from Table 1 allow to significantly reduce the K_d variability. For example, the total $GSD(K_d)$ of Cu and Ca for SS in *in situ* conditions that initially equal 4.6 and 7.8 respectively (Table S.2) are reduced to 2-3 and 2-4 by considering m/V (Fig. 4). Thus, the variability of their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

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

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

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

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



376

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.

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

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 ² (<i>p</i> -value)	Equation	R ²	
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

N* - size of window (number of data)

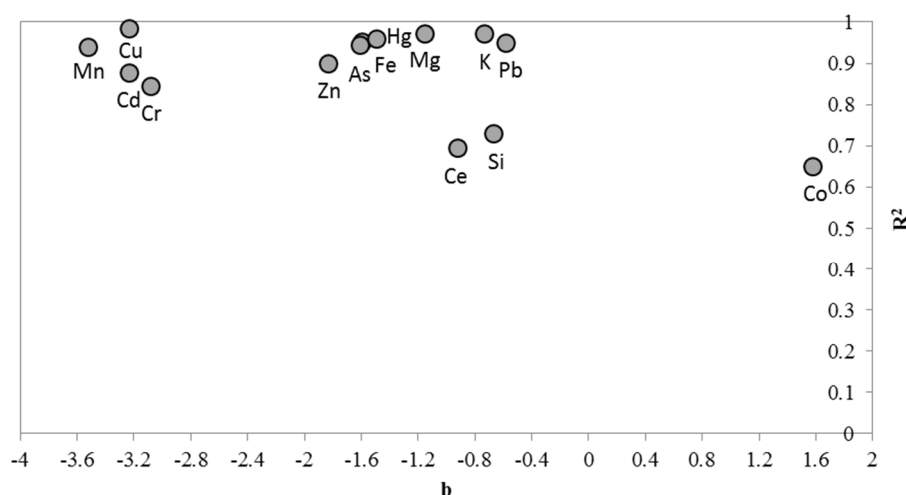


Fig. 7. R^2 as a function of b for the relationship $GM(K_d) = a \cdot DOC^b$.

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

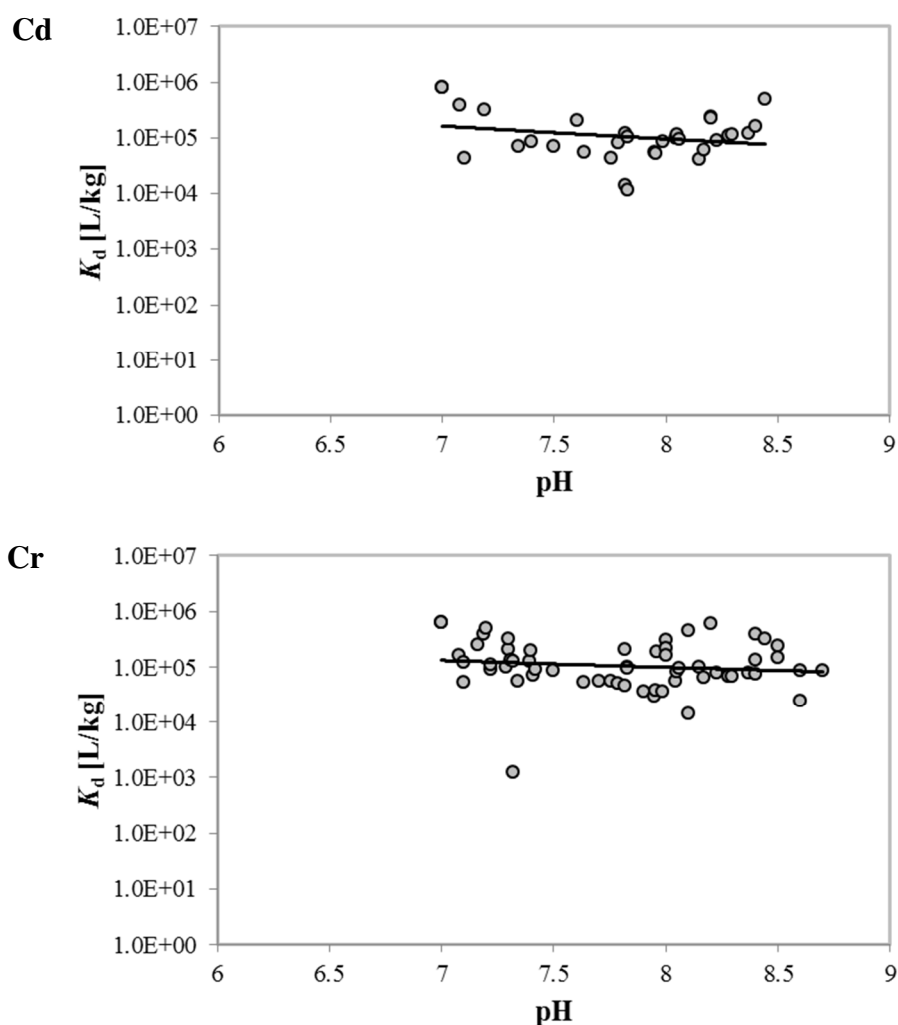
The elements less sensitive to the DOC concentrations are Co and Si. In particular, Co is the only element for which the slope b is positive and, for Si, this result is in accordance with the work of Veselý et al. (2001). At this stage, it can also be noted that the K_d distributions of Si and Co are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

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

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

Obviously pH is a relevant parameter to consider in order to reduce the variability of K_d distributions, because a large fraction of metals in freshwaters is present as free ions under acidic conditions, whereas they precipitate with oxy-hydroxyde under alkaline conditions (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: $K_d = a \cdot pH^b$ (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	$K_d = 2.92 \cdot 10^3 \cdot (pH)^{1.66}$	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

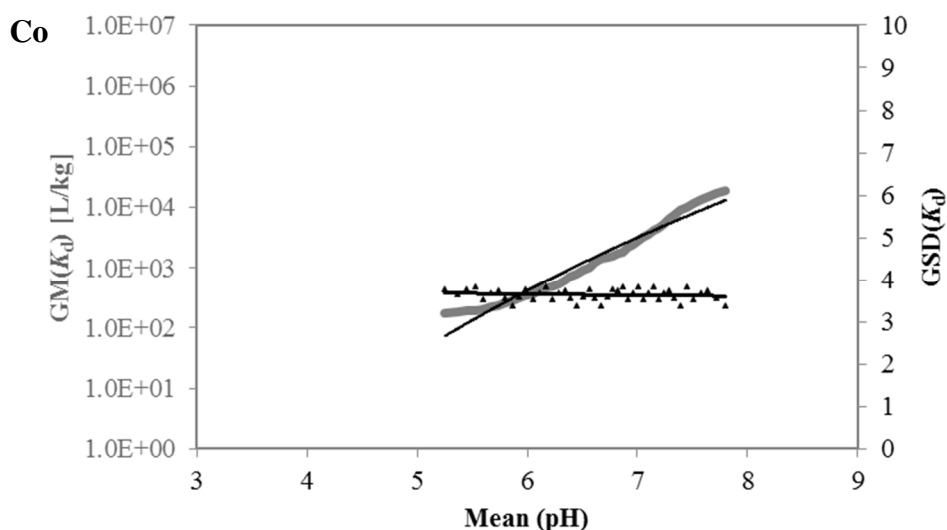
427 0.24. K_d of As, Co, Cu, Mn and Zn are characterized by a smooth decrease with increasing pH

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).



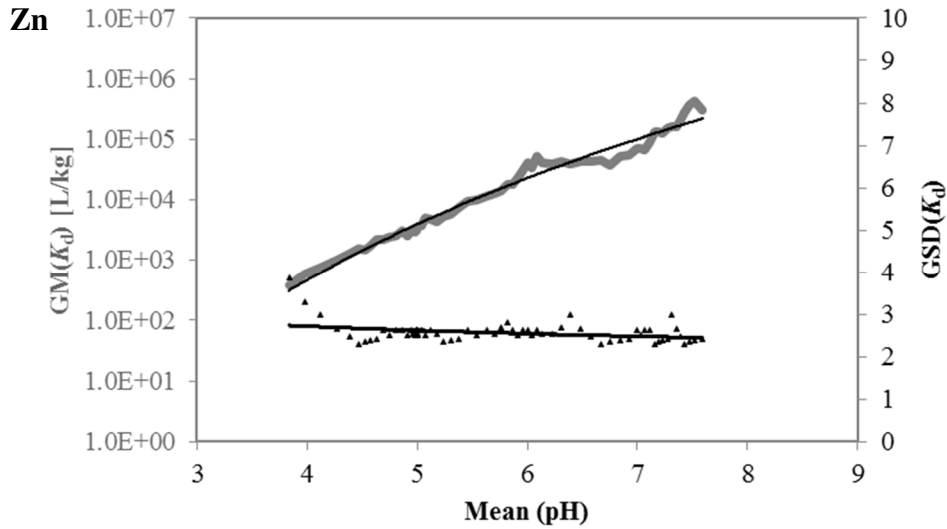


Fig. 9. K_d log-normal distributions ($GM(K_d)$ — and $GSD(K_d)$ ▲) as a function of pH for DS under adsorption conditions.

Table 4 presents the relationships obtained for the variations of $GM(K_d)$ and $GSD(K_d)$ of DS as a function of pH. The best correlations were obtained by applying here again the following 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 statistically significant (p -value $\ll 0.5$), whatever the conditions.

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

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

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

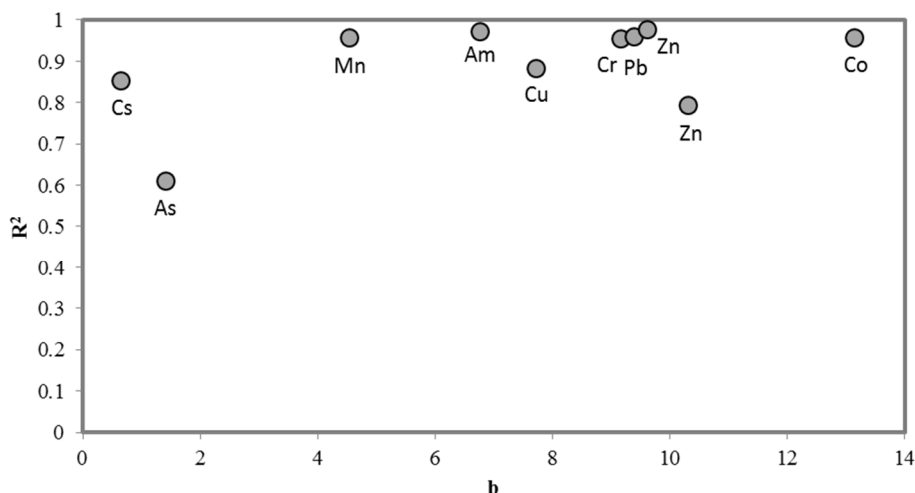


Fig. 10. R^2 as a function of b for the relation $GM(K_d) = a \cdot pH^b$.

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

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

4. Conclusions

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

in Boyer et al. (2018). After this update, the freshwater K_d database contains 8564 K_d values for 50 elements: Ag, Al, Am, As, B, Ba, Be, Ca, Cd, Ce, Cm, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Hf, Hg, Ho, I, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Po, Pr, Pu, Ra, Rb, Ru, S, Sb, Se, Si, Sn, Sr, Th, Ti, U, V, Zn. For each element, the K_d values are classified as a function of three exchange conditions (*in situ*, adsorption, desorption), two environmental components (suspended and deposited sediments) as well as for stable and unstable nuclides. Moreover, each K_d value is associated to several co-factors such as m/V, DOC and pH, when they were available. The new statistical distributions obtained for the different combinations between elements, exchange conditions and components do not show significant changes with those of the previous version of the database that reinforces the robustness of their representativeness. In the same way, it is again observed, for a large majority of elements, that $GM(K_d)$ for SS under *in situ* conditions is two orders of magnitude higher than for DS.

However, the main objective of this paper was to determine conditional statistical distributions of K_d as a function of m/V, DOC and pH values. These distributions were assumed log-normal and obtained by applying a sliding window method which showed that $GM(K_d)$ and $GSD(K_d)$ change as power laws of m/V, DOC and pH. Although freshwater K_d are characterized by high variability, it was shown that for most elements these relationships between the log-normal K_d distributions and the key parameters m/V, DOC and pH allowed reducing, by several orders of magnitudes, the variability of global K_d distributions for environmental components and sorption conditions. These relationships are thus very useful for decreasing the uncertainties in the prediction of the elements mobility in freshwater systems when the K_d approach is applied and *in situ* data not available.

The new database of freshwater K_d compiled for this work contains 8564 K_d values for 50 elements. For each element, the K_d values were classified as a function of three exchange conditions (*in situ*, adsorption, desorption), two environmental components (suspended and deposited sediments) and separated between stable and unstable nuclides. Moreover, each K_d value was associated to several co-factors such as m/V, DOC and pH when available.

For a large majority of elements, $GM(K_d)$ for suspended sediments under *in situ* conditions is two orders of magnitude higher than for deposited sediments. Statistical distributions of K_d were defined as a function of m/V, DOC and pH values. These distributions were assumed log-normal and obtained by applying a sliding window method which showed that $GM(K_d)$ and $GSD(K_d)$ change as power laws of m/V, DOC and pH. Although freshwater K_d are characterized by high variability, it was shown that for most elements these relationships between the log-normal K_d distributions and the key parameters m/V, DOC and pH allowed to

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

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