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A method to determine the soil-solution distribution
coefficients and the concentrations for the free ion and
the complexes of trace metals: Application to
cadmium

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Abstract

Partitioning of metals between the soil solid phase and the solution is an important topic in environmental sciences because it determines the metal transfers to aquifers and biological organisms. Complexation of metals with ligands in the soil solution strongly influences the sorption/desorption (SD) of metals, in particular that of the free ion. Because the latter is the metal species principally absorbed by biological organisms, the bioavailability of a metal is better reflected by the soil-solution distribution coefficients of the free ion as compared to that of the total metal (sum of the free ion and of the complexes). The present work proposed a modeling approach to determine the distribution coefficients for the free ion and for the metal complexes from SD experiments. The method does not require estimating the mobile pool of the metal sorbed onto the solid phase by any chemical extraction as the modeling relies on the variation of the sorbed metal, which is experimentally exactly estimated from the variation of the amount of metal in solution during the SD experiment. Tested for cadmium (Cd), the model reproduced very well the SD curves observed for the total metal. For any solution:soil ratio including that at field soil moisture, the model gives estimates of important variables including the distribution coefficient for the free ion, the complex, the ligands and the total metal, the concentration of these species in the soil solution and onto the solid phase. The model can be applied as long as the range of the concentration investigated allows to assume a linear sorption of the metal.

Keywords : Complexation; Distribution coefficient; Modeling, Sorption-desorption; Trace metals

1 Introduction

Trace metals in soils is an important research topic because on one hand, as micronutrients, they contribute to plant health and to the nutritional value of food and feed crop products and on the other hand, excess of toxic or essential metals in soils due to anthropogenic inputs has negative environmental and agricultural impacts. In soil, most of trace metals are distributed between the solid phase, the biomass and the solution. The partitioning between the solid phase and the solution is of particular importance because it governs the physical transfers of metals (e.g. leaching) and their uptake by biological organisms (Kabata-Pendias, 2004; Posch and de Vries, 2009; de Vries and Groenenberg, 2009; de Vries et al., 2011). In the soil solution, cationic trace metals form complexes of variable stability with ligands, generally dominated by organic molecules including the ubiquitous organic macromolecules fulvic and humic acids (Ren et al., 2015; Weng et al., 2002). Biological organisms, including plant roots, generally absorb metals preferentially as free hydrated ions and not or very little as organo-metallic complexes (Custos et al., 2014; Lin et al., 2014, 2016). As the result of various physical and chemical interactions, both the free metal ion and the metal complexes can exchange from the solution onto the solid phase (sorption) and conversely from the solid phase to the soil solution (desorption) (Selim, 2013). The partitioning of an element between the solid phase and the solution can be characterized by the distribution coefficients (K_d), *i.e.* the concentration ratio of the sorbed to the soluble metal and this, for the total metal ($K_{d,Mtot}$), for its free ion ($K_{d,M}$) or for the complexes ($K_{d,ML}$) (Degryse et al., 2009; Filipović et al., 2016; Legind et al., 2012). Due to the numerous physical and chemical mechanisms responsible for the sorption and desorption of metals, depending on the soil characteristics and on the range of the metal concentration, the distribution coefficient can be deduced from different mathematical models, the most common one being the linear model, the curvilinear model without (Freundlich model) or with (Langmuir model) a saturation plateau (Selim, 2013). Furthermore, the kinetics of the SD reactions can make the partitioning coefficient depend on time (Fardeau et al., 1991; Gray et al., 1999).

Experimentally, the distribution coefficient for the total metal ($K_{d,Mtot}$) can be estimated by different approaches. The SD experiments are the most common one and consist

66 in determining the metal concentration in the solution after addition of the metal at
 67 a concentration higher than the one of the soil solution for a given solution:soil ratio
 68 (sorption) or by increasing the water:soil ratio with no addition of metal to the solution
 69 (desorption). Frequently, the distribution coefficient is calculated from the determination
 70 of the pool of metal that is reversibly sorbed onto the solid phase. One main issue
 71 of the SD approach lies in the determination of this pool, which is generally based on
 72 chemical extractions. Indeed, an over or underestimation of this pool makes the estimated
 73 $K_{d,Mtot}$ strongly depend on the experimental conditions including the solution:soil ratio in
 74 a manner that is difficult to interpret and particularly confusing (see the demonstration
 75 in the Supplementary Information (SI)). The second approach is the so-called isotopic
 76 dilution and is based on the partition of a radioactive or stable isotope of the metal added
 77 to a soil suspension at a low concentration so that it is assumed to not significantly modify
 78 the partition equilibrium (Tiller et al., 1972; Sivry et al., 2006; Gérard et al., 2000). The
 79 isotopic dilution is likely the most attractive method to estimate the pool of metal that
 80 is reversibly sorbed onto the solid phase from the partitioning of the isotope (Schneider
 81 and Morel, 2000; Degryse et al., 2009; Sterckeman et al., 2004; Schneider et al., 2003),
 82 but the use of isotopes can be difficult to implement.

83 Both the isotope dilution and the SD experiments approaches are generally performed at
 84 a solution:soil ratio (r) much higher than the one corresponding to the soil moisture in the
 85 field (Degryse et al., 2009). For a practical use, this is a concern because the distribution
 86 coefficient was observed to increase with r (Di Toro et al., 1986; Ponizovsky et al., 2006).
 87 The possible explanations evoked to explain this dependence to r are the occurrence
 88 of colloid particles in the solution that are not removed by filtration, the interactions
 89 between soil particles (Di Toro et al., 1986; O'Connor and Connolly, 1980), or the SD
 90 of organic matter, which in turn affects the complexation of the metals in solution (Yin
 91 et al., 2002). The latter hypothesis has frequently been pointed out to explain the shape
 92 of the SD curve (Elliott and Denny, 1982; Christensen, 1985, 1989; Neal and Sposito,
 93 1986; Boekhold et al., 1993; Temminghoff et al., 1995; Singh and Pandeya, 1998; Zhou
 94 and Wong, 2001). Besides, some experimental conditions can also strongly influence the
 95 partitioning of the metal between the solid phase and the solution, making the estimate

be significantly different from that of the field conditions (Harter and Naidu, 2001; Shi et al., 2007; Degryse et al., 2009). An important one is the Ca concentration, which is generally fixed for SD experiments but not necessarily at a value corresponding to realistic soil water contents (Christensen, 1984; Degryse et al., 2009; Staunton, 2004).

If bioavailability of the metal is the topic of investigation, the distribution coefficient for the total metal ($K_{d,Mtot}$) is expected to be of limited value and it is necessary to estimate the distribution coefficient for the free metal ($K_{d,M}$), for the complex ($K_{d,ML}$) and to understand complexation in solution (Filipović et al., 2016; Legind et al., 2012; Lin et al., 2016; Schneider et al., 2018). Generally, in literature, authors do not consider the speciation of the metal in solution and report the partition coefficient for the total metal assuming that only M but not ML sorbed onto the soil matrix (e.g. Yin et al., 2002; Ponizovsky et al., 2006). It is still a challenge to estimate the distribution coefficient for the free metal and for the complex and to determine the metal speciation in solution, particularly at a solution:soil ratio consistent with the water content of soil *in situ*. There is a need for a method as simple as possible to estimate the partition coefficients of a metal that also consider complexation. Therefore, this study aimed at i) developing a model for the SD of a trace metal in soil that takes into account the complexation and its associated experimental approach in order to estimate the partition coefficients for the free ion and for the complexes and also the concentrations of these species in the soil solution at realistic solution:soil ratios, ii) to apply the approach to cadmium (Cd), a metal of particular interest for both agricultural and environmental issues.

2 Materials and Methods

2.1 Considerations about the distribution coefficient

The distribution coefficient of an element (L kg^{-1}) is generally defined as :

$$K_d = \frac{q}{c} \quad (1)$$

where q is the content sorbed onto the solid phase. If q does not include the fraction

121 of the element that is irreversibly sorbed onto the solid phase, q is the so-called 'mobile
 122 pool' that can exchange with the solution (Schneider and Morel, 2000; Schneider, 2003).
 123 The distribution of an element between the solution and the solid phase depends on time
 124 because the sorbed species is generally constituted by at least two pools showing different
 125 kinetics. The pool that reacts the most slowly is responsible for what is called "ageing" of
 126 the trace elements. Here, we consider a time scale for which the fast SD reactions are more
 127 or less completed and the slowest reactions are not significantly involved (Selim, 2013).
 128 The variable c is the concentration in the solution at equilibrium with the solid phase.
 129 If q is actually the mobile pool, it tends towards zero when the species concentration
 130 in solution also tends towards zero, and conversely. Therefore, the theoretical SD curve,
 131 linear or not, should pass through the origin point. We also consider a time scale for which
 132 the fast SD reactions are completed and therefore the system is at pseudo-equilibrium,
 133 which means that after, K_d changes little. In order to assume that the distribution
 134 coefficient is constant, the metal added to the soil during sorption or the solution:soil
 135 ratio during desorption must be sufficiently low so as the final metal concentration in
 136 solution does not differ too much from the concentration of the soil solution of the soil in
 137 its initial state (Schneider, 1997).
 138 An important issue of SD experiments is that none method can perfectly determines
 139 the mobile pool. If the pool of the metal sorbed onto solid phase that is determined
 140 experimentally does not match the mobile pool, the interpretation of the SD curves is
 141 biased (see the demonstration in the SI). One way to solve this problem is to define the
 142 distribution coefficient as the buffer power (Barber, 1995) :

$$K_d = \frac{dq}{dc} \quad (2)$$

143 and to analyze SD experiments by considering the variation of the mobile pool of the metal
 144 sorbed onto the solid phase $\Delta q = (q_f - q_0)$ where the q_f and q_0 correspond to the mobile
 145 pool after and before the sorption or desorption, respectively. During SD experiments,
 146 because the system is closed, any variation of the amount of the metal in the solution is
 147 balanced by the opposite variation of the amount of metal onto the solid phase. Hence,
 148 Δq can always be estimated from the measurement of the variations of the concentration

of the metal in the solution by using the mass balance equation. In case of desorption, the mobile pool decreases and its variation Δq is negative while in parallel, the concentration in solution increases. Conversely, in case of sorption, the amount in solution decreases while the mobile pool increases and Δq is positive.

For a given soil, q_0 is constant for the different SD experiments whereas q_f varies. So, $d(\Delta q) = d(q_f - q_0) = dq_f$ and Eq. 2 can be written as :

$$K_d = \frac{d(\Delta q)}{dc} \quad (3)$$

2.2 Modeling of the distribution coefficient by taking into account the speciation in the soil solution

2.2.1 Conceptual model and assumptions

The aim is to model the concentrations of a metal both in the solution and onto the solid phase, during SD experiments, taking into account the complexation in solution in order to estimate the distribution coefficient for both the metal free ion and its complexes (Variable description in Table 1).

Assumption 1. : A single virtual complex ML mimics the presence of the actual various complexes in the soil solution (Schneider, 2006, 2008; Lin et al., 2016). Therefore, only two metal species are considered in solution, the free ion M (c_M , M) and the complex ML (c_{ML} , M) formed with a mean free ligand L (c_L , M)

The initial state is a mass m (kg) of air-dried soil with a volume V_r (L) of residual solution. The soil contents in M , ML , L reversibly sorbed onto the solid phase are $q_{M,0}$, $q_{ML,0}$, $q_{L,0}$ (mol kg⁻¹), respectively, which are in equilibrium at the time of sampling with the concentrations of the corresponding species in the residual solution $c_{M,0}$, $c_{ML,0}$, $c_{L,0}$ (M), respectively. The total initial content/concentration for M is $q_{Mtot,0} = (q_{M,0} + q_{ML,0})$ and $c_{Mtot,0} = (c_{M,0} + c_{ML,0})$ and for L, $q_{Ltot,0} = (q_{L,0} + q_{ML,0})$ and $c_{Ltot,0} = (c_{L,0} + c_{ML,0})$.

The mass of soil is put into contact with a volume V (L) of an aqueous solution containing initially only M at a defined concentration $c_{M,i}$ (M). At equilibrium, the final soil contents of M , ML , L sorbed onto the solid phase are $q_{M,f}$, $q_{ML,f}$, $q_{L,f}$, respectively, which

are in equilibrium with the concentrations of the corresponding species in the solution
 $c_{M,f}$, $c_{ML,f}$, $c_{L,f}$, respectively. The proportion of metal irreversibly sorbed is neglected
at the time scale of SD experiments. The total final contents/concentrations for M is
 $q_{Mtot,f} = (q_{M,f} + q_{ML,f})$ and $c_{Mtot,f} = (c_{M,f} + c_{ML,f})$ and for L $q_{Ltot,f} = (q_{L,f} + q_{ML,f})$ and
 $c_{Ltot,f} = (c_{L,f} + c_{ML,f})$.

The mass balance for the total metal writes :

$$mq_{Mtot,0} + V_r c_{Mtot,0} + V c_{M,i} = mq_{Mtot,f} + (V + V_r) c_{Mtot,f} \quad (4)$$

and for L_{tot}

$$mq_{L,0} + mq_{ML,0} + V_r c_{Ltot,0} = mq_{L,f} + mq_{ML,f} + (V + V_r) (c_{L,f} + c_{ML,f}) \quad (5)$$

Assumption 2. : The volume of added solution V is much greater than V_r so that
 $(V + V_r) \simeq V$

Assumption 3. : The ligand is always in excess compared to the complex, both in
solution and onto the solid phase: $(c_{L\{0,f\}} \gg c_{ML,\{0,f\}})$ so $c_{L,\{0,f\}} \simeq c_{Ltot,\{0,f\}}$ and
 $(q_{L,\{0,f\}} \gg q_{ML,\{0,f\}})$ so $q_{L,\{0,f\}} \simeq q_{Ltot,\{0,f\}}$

Assumption 4. : The SD of M , ML , and L are linear; $K_{d,M}$, $K_{d,ML}$ and $K_{d,L}$ are constant.

$$K_{d,M} = \frac{d(\Delta q_M)}{dc_M} = \frac{q_{M,0}}{c_{M,0}} = \frac{q_{M,f}}{c_{M,f}} \quad (6)$$

$$K_{d,ML} = \frac{d(\Delta q_{ML})}{dc_{ML}} = \frac{q_{ML,0}}{c_{ML,0}} = \frac{q_{ML,f}}{c_{ML,f}} \quad (7)$$

$$K_{d,L} = \frac{d(\Delta q_L)}{dc_L} = \frac{q_{L,0}}{c_{L,0}} = \frac{q_{L,f}}{c_{L,f}} \quad (8)$$

So

$$\Delta q_M = (q_{M,f} - q_{M,0}) = K_{d,M}(c_{M,f} - c_{M,0}) \quad (9)$$

$$\Delta q_{ML} = (q_{ML,f} - q_{ML,0}) = K_{d,ML}(c_{ML,f} - c_{ML,0}) \quad (10)$$

$$\Delta q_L = (q_{L,f} - q_{L,0}) = K_{d,L}(c_{L,f} - c_{L,0}) \quad (11)$$

Assumption 5. : The amounts of M , of L and of ML in V_r are negligible compared to the corresponding amounts initially sorbed onto the solid phase : $V_r c_{M,0} \ll m q_{M,0}$, $V_r c_{L,0} \ll m q_{L,0}$, $V_r c_{ML,0} \ll m q_{ML,0}$, respectively. This means $\frac{q_{M,0}}{c_{M,0}} = K_{d,M} \gg \frac{V_r}{m}$, $\frac{q_{L,0}}{c_{L,0}} = K_{d,L} \gg \frac{V_r}{m}$ and $\frac{q_{ML,0}}{c_{ML,0}} = K_{d,ML} \gg \frac{V_r}{m}$. Starting from an air-dried soil with $\frac{V_r}{m}$ being generally below 5%, the condition is $\{K_{d,M}; K_{d,L}; K_{d,ML}\} \gg 0.05 \text{ L kg}^{-1}$. Starting from a wet soil with $\frac{V_r}{m}$ around 0.3 L kg^{-1} , the condition becomes $\{K_{d,M}; K_{d,L}; K_{d,ML}\} \gg 0.3 \text{ L kg}^{-1}$.

From assumptions 2 and 5 , Eq. 4 becomes :

$$\Delta q_{Mtot} = (q_{Mtot,f} - q_{Mtot,0}) = \Delta q_M + \Delta q_{ML} \simeq r(c_{M,i} - c_{Mtot,f}) \quad (12)$$

and additionally with assumption 3, Eq. 5 becomes :

$$\Delta q_L = (q_{L,f} - q_{L,0}) \simeq -r c_{L,f} \quad (13)$$

where $r = V/m$.

Eq. 9 and 10 are substituted in Eq. 12 to give :

$$r(c_{M,i} - c_{Mtot,f}) = K_{d,M}(c_{M,f} - c_{M,0}) + K_{d,ML}(c_{ML,f} - c_{ML,0}) \quad (14)$$

From Eq. 11 and Eq. 13 :

$$-r c_{L,f} = K_{d,L}(c_{L,f} - c_{L,0}) \quad (15)$$

$$c_{L,f} = \frac{c_{L,0} K_{d,L}}{K_{d,L} + r} \quad (16)$$

At equilibrium, the three concentrations of M , ML and L are linked by the complex

204 conditional formation constant :

$$K = \frac{c_{ML,f}}{c_{M,f}c_{L,f}} = \frac{c_{ML,0}}{c_{M,0}c_{L,0}} \quad (17)$$

205 The initial fraction of the free metal M is :

$$F_{M,0} = \frac{c_{M,0}}{c_{Mtot,0}} = \frac{1}{1 + Kc_{L,0}} = \frac{1}{1 + K_0^*} \quad (18)$$

206 with $K_0^* = Kc_{L,0}$.

207 The fraction of the free metal at equilibrium after the addition of the solution is :

$$F_{M,f} = \frac{c_{M,f}}{c_{Mtot,f}} = \frac{1}{1 + Kc_{L,f}} = \frac{1}{1 + \frac{K_0^*K_{d,L}}{r + K_{d,L}}} \quad (19)$$

208 For ML , it is

$$F_{ML,f} = \frac{c_{ML,f}}{c_{Mtot,f}} = (1 - F_{M,f}) \quad (20)$$

209 It should be noticed that in SD experiments, $F_{M,f}$ and therefore $F_{ML,f}$ only depend on r
 210 since K_0^* and $K_{d,L}$ are constant.

211 In Eq. 14, $c_{M,f}$ and $c_{ML,f}$ are replaced by their formulation from Eq. 19 and 20, respec-
 212 tively, which gives :

$$C_{Mtot,f} = \frac{(rc_{M,i} + K_{d,M}c_{M,0} + K_{d,ML}c_{ML,0})}{r + F_{M,f}K_{d,M} + F_{ML,f}K_{d,ML}} \quad (21)$$

213 This equation shows that, for a given soil, the final concentration of the total metal in
 214 solution is the ratio of its initial total amount in the system (initial supply + initial
 215 contents of the mobile pools of M and ML in the dried soil) divided by the partitioning
 216 coefficient for M and ML at the given r value and for a final composition of the solution
 217 $(F_{M,f}, F_{ML,f})$.

218 From Eq. 19 and 20, it gives :

$$C_{Mtot,f} = \frac{(rc_{M,i} + c_{M,0}(K_{d,M} + K_0^*K_{d,ML}))(r + K_{d,L} + K_0^*K_{d,L})}{r(r + K_{d,L} + K_0^*K_{d,L}) + (r + K_{d,L})K_{d,M} + K_0^*K_{d,L}K_{d,ML}} \quad (22)$$

and from Eq. 19 :

$$C_{M,f} = \frac{(rc_{M,i} + K_{d,M}c_{M,0} + K_{d,ML}c_{ML,0})F_{M,f}}{r + F_{M,f}K_{d,M} + F_{ML,f}K_{d,ML}} \quad (23)$$

2.2.2 Distribution coefficient for the total metal

The distribution coefficient for the total metal is

$$K_{d,Mtot,f} = \frac{dq_{Mtot,f}}{dc_{Mtot,f}} = \frac{d(\Delta q_{Mtot})}{dc_{Mtot,f}} = \frac{d(r(c_{M,i} - c_{Mtot,f}))}{dc_{Mtot,f}} \quad (24)$$

Let us consider experiments where r is constant and only $c_{M,i}$ varies. Then, isolating $c_{M,i}$ from Eq. 21 and substituting it in Eq. 24 gives the distribution coefficient for the total metal at a fixed r value :

$$K_{d,Mtot,f} = F_{M,f} K_{d,M} + F_{ML,f} K_{d,ML} \quad (25)$$

The sorption of M and ML being linear, $K_{d,M}$ and $K_{d,ML}$ are constant (assumption 4). Moreover, $F_{M,f}$ and therefore $F_{ML,f}$ only depend on r (Eqs. 19 and 20). As a consequence, for a given r , the distribution coefficient $K_{d,Mtot}$ for the total metal ($M + ML$) is constant. From (Eq. 24), it means that plotting $r(c_{M,i} - c_{Mtot,f}) = \Delta q_{Mtot}$ against $c_{Mtot,f}$ should produce one linear relationship by r value, the slope of which is $K_{d,Mtot,f}$. The intercept with the y -axis is the initial content of sorbed metal $q_{Mtot,0} = K_{d,Mtot,f} c_{Mtot,0}$ so that $\Delta q_{Mtot} = 0$ when the added solution has a concentration of total metal $c_{M,i} = c_{Mtot,0}$. The initial content of sorbed metal is the so-called mobile pool for fast reactions of SD. It is a constant for a given soil and it has a great environmental importance. Its estimation by modeling is of great interest because it is difficult to determine experimentally.

To summarize :

$$\begin{aligned} \Delta q_{Mtot} &= r(c_{M,i} - c_{Mtot,f}) \\ &= K_{d,Mtot,f} (c_{Mtot,f} - c_{Mtot,0}) \\ &= K_{d,Mtot,f} c_{Mtot,f} - q_{Mtot,0} \end{aligned} \quad (26)$$

236 and $K_{d,Mtot,f}$ depends on r (Eq. 25).

237 When r is large enough so that $F_{M,f}$ tends to 1 ($r \gg K_{d,L}(K_0^* - 1)$, Eq. 19), Eq. 25
 238 shows that $K_{d,Mtot,f}$ tends to $K_{d,M}$. Conversely, when r tends towards 0, $F_{M,f} \rightarrow \frac{1}{1+K_0^*}$.
 239 Extrapolating $F_{M,f}$ for $r \rightarrow 0$ provides an estimate of K_0^* .

240 **2.2.3 Estimation of $K_{d,M}$, $K_{d,ML}$ and $c_{M,0}$ from the experimental determination** 241 **of F_M**

242 If the free ion metal M can be quantified in the soil solution by any method such as a
 243 specific electrode or a resin exchange method, the experimental determination of $F_{M,f}$
 244 and of $c_{Mtot,f}$ from a set of SD experiments can be utilized to fit the modeled $c_{Mtot,f}$ (Eq.
 245 21) or $c_{M,f}$ (Eq. 23) to estimate $K_{d,M}$, $K_{d,ML}$ and $c_{M,0}$. The experimental values of $F_{M,f}$
 246 can also be used to fit Eq. 19 to first estimate K_0^* and $K_{d,L}$. Then, together with the
 247 experimental values of $c_{Mtot,f}$, $K_{d,M}$, $K_{d,ML}$ and $c_{M,0}$ can be estimated from Eq. 22.

248 **2.2.4 Estimation of $K_{d,M}$, $K_{d,ML}$ and $c_{M,0}$ from the modeling of the desorption** 249 **of the dissolved organic carbon (DOC)**

250 It is not always possible or easy to determine the free ion concentration and therefore, at
 251 a cost of an additional assumption, $K_{d,M}$, $K_{d,ML}$ and $c_{M,0}$ can also be estimated from the
 252 modeling of the desorption of the dissolved organic carbon (DOC).

253 **Assumption 6.** : The ligand behaves as a fraction $\alpha \leq 1$ of the DOC (c_{DOC} , M) :

$$c_{Ltot} = \alpha c_{DOC} \quad (27)$$

$$K_{d,L} = K_{d,DOC} \quad (28)$$

$$K = \frac{K_{DOC}}{\alpha} \quad (29)$$

254 where $K_{d,DOC}$ is the distribution coefficient of the DOC and K_{DOC} (M^{-1}) and K (M^{-1})

are the conditional formation constants of the complex between M and the DOC or L ,
(Eq. 17), respectively.

This assumption means that complexation with inorganic ligands is neglected, unless they
behave like the DOC. If inorganic complexation is dominating, the modeling approach can
easily be adapted by replacing the DOC by the concentration of the dominating inorganic
ligand.

With this additional assumption, the modeling of $c_{L,f}$ (Eq. 16) becomes

$$c_{DOC,f} = \frac{c_{DOC,0}K_{d,DOC}}{K_{d,DOC} + r} \quad (30)$$

and that of $F_{M,f}$ (Eq. 19) becomes :

$$F_{M,f} = \frac{1}{1 + \frac{K_{DOC,0}^*K_{d,DOC}}{r + K_{d,DOC}}} \quad (31)$$

where

$$K_0^* = K_{DOC,0}^* = K_{DOC}c_{DOC,0} \quad (32)$$

The experimental final concentrations of the DOC in the SD experiments are utilized
to fit Eq. 30 to estimate $K_{d,DOC}$ and $c_{DOC,0}$. Then, from these two estimated values,
Eq.22 is fitted to the experimental data of $c_{Mtot,f}$, assuming that $K_{d,L} = K_{d,DOC}$ and
 $K_0^* = K_{DOC,0}^* = K_{DOC}c_{DOC,0}$ (Eq. 32), which gives the estimates of $K_{d,M}$, $K_{d,ML}$, $c_{M,0}$
and K_{DOC} .

2.2.5 Partitioning and speciation of the metal at low r values corresponding to the soil moisture in field conditions

The previous modeling gives estimates of $K_{d,M}$, $K_{d,ML}$ and $K_{d,L}$, which are assumed to
be independent from r (assumption 4) and therefore, they are valid for soil moisture
consistent with field conditions. Estimating K_0^* or $K_{DOC,0}^*$ and $K_{d,L}$ or $K_{d,DOC}$ makes it
possible to calculate $F_{M,f}$ at any r values (Eqs. 19 and 31). Therefore, $K_{d,Mtot,f}$ can also
be calculated for field conditions regarding the soil moisture (Eq. 25). From $K_{d,M}$, $K_{d,ML}$,

$K_{d,L}$, K_0^* or $K_{DOC,0}^*$, $K_{d,L}$ or $K_{d,DOC}$ and $F_{M,f}$ the concentrations of the total metal and of the free ion can be estimated at any r values by Eqs. 21, 22 and 23 by setting $c_{M,i} = 0$. It can be noticed that if the SD experiments are performed from the moist soil instead of an air-dried soil, then, $c_{M,0}$ becomes the concentration of the free metal at the targeted soil water content. Working with moist soil has the advantage of limiting the microbial flush that can occur during the equilibration of the soil with the added solution.

2.3 Experiments

2.3.1 Soils

Samples from six different soils were studied to estimate the concentrations and the distribution coefficients of Cd^{2+} and of its complexes by using the proposed modeling approach. Sample S1 was collected in 2011 at Lusignan (France), from the top 15-20 cm of a loamy agricultural soil. Soil S2 was sampled in 2000, in the ploughed layer of a cultivated Podzol (Pierroton, France) supplied with sewage sludge for three years at 10 t DM ha⁻¹year⁻¹. Soil S3 was collected in 2004 in the 0-20 cm layer of a cultivated soil (Mortagne-du-Nord, France), contaminated with Cd, Pb, and Zn by atmospheric fallouts from a zinc and lead smelter. Soil S4 was sampled in 2001 in the ploughed layer of an agricultural soil located in the plaine of Pierrelaye (France), contaminated by the spreading of Paris wastewaters for about one century. Soil S5 was sampled in 1998 from the 20-40 cm layer of a soil of a woody fallow land (Auby, France). Soil S6 was sampled in 2004 from the ploughed horizon of a cultivated soil at Noyelles-Godault (France). Soils S5 and S6 were contaminated with Cd, Pb, and Zn by the atmospheric fallouts from a proximate smelter for almost one century.

The soil samples were air-dried and sieved at 2 mm before use. The following characteristics were determined with standardized methods by the Laboratoire d'Analyses des Sols of INRA (Arras, France, <https://www6.hautsdefrance.inra.fr/las/Methodes-d-analyse/Sols>): particle size distribution (pipette method, NF X 31-107), organic carbon content (SOC, dry combustion method, NF ISO 10694), $\text{pH}_{\text{H}_2\text{O}}$ (NF ISO 10390), total carbonates (CaCO_3 , volumetric method, NF ISO 10693), cation exchange capacity (CEC, Metson's method, NF X 31-130), and total Cd concentrations (HF - HClO_4 solubilization,

NF X 31-147 and quantification by ICP-MS) (Table 2) .

2.3.2 Sorption-desorption experiments

Three different full factorial experiments were performed (Table 3). The $c_{M,i}$ were adapted to be around the metal concentrations in the soil solution of the wet soils. The first experiment was dedicated to show the strong influence of the Ca concentration of the solution and therefore to demonstrate that SD operations should be performed at a Ca concentration close to that of the soil solution at the soil water holding capacity. Experiments 2 and 3 aimed at testing the modeling approach for estimating $K_{d,M}$, $K_{d,ML}$ and $c_{M,0}$ (Eq. 22). In experiment 2, the experimental measurements of F_M were utilized (section 2.2.3) whereas for experiment 3 the approach depended on the modeling of the DOC desorption (section 2.2.4). For experiments 2 and 3, the Ca concentration of the solutions added to the soil ($c_{Ca,i}$; Table 3) was set equal to the sum of the concentrations of Ca and Mg previously measured in the soil-pore solution extract at the soil water holding capacity as determined by displacement by centrifugation of the wet soil with a solvent non miscible to water (Schneider, 2003) or by extraction from the soil incubated at its water holding capacity for one month by a 2.5 mm Rhizon® (MOM model). The total Cd concentration was also measured on these soil solution extracts obtained by Rhizon® ($c_{SS,Cd}$; Table 3). The salts used for preparing the solutions were $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ because Cd forms very weak complexes with nitrate. The solutions for sorption contained both Ca and Cd whereas that for desorption contained only Ca. After addition of the solution to the dry soil, the suspension was shaken on a roller (40 cycles min^{-1} , 17-23°C) for 24 h. The suspension was then centrifuged (48 000 g , 15 min , 20 °C). The supernatant was filtered (0.2 μm pore-size cellulose acetate filter). The Cd concentration was determined on a subsample of the filtrate acidified at 5% HNO_3 by graphite-furnace atomic absorption spectroscopy (Solaar M6; Thermo Elemental, Cambridge, UK). For experiment 2, the free ionic fraction of Cd in solution ($F_{M,f}$) was estimated following an ion exchange method (Schneider, 2006). For experiment 3, the total dissolved carbon and inorganic carbon concentrations in the final solutions were determined by combustion catalytic oxidation and non-dispersive infrared gas analysis detection method (Shimadzu

TOC-VCSH, Kyoto, Japan) and the dissolved organic carbon (DOC) concentration was calculated by difference between the two measurements.

2.3.3 Calculations and statistical analyses

Data processing and analyses were performed with R (R Code Team, 2013). The Eq. 19, 21, 22 and 30 were fitted to the experimental observations by the “port” algorithm of the non-linear least-squares *nls()* function (stats package). Confidence intervals ($p=0.05$) of predicted values (*e.g.* $c_{Mtot,f}$ from Eq. 22 , $K_{d,Mtot,f}$ from Eq. 24) were derived from Monte Carlo simulations (100 000 replicates) using the estimated parameters values and their asymptotic standard errors returned by the *nls()* function.

3 Results

3.1 Influence of the Ca concentration of the solution added to the soil on the sorption-desorption results

As predicted by the modeling (section 2.2.2), the change in the sorbed metal ($\Delta q_{Mtot,f}$) calculated from Eq. 12 plotted against the concentration of the total metal in the solution at equilibrium was linear (Eq. 26) for each Ca concentration (Fig. 1a). The intercepts of the linear relationships with the y-axis, which give the initial mobile pool of sorbed Cd for the dried soil ($q_{Mtot,0}$) was not affected by the Ca concentrations. This makes sense because at the time scale of the SD experiments, this pool being related to the dry soil before the contact with the Ca solution, it is not depending on the latter. By contrast, the slope of the relationships, which gives $K_{d,Mtot,f}$ decreased when the Ca concentration increased. An inverse relationship between $K_{d,Mtot,f}$ and the final Ca concentration in solution ($c_{Ca,f}$) fitted relatively well the data (Fig. 1b). This means that the initial concentration of total Cd in the residual soil solution in equilibrium with $q_{M,0}$ increased with $c_{Ca,f}$ (Fig. S5a in SI). The final pH of the suspensions was independent of $c_{M,i}$ but decreased from 5.8 to 5.1 when $c_{Ca,f}$ increased from 1 mM to 100 mM (Fig. S5b in SI).

3.2 Goodness of fit of the models for

$$K_{d,L}, K_0^*, c_{DOC,0}, K_{d,DOC}, K_{DOC}, K_{d,M}, K_{d,ML}, c_{M,0}$$

If it is possible to measure the free ion fraction $F_{M,f}$, the partitioning coefficient for the ligand ($K_{d,L}$) and the product $K_0^* = K c_{L,0}$ must be first estimated in order to further determine the partitioning coefficient for the free metal ($K_{d,M}$), the complex ($K_{d,ML}$), and the initial concentration of the free ion in the soil solution ($c_{M,0}$) (see section 2.2.3). $F_{M,f}$ was measured on soils S2 and S3. The covariance analysis of $F_{M,f}$ as a function of r and $c_{M,i}$, with $c_{Mtot,f}$ as covariate, indicated that only r had a significant effect for both soils ($P < 10^{-4}$, not shown). This is consistent with Eq. 19. There was no significant effect of $c_{Mtot,f}$ on $F_{M,f}$ and consequently on $c_{L,f}$ (Eq. 19, see Fig. S6 in SI). The independence between $c_{Mtot,f}$ and $c_{L,f}$ indicates that L was in excess compared to ML , *i.e.* $c_{ML,f} \ll c_{L,f} \simeq c_{Ltot,f}$. This shows that assumption 3 is likely valid.

For the soils S2 and S3, $F_{M,f}$ ranged between 0.61 and 0.93. This indicates that Cd in solution after the addition of the solution to the soil was mainly as free Cd^{2+} . $F_{M,f}$ increased when r increased (Fig. 2) as expected from Eq. 19, which fitted relatively well the data for the soil S2. For the soil S3, the model overestimated $F_{M,f}$ at the highest r value (100 L kg^{-1}) because $F_{M,f}$ tended towards an asymptotic value below 1 (Fig. 2b). The two parameters $\{K_{d,L}; K_0^*\}$ were quite accurately estimated as illustrated by their asymptotic standard errors (Fig. 2). The two soils essentially differed by their $K_{d,L}$: soil S2 showed a higher value, explaining why $F_{M,f}$ increased more slowly with r than in the case of soil S3.

If $F_{M,f}$ cannot be determined, another approach for estimating $K_{d,M}$, $K_{d,ML}$ and $c_{M,0}$ relies on the modeling of the desorption of the DOC to first estimate the initial DOC concentration in the dry soil ($c_{DOC,0}$) and the distribution coefficient of the DOC $K_{d,DOC}$ (see section 2.2.4). Therefore, for soils S4-S6, the final concentration of the DOC ($c_{DOC,f}$) in solution was used to fit Eq. 30. Figure 3 shows that $c_{DOC,f}$ decreased when r increased as expected from Eq. 30, which fitted well the data for the three soils. Indeed, as shown in Fig. 3, the parameters $c_{DOC,0}$ and $K_{d,DOC}$ were accurately estimated based on their asymptotic standard error.

In the F_M -based approach (see section 2.2.3, soils S2 and S3), the previously estimated

$\{K_{d,L}; K_0^*\}$ were applied in Eq. 22, which was then fitted to the observed concentration of total Cd in solution ($c_{Mtot,f}$). This allowed to estimate $K_{d,M}$, $K_{d,ML}$, $c_{M,0}$ and K_{DOC} . In the DOC-based approach (see section 2.2.4, soils S4 to S6), the estimated $\{c_{DOC,0}; K_{d,DOC}\}$ were applied in Eq.22 to estimate $K_{d,M}$, $K_{d,ML}$, and $c_{M,0}$ by replacing K_0^* by $K_{d,DOC} c_{DOC,0}$ (Table 4). The influence of r on $c_{Mtot,f}$ depended on both the range of r and on the soil (Figure 4). When $r \geq 10 \text{ L kg}^{-1}$, the relationship between $c_{Mtot,f}$ and r was more or less linear, with a slope that was negative when $c_{M,i} = 0$ and that increased with $c_{M,i}$. When $r \leq 10 \text{ L kg}^{-1}$, the slope was still negative when $c_{M,i} = 0$ and $c_{Mtot,f}$ generally increased when r tended towards 0. For soil S4, and particularly for soil S3, whatever the value of $c_{M,i}$, the relationship was curved with a local slope that becomes more negative as r decreases. This complex relationship between $c_{Mtot,f}$ and r was well illustrated by Eq. 22. Indeed, the linear regression between the observed and the predicted $c_{Mtot,f}$ indicated a very good fit ($R^2 > 0.91$) and no significant bias (slope and intercept never significantly different from 1 and 0, respectively, Figure S7 in SI) . Figure 5 shows the relationships between Δq_{Mtot} and $c_{Mtot,f}$ for the five soils, *i.e.* the observed SD curves. As predicted by the modeling (see section 2.2.2), for a given r value, the relationship between Δq_{Mtot} and $c_{Mtot,f}$ was linear. Because $K_{d,M} > K_{d,ML}$ (Table 4) and because $F_{M,f}$ increases with increasing r values (Eq. 19), the model of Eq. 25 also predicts an increase of $K_{d,Mtot,f}$ (the slope) if r increases. This was confirmed by the experimental observations (Fig. 5).

3.3 Values of the estimated parameters

$$\{K_{d,L}; K_0^*; c_{DOC,0}; K_{d,DOC}; K_{d,M}; K_{d,ML}; c_{M,0}\}$$

Soil S5 showed a high $K_{d,DOC}$ value (8 L kg^{-1}) compared to the two other soils but all $K_{d,DOC}$ estimates fall in the range of 0.4–101 L kg^{-1} (median 11 L kg^{-1}) reported by (Neff and Asner, 2001; Vandenbruwane et al., 2007). For soils S4, S5, and S6, the DOC extracted during the SD experiments at $r = 2 \text{ L kg}^{-1}$ were 0.17, 0.05, and 0.43% of the soil organic carbon, respectively. These values are in the range of 0.05–0.4% reported in Haynes’ literature review (2005).

Table 4 shows that generally, $K_{d,M}$ was much higher than $K_{d,ML}$, which itself was generally

418 but not systematically higher than $K_{d,L}$. Indeed, for soil S2, $K_{d,ML}$ was not significantly
 419 different from 0 and for soil S5, $K_{d,ML}$ and $K_{d,L}$ were similar. Regarding the parameter
 420 $K_0^* = K_{CL,0} = c_{ML,0}/c_{M,0}$, the higher it is, the stronger the complexation in the residual
 421 solution of the dry soil and when $K_0^* > 1$, ML dominates over M . K_0^* varied by two
 422 orders of magnitude and was particularly high for soil S6 ($K_0^* = 59$). This means that
 423 ML was largely predominant in the residual solution compared to M (Table 4).
 424 Estimates for the sorbed M ($q_{M,0}$) and ML ($q_{ML,0}$) in the dry soil varied strongly from
 425 one soil to another. For soil S2, $q_{M,0}$ was much higher than the total Cd probably because
 426 the later being very low (0.1 mg kg^{-1}), the estimated $q_{M,0}$ was highly uncertain.
 427 For the other soils, the total sorbed Cd ($q_{M,0} + q_{ML,0}$) was 67%, 116%, 84%, and 11% of
 428 the soil total Cd for soils S3, S4, S5, and S6, respectively. For soils S2 and S3, the modeling
 429 does not enable the estimation of the sorbed ligand, $q_{L,0}$ because only $K_0^* = K_{CL,0}$ was
 430 derived (Table 4). In the DOC desorption approach (section 2.2.4), $c_{DOC,0}$ was estimated,
 431 which makes possible to calculate the sorbed DOC for the dry soil $q_{DOC,0} = K_{d,L}c_{DOC,0}$.
 432 For soils S4 to S6, $q_{ML,0}$ (mol kg^{-1}) was at the most 0.4% of $q_{DOC,0}$ (mol kg^{-1}). Similarly,
 433 for these soils, $c_{ML,0}$ (M) \ll $c_{DOC,0}$ (M). These results give some confidence in assumption
 434 3 ($q_{ML} \ll q_L$).
 435 For the studied soils, when the soil pH increased, $K_{d,M}$, $K_{d,ML}$ and the DOC concentration
 436 in the residual water increased whereas $K_{d,L}$ decreased (Fig. S8a, S8b, and S8c in SI).
 437 When $c_{DOC,0}$ increased, $K_{d,ML}$ also increased whereas the initial content of sorbed ML
 438 ($q_{ML,0}$) decreased (Fig. S8f and S8g). This was unexpected because $q_{ML,0}$ was calculated
 439 as $q_{ML,0} = K_{d,ML} c_{ML,0} = K_{d,ML} K_{CL,0} c_{M,0} = K_{d,ML} K_{DOC} c_{DOC,0} c_{M,0}$ (Eq. 17, 27 and
 440 29, assumption 3).

4 Discussion

4.1 Importance of Ca concentration of the sorption/desorption solutions

The SD curves and consequently the partitioning coefficients and the metal concentrations deduced from their modeling were shown to be affected by the Ca concentration of the SD solution. The $K_{d,Mtot}$ was found inversely proportional to the latter (Fig. 1) and $c_{Mtot,0}$ proportional to it (Fig. S5 in SI). This is consistent with previous observations for which the effects of Ca were however generally less strong (Christensen, 1984; Boekhold et al., 1993; Voegelin et al., 2001). For Ni, Staunton (2004) reported a very variable effect of the background Ca concentration on the $K_{d,Mtot}$ for thirteen French soils. The most probable reason for the effect of Ca on the SD of Cd could be a competitive exchange of Cd by Ca, leading to a lower $K_{d,Mtot}$ and a greater $c_{Mtot,0}$ when the Ca concentration increased. For some soils like S1, it cannot be excluded that an additional effect of the pH happened, *i.e* a desorption of Cd by some additional H desorbed by Ca. Because of the potential strong effect of Ca on the sorption of cations like Cd, it is important to perform the SD experiments at the Ca concentration of the soil solution at the field moisture. The latter may importantly differ from the Ca concentrations of the SD solutions commonly reported in the literature, typically 10 mM. Indeed, from a study on 45 soils coming from 15 French sites, the (Ca+Mg) concentration in the soil solution was observed to range from 0.9 to 17.6 mM, with a median value of 2.9 mM (Schneider, 2003). For simplification, in our work, the Ca concentration in the SD experiments was set at the concentration of (Ca+Mg) and therefore, further investigations should determine if Ca is a good proxy of Mg or if Mg should be also adjusted in the SD experiments.

4.2 Modeling of the free metal fraction F_M

The free Cd fractions ($F_{M,f}$) experimentally determined at the end of the SD experiments for soils S2 and S3 were found to be greater than 0.6. Similarly, in the residual soil water, $F_{M,0} = c_{M,0}/(c_{M,0}+c_{ML,0})$ was 0.59 and 0.61, respectively (Table 4). Assuming that the ligand was in excess compared to the metal (assumption 3), this indicates a moderate

complexation, either because of a low thermodynamical affinity of the ligand for M or because of the competition of other cations for complexation, probably mainly Ca .

For soil S6, Cd was mainly as ML in solution since $F_{M,0} = 0.017$. In this soil the ligands may have had an especially high affinity for Cd ($\text{Log}_{10}(K_{DOC}) = 4.0$). However, as the complex formation constants defined here are conditional ones, this can also be related to the high pH (8.1) of this soil, which is expected to reduce the protonation of the complexing groups of the ligand compared to a lower pH . A least protonated *i.e* more negatively charged ligand is also expected to result in a lower sorption due to repulsion from the net negatively charged soil surface, resulting in a higher concentration in solution (Fig. S8d in SI).

For soil S3, the measured fraction of free Cd^{2+} ($F_{M,f}$) reached a plateau at the value of around 0.9 (Fig. 2b) when r increased. However, the modeling predicts that the asymptotic value should be 1 (Eq. 19) because K_0^* and $K_{d,L}$ are assumed to be constant. For this soil, the latter condition was probably not fulfilled and K_0^* and/or $K_{d,L}$ may have increased with r . One possible explanation could be the non validity of the assumption of a mean unique ligand (Assumption 1). At high r , ligands with low $K_{d,L}$ may have been almost completely desorbed. Consequently the contribution of ligands with a higher $K_{d,L}$ becomes greater and the resulting mean behavior is an increase of $K_{d,L}$ with r . Under these conditions, the asymptotic value of 1 for F_M is reached at much higher r value than if $K_{d,L}$ was constant. Moreover, it cannot be excluded that in parallel, the complex formation constant and therefore, K_0^* also increased with r . This kind of problem can only be detected if F_M is experimentally determined.

For the other soils, the modeling of $F_{M,f}$ (Eq. 19), of $c_{DOC,f}$ (Eq. 30) and thereafter of $c_{Mtot,f}$ (Eq. 22) generally predicted well the experimental observations (Figs. 2, 3 and 4). This does not question the validity of the different assumptions except part of assumption 3, which states that $ML \ll L$ both in the solution and sorbed onto the solid phase. The observations that $c_{ML,0} \ll c_{DOC,0}$ and $q_{ML,0} \ll q_{DOC,0}$ give a high degree of confidence to assumption 3 in the case where the ligand is considered to be a significant part of the DOC . By contrast, if the mean ligand is inorganic or is a minor fraction of the DOC , assumption 3 can be questioned.

4.3 $K_{d,M}$, $K_{d,ML}$ and $K_{d,L}$

The estimated distribution coefficients follow the ranking $K_{d,M} > K_{d,ML} > K_{d,L}$ (Table 4). For soil S2, the nil estimate of $K_{d,ML}$ might be explained by the important amount of sewage sludges supplied to the soil before its sampling. This might confirm the results of Neal and Sposito (1986) who found that sewage sludges application to soils reduced the sorbed Cd because of the formation of Cd organic complexes that did not sorbed onto the solid phase. Generally $K_{d,ML}$ was much closer to $K_{d,M}$ than to $K_{d,L}$. This suggests that, despite the supposed macromolecular nature of L , the complex behaves more like the free metal than like the ligand. Consistent with this, $K_{d,M}$ and $K_{d,ML}$ were positively correlated and both increased with increasing soil pH (Fig. S8a, S8b, and S8c in SI). This may indicate that the complex is positively charged and attracted by the anionic charge of the soil surface, which increases with the pH. Conversely, $K_{d,L}$ decreased with increasing pH. This suggests that the ligand was globally negatively charged. All these observations indicate that generally, $K_{d,ML}$ should not be supposed close to $K_{d,L}$ (as done by Lin et al., 2016) and it cannot be considered nil.

4.4 Effect of complexation on the SD curves

The observed relationships between Δq_{Mtot} and $c_{Mtot,f}$ were linear. The slope is $K_{d,Mtot,f}$, which only depended on r and not on $c_{M,i}$ (Fig. 5). The reason for the linearity is attributed to the quite narrow range of $c_{M,i}$ and r (Table 3). The linearity also validates the hypothesis of a constant $K_{d,M}$, $K_{d,ML}$ and $K_{d,L}$. In similar conditions previous results also reported linear SD isotherms for total Cd (García-Miragaya and Page, 1978; Boekhold et al., 1993; Gray et al., 1999). Therefore, the proposed modeling approach may not be valid for SD experiments involving a very large range of variation of total metal. In this case, the observed sorption of M and ML may become no longer linear ($K_{d,M}$ and $K_{d,ML}$ can no longer be assumed constant).

The linear relationships between Δq_{Mtot} and $c_{Mtot,f}$ for each r value have an intercept with the x-axis that corresponds to equilibrium (at the studied time scale) between the solid phase and the solution ($\Delta q_{Mtot} = 0$, Fig. 5). The concentration of the total metal in solution ($c_{Mtot,f}$) increased with decreasing r as shown by the shift of the observed SD

isotherms for the total Cd towards the right along the $c_{Mtot,f}$ axis (Fig. 5). This can be explained by an increasing importance of complexation in solution with decreasing r . This is illustrated by the concomitant increase of the measured DOC and of the modeled concentration of the ligand ($c_{L,f}$, Eq. 16, Fig. 3) and by the decrease of the free Cd fractions ($F_{M,f}$). This increasing importance of complexation with decreasing r was much less marked for soil S6 because in the dry soil ML was strongly dominating so that the speciation did not vary a lot when r increased (Fig. S9 in SI). The shift of the observed SD isotherms along the $c_{Mtot,f}$ axis with r values was much lower compared to the other soils (Fig. 5).

As shown by Eq. 25, the partitioning coefficient for the total Cd ($K_{d,Mtot,f}$) depends on r due to the effect of complexation. Experimentally, this was demonstrated by the lower slope of the plot of Δq_{Mtot} against $c_{Mtot,f}$ (Eq. 26, Fig. 5) when r decreased. This is well reproduced by the model. When r is high, $F_{M,f}$ is also high (Eq. 19) and $K_{d,Mtot}$ tends towards the distribution coefficient for the free metal ($K_{d,M}$, Eq. 25). Conversely, when r decreases, $F_{M,f}$ decreases and $K_{d,Mtot}$ is increasingly depending on the distribution coefficient of the complex ($K_{d,ML}$, Eq. 25).

Many authors assumes that $K_{d,M} \gg K_{d,ML}$ and they model sorption and desorption by considering that only the ionic form of the metal can sorb onto soil particles (Boekhold et al., 1993; Temminghoff et al., 1995; Lee et al., 1996; Weng et al., 2002; Shi et al., 2007; Ponizovsky et al., 2006). Our results are in line with the common opinion that the free metal ion is the most reactive species for the sorption onto the solid phase and therefore that $K_{d,M} > K_{d,ML}$ (Table 4). However, our results also show that the sorption of ML onto the soil solid phase cannot be neglected. Some other authors recognize implicitly that complexation can be responsible for the non linearity of the SD curves. For example, for soils having received sewage sludges, Neal and Sposito (1986) modeled the Cd sorption curves by a S-shape model by considering that it was due to the formation of soluble Cd-organic complexes in solution that were not sorbed by the soil solid phase. Singh and Pandeya (1998) found that the partition coefficient of Cd in soils was generally smaller when a Cd-fulvic acid complex was added than when soils received $CdCl_2$. Here, we proposed a mechanistic approach for modeling and understanding the SD curve for the

total metal by considering the complexation. For example, considering that $F_{M,f}$ increases with r , (Eq. 19, Fig. 2), the model for $K_{d,Mtot,f}$ (Eq. 26) explains why $K_{d,Mtot,f}$ increases when r increases for $K_{d,M} > K_{d,ML}$ (Table 4) and predicts that when r increases, $K_{d,Mtot,f}$ will decrease if $K_{d,M} < K_{d,ML}$ and will be unchanged if $K_{d,M} = K_{d,ML}$.

4.5 A simplified procedure for estimating the parameters

There is a great interest in easily determining $K_{d,Mtot}$, $K_{d,M}$ and $K_{d,ML}$ in environmental and agricultural sciences for studying the transfers and bioavailability of metals (Lin et al., 2016; Schneider et al., 2018). As demonstrated in this work, due to complexation, $K_{d,M}$ cannot be approximated by $K_{d,Mtot}$. Furthermore, because $K_{d,Mtot}$ depends on r , SD experiments usually performed at a unique r value (commonly 10 L kg^{-1}) poorly reflects the values of $K_{d,Mtot}$ and $K_{d,M}$ at the field soil moisture. Our approach allows estimating $K_{d,Mtot}$, $K_{d,M}$, $K_{d,ML}$, $c_{M,0}$ and $c_{ML,0}$, including for field soil moisture by extrapolating the relationship between $K_{d,Mtot}$ and r at the appropriate r value (Fig. S9 in SI). An alternative would be to study moist soils instead of air-dried soils. This could avoid problems due to re-wetting, including the microbial flush.

Our approach requires a time consuming factorial design combining the additions of the metal ($c_{M,i}$) with different r . This may be a limitation if the number of soils is large. Therefore, we propose a simplified experimental design that consists in only four experiments but that enables to estimate the above-mentioned parameters, provided that the free ion fraction could be determined.

- Experiment 1 ($E1$) is a desorption experiment consisting in re-wetting the air-dried soil to the low r_{low} (field moisture) value with pure water ($c_{M,i,1} = 0$). After one day of equilibration, the soil solution is extracted and filtered at $0.2 \mu m$. The Ca, Mg, total M ($c_{Mtot,f,1}$) concentrations and the fraction of free M ($F_{M,f,1}$) are measured in the solution.
- Experiment 2 ($E2$) is a sorption experiment for which the soil is also re-wetted to r_{low} (field moisture) but with one aqueous solution of M, having a concentration of $c_{M,i,2}$ so that the amount of added M is a fraction (< 1) of the initial total M

content in the soil. $c_{M,i,2}$ could increase with the expected $K_{d,Mtot}$, which can be estimated from pedotransfer functions based on the soil pH, clay and/or organic matter content, etc.

- Experiments 3 ($E3$) is a desorption experiment performed at a very high r_{high} value, 1000 L kg⁻¹ for instance, with a M -free solution ($c_{M,i,3} = 0$) containing only Ca and Mg at the concentrations determined in $E1$.
- Experiments 4 ($E4$) is a sorption experiment, also performed at r_{high} , with a solution containing Ca and Mg as previously, together with M at a concentration $c_{M,i,4}$ that must also be chosen so that the amount of added M is a fraction (< 1) of the initial total M content in the soil. Therefore, $c_{M,i,4} \ll c_{M,i,2}$ because $r_{low} \ll r_{high}$.

The soil solutions of $E2$, $E3$, and $E4$ are collected following the protocol of $E1$ and the total M concentrations are determined : ($c_{Mtot,f,2}$, $c_{Mtot,f,3}$, $c_{Mtot,f,4}$, respectively).

In these conditions, $c_{Mtot,f,1}$ approximates $c_{Mtot,0}$. $F_{M,f,1}$ together with Eq. 18 gives K_0^* and also $c_{M,0}$ and finally $c_{ML,0}$. The changes in the contents of sorbed M are calculated from Eq. 26 for the four experiments:

$$E1 : \Delta q_1 = -r_{low}c_{Mtot,f,1} \quad (33)$$

$$E2 : \Delta q_2 = r_{low}(c_{M,i,2} - c_{Mtot,f,2}) \quad (34)$$

$$E3 : \Delta q_3 = -r_{high}c_{Mtot,f,3} \quad (35)$$

$$E4 : \Delta q_4 = r_{high}(c_{M,i,4} - c_{Mtot,f,4}) \quad (36)$$

Then, the distribution coefficients for total M ($K_{d,Mtot}$) are calculated by r value following Eq.26 :

$$K_{d,Mtot,r_{low}} = \frac{\Delta q_2 - \Delta q_1}{c_{Mtot,f,2} - c_{Mtot,f,1}} \quad (37)$$

$$K_{d,Mtot,r_{high}} = \frac{\Delta q_4 - \Delta q_3}{c_{Mtot,f,4} - c_{Mtot,f,3}} \quad (38)$$

At high r , $F_{M,f} \rightarrow 1$ (Eq. 19) and therefore $K_{d,Mtot,r_{high}} \simeq K_{d,M}$ (Eq. 25). Eq. 25 for r_{low} becomes

$$K_{d,Mtot,r_{low}} = F_{M,f,1}(K_{d,Mtot,r_{high}} - K_{d,ML}) + K_{d,ML} \quad (39)$$

and then

$$K_{d,ML} = \frac{K_{d,Mtot,r_{low}} - F_{M,f,1}K_{d,Mtot,r_{high}}}{1 - F_{M,f,1}} \quad (40)$$

5 Conclusions

This work proposed a modeling of SD curves for determining the soil-solution distribution coefficients and concentrations for the free ion and the complexes of trace metals. Experimental results indicated that the approach was valid for Cd and further works should be dedicated to test it for other cationic metals and also for more soils having a broader range of characteristics. The partitioning of the free ion between the solid phase and the solution is a major mechanism of metal bioavailability since it governs not only the initial concentration of the free metal in the soil solution and therefore the initial rate of uptake by a biological organisms but also the capacity of the soil to buffer this concentration during depletion. Therefore, the significance of this work is potentially important for environmental sciences.

6 Acknowledgments

The authors are grateful to Sylvie Bussière, Cécile Coriou, and Alain Vivès for their technical assistance. The financial support for this work was provided by different organisms: i) French Ministry of Environment (programme inter-organism CEA-CNRS-INRA-INSERM, Toxicologie Nucléaire Environnementale), ii) Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME, convention n° 01 75 017), iii) Agence Nationale de la Recherche (SimTraces project, ANR 2011 CESA 008 01).

The authors declare that they have no conflict of interest.

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Table 1 : Description of the different variables of the modeling with their respective units. The terms 'initial' and 'final' correspond to sorption/desorption (SD) experiments, namely before and after the addition of the solution to the air-dried soils. M, L, ML and DOC stands for the free metal, the free ligand, the metal complex and the dissolved organic carbon, respectively. $M_{tot}=(M+ML)$, $L_{tot}=(L+ML)$.

Variables	Description	Units
$c_{M,0}$, $c_{L,0}$, $c_{DOC,0}$, $c_{ML,0}$, $c_{Mtot,0}$, $c_{Ltot,0}$	Initial concentrations of M, L, DOC, ML, M_{tot} , L_{tot} in the residual solution of the air-dried soil in equilibrium with the initial contents of M, L, DOC, ML, M_{tot} , L_{tot} sorbed onto the soil, respectively	M
$c_{M,i}$	Initial concentrations of M in the solution added to the air-dried soil	M
$c_{M,f}$, $c_{L,f}$, $c_{DOC,f}$, $c_{ML,f}$, $c_{Mtot,f}$, $c_{Ltot,f}$	Final concentrations of M, L, DOC, ML, M_{tot} , L_{tot} in solution, respectively	M
$F_{M,0}$	M as a fraction of the total metal in the residual solution of the air-dried soil	Dimensionless
$F_{M,f}$, $F_{ML,f}$	M, ML as a fraction of the total metal in the final solution, respectively	Dimensionless
K	Conditional formation constant of ML	M^{-1}
K_0^*	$= K c_{L,0}$	Dimensionless
K_{DOC}	Conditional formation constant of the complex between the DOC and M	M^{-1}
$K_{DOC,0}^*$	$= K_{DOC} c_{DOC,0}$	Dimensionless
$K_{d,M}$, $K_{d,L}$, $K_{d,DOC}$, $K_{d,ML}$, $K_{d,Mtot}$	Soil-solution partitioning coefficients of M, L, DOC, ML, M_{tot} , respectively	$L\ kg^{-1}$

Continued next page.

764 Table 1 (continued)

765

Variables	Description	Units
m	Soil mass	kg
$q_{M,0}, q_{L,0},$ $q_{DOC,0}, q_{ML,0},$ $q_{Mtot,0}, q_{Ltot,0}$	Initial soil contents in M, L, DOC, ML, M_{tot} , L_{tot} sorbed onto the solid phase of the air-dried soil in equilibrium with the concentrations of M, L, DOC, ML, M_{tot} , L_{tot} in the residual solution of the air-dried soil, respectively	mol kg^{-1}
$q_{M,f}, q_{L,f},$ $q_{DOC,f}, q_{ML,f},$ $q_{Mtot,f}, q_{Ltot,f}$	Final soil contents in M, L, DOC, ML, M_{tot} , L_{tot} sorbed onto the solid phase in equilibrium with the concentration of M, L, DOC, ML, M_{tot} , L_{tot} in solution, respectively	mol kg^{-1}
$\Delta q_M, \Delta q_L,$ $\Delta q_{DOC}, \Delta q_{ML},$ $\Delta q_{Mtot}, \Delta q_{Ltot}$	Variations of the mobile pools of M, L, DOC, ML, M_{tot} , L_{tot} sorbed onto the soil solid phase during the SD experiments, respectively	mol kg^{-1}
α	Fraction of the DOC that is assumed to behave as the ligand L	Dimensionless
r	Solution volume : soil mass ratio	L kg^{-1}
V	Volume of solution added to the air-dried soil mass	L
V_r	Volume of the residual solution in the the air-dried soil	L

766 Table 2: Selected physical and chemical characteristics of the six studied soils.

Soil	Clay	Silt	Sand	CaCO ₃	SOC	pH	CEC [†]	Total Cd
	%						cmol ⁺ kg ⁻¹	mg kg ⁻¹
S1	22.4	63.5	14.2	<0.1	1.3	6.1	7.2	0.2
S2	3.1	2.9	94.0	<0.1	2.1	5.8	4.6	0.1
S3	10.4	36.7	52.9	0.2	1.5	6.4	6.8	3.8
S4	9.4	18.6	72.0	3.9	3.1	7.3	7.3	5.0
S5	19.4	47.7	32.9	<0.1	3.2	6.0	12.8	18.2
S6	16.0	60.8	23.2	1.1	1.8	8.1	10.7	18.9

768 †: Metson's method

769 Table 3: Combinations of the factors studied in the three experimental series.

770

Series	Soil	$c_{Ca,i}$	$c_{SS,Cd}$	r	$c_{M,i}$	n^d	N^e
		mM	$\mu\text{g L}^{-1}$	L kg^{-1}	nM		
1	S1	1.0, 1.8 ^a , 10.0, 100.0	-	10	0, 050, 100	2	24
2	S2	2.0 ^a	-	10, 20, 40	0, 200	3	18
2	S3	2.0 ^a	-	2, 5, 10, 25, 100	0, 85, 170	4	60
3	S4	4.1 ^b	9.1 ^{b,c}	2, 10, 25, 100	0, 400, 800, 1200	3	48
3	S5	4.8 ^b	406.4 ^{b,c}	2, 10, 25, 100	0, 4000, 8000, 12000	3	48
3	S6	6.1 ^b	3.6 ^{b,c}	2, 10, 25, 100	0, 300, 600, 900	3	48

771

772 ^a: Sum of the concentrations of Ca and Mg ($c_{Ca,i}$) and concentration of Cd ($c_{SS,Cd}$)
773 measured in a soil solution extract obtained either by centrifugation of the wet soil or, ^b:
774 by using Rhizon® samplers.

775 ^c: One replicate of measurement of $c_{SS,Cd}$.

776 ^d: Number of replicates of the SD experiments.

777 ^e: Total number of SD experiments.

778 Table 4: Parameters estimated by the fitting of the models to the data and calculated characteristics ($c_{ML,0}$, $q_{DOC,0}$, $q_{M,0}$, $q_{ML,0}$).
779

Soil	$K_{d,L}$ L kg ⁻¹	K_0^*	K_{DOC} M ⁻¹	$c_{DOC,0}$ mg L ⁻¹	$K_{d,M}$ L kg ⁻¹	$K_{d,ML}$	$c_{M,0}$ μg Cd L ⁻¹	$c_{ML,0}^c$	$q_{DOC,0}^d$	$q_{M,0}$ mg kg ⁻¹	$q_{ML,0}$
S2	9	0.7	-	-	422	0	0.4	0.3	-	0.2	0.0
S3	5	0.6	-	-	385	38	6.2	4.0	-	2.4	0.15
S4	3 ^a	3.2 ^b	834	47	1056	343	2.7	8.7	120	2.8	3.0
S5	8 ^a	2.8 ^b	2367	14	90	14	119.0	328.0	113	10.6	4.6
S6	3 ^a	59.0 ^b	10421	68	1256	511	0.1	4.1	196	0.1	2.1

780 ^a: In fact $K_{d,DOC}$.
781

^b: Calculated as $K_{DOC} c_{DOC,0}$.
782

^c: Calculated as $K_0^* c_{M,0}$.
783

^d: Calculated as $K_{d,L} c_{DOC,0}$

7 Figure captions

Figure 1: Effect of the background Ca concentration on the sorption/desorption (SD) experiments. Fig 1a: Variation of the mobile pool of total Cd (Δq_{Mtot}) as a function of the concentration of total Cd in solution ($c_{Mtot,f}$, points) and linear regressions (lines) with slopes ($K_{d,Mtot}$) and intercept ($-q_{Mtot,0}$) given inset (standard errors in parentheses). Fig 1b: $K_{d,Mtot}$ as a function of the Ca concentration in solution at the end of the SD experiments ($c_{Ca,f}$); the vertical bars are the confidence intervals ($P = 0.05$); the curve is the inverse relationship ($y = a/x$) fitted to the data the equation of which is given in inset.

Figure 2: Observed free Cd fraction ($F_{M,f}$) as a function of the solution volume:soil mass ratio (r) for soils S2 and S3. The colors indicate the tested soil solution:soil mass ratio (r) and the different symbols show the different tested values of $c_{M,i}$ (circles : $c_{M,i}=0$, diamond and square symbols for increasing non null $c_{M,i}$; see Table 3). The thick line is the model of Eq. 19 fitted to the data; the thin lines are the confidence interval ($P = 0.05$) for the predicted $F_{M,f}$; the estimated values of $K_{d,L}$ (L kg⁻¹) and of K_0^* (dimensionless) are given in each graph as well as the corresponding standard errors (in parentheses).

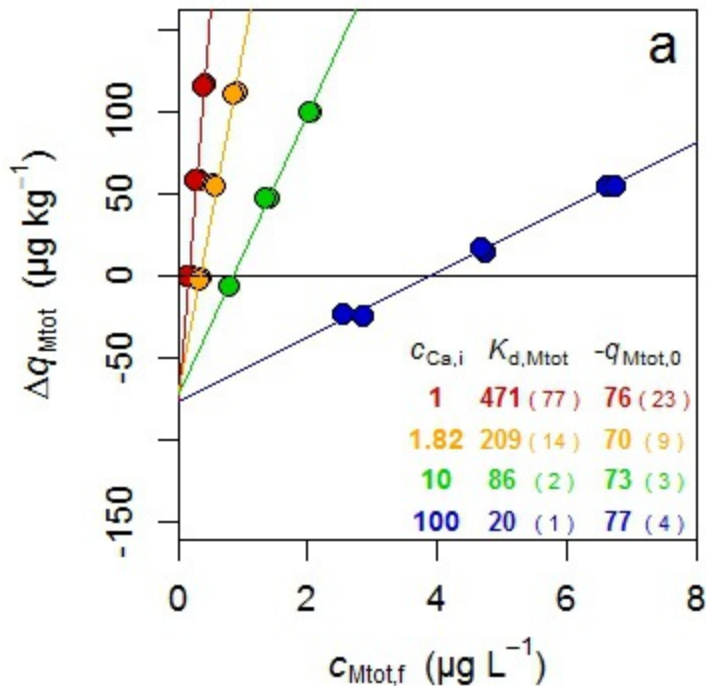
Figure 3: Observed final DOC concentration ($c_{DOC,f}$) as a function of the solution volume:soil mass ratio (r) for soils S4-S6. The colors indicate the tested soil solution:soil mass ratio (r) and the different symbols show the different tested values of $c_{M,i}$ (circles : $c_{M,i}=0$, diamond and square symbols for increasing non null $c_{M,i}$; see Table 3). The thick line is the model of Eq. 16 fitted to the data; the thin lines are for the corresponding confidence interval ($P = 0.05$) of the predicted values; the estimated values of $K_{d,DOC}$ (L kg⁻¹) and of $c_{DOC,0}$ (mg L⁻¹) are given in each graph as well as their standard error (in parentheses).

Figure 4: Observed (points) and modeled (Eq. 22, lines) $c_{Mtot,f}$ values as a function of the solution volume:soil mass ratio (r). The colors indicate the tested soil solution:soil mass ratio (r) and the different symbols show the different tested values of $c_{M,i}$ (circles : $c_{M,i}=0$, diamond and square symbols for increasing non null $c_{M,i}$; see Table 3).

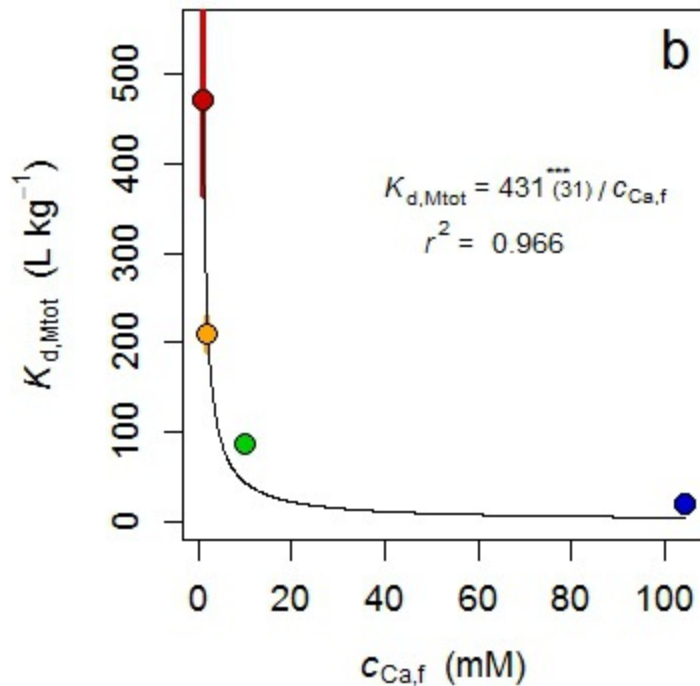
Figure 5: Observed (points) and modeled (lines) SD curves of total Cd. The points

813 show the observed SD curves between q_{Mtot} calculated (Eq. 12) from the observed final
 814 concentrations of total Cd ($c_{Mtot,f}$) and observed $c_{Mtot,f}$. The lines stand for the modeled
 815 values, i.e. the relationship between q_{Mtot} calculated (Eq. 12) from the predicted $c_{Mtot,f}$
 816 (Eq. 22) and the predicted $c_{Mtot,f}$. Symbols and colors stand for the different values of
 817 the initial Cd concentration in the solution ($c_{M,i}$) and of the solution volume:soil mass
 818 ratio (r) (Table 3), respectively. The estimated values of $K_{d,M}$ ($L\ kg^{-1}$), of $c_{M,0}$ ($\mu g\ L^{-1}$),
 819 of $K_{d,ML}$ ($L\ kg^{-1}$) and, for soils S4-S6, of (K_{DOC}) (M^{-1}) are given in each graph (with
 820 their asymptotic standard error in parentheses).

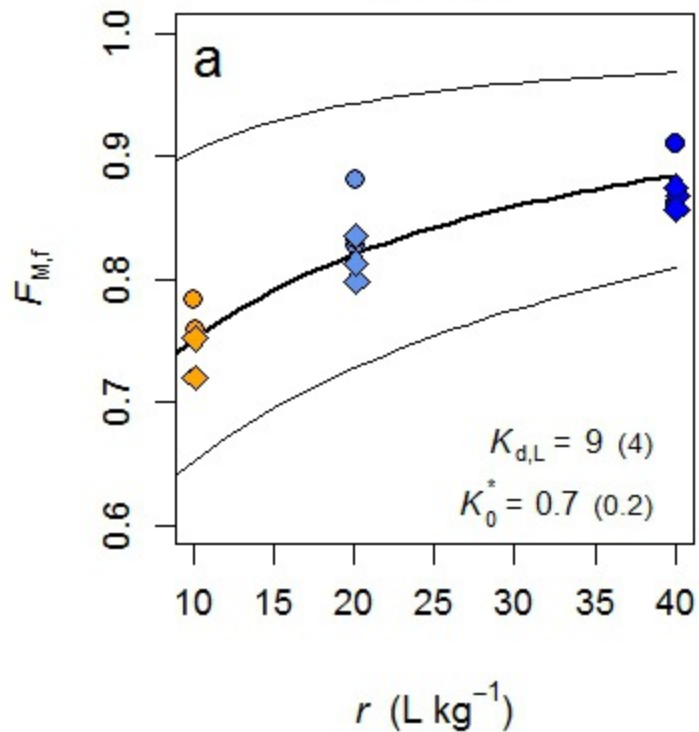
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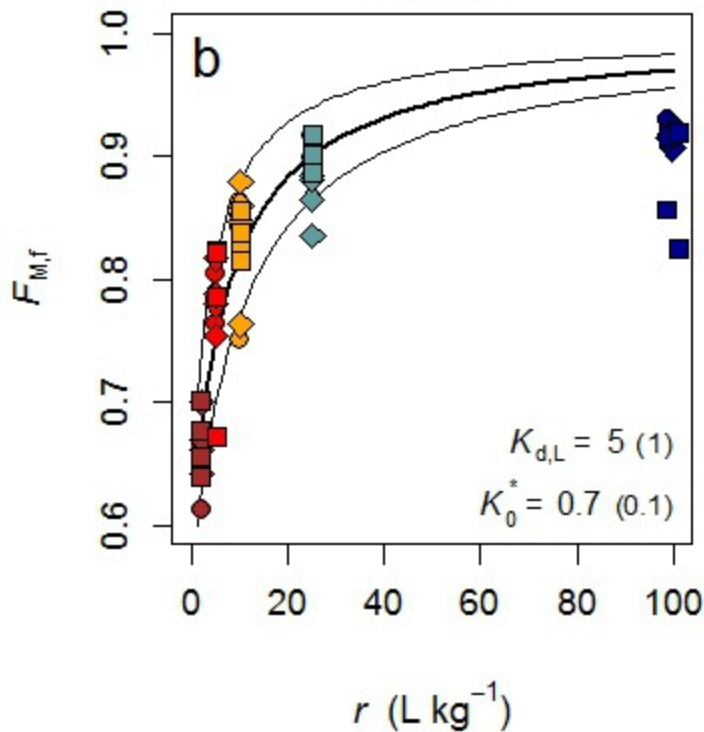
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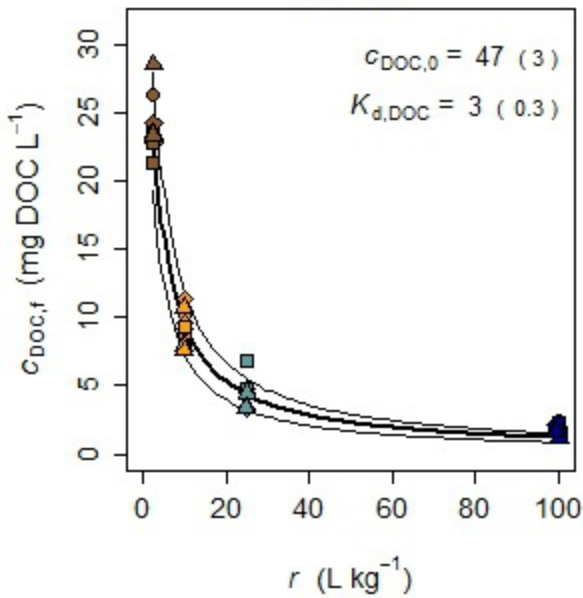
Soil S2



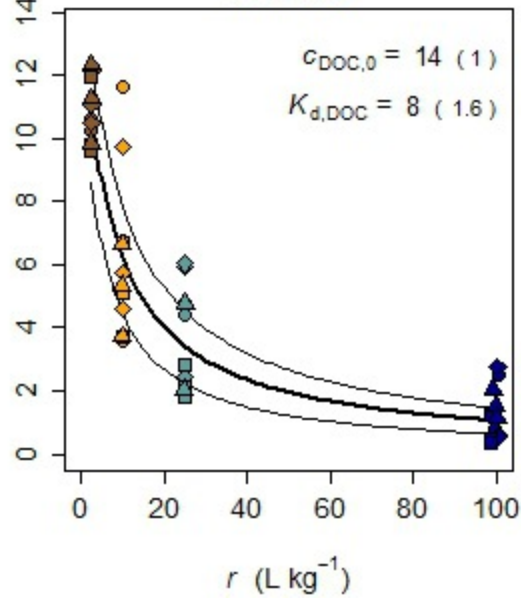
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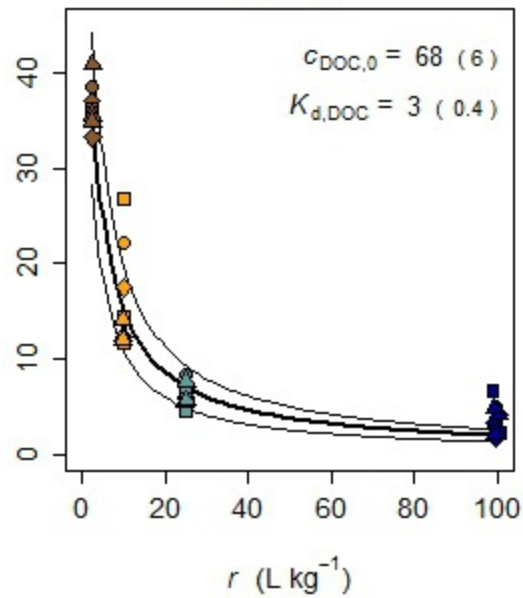
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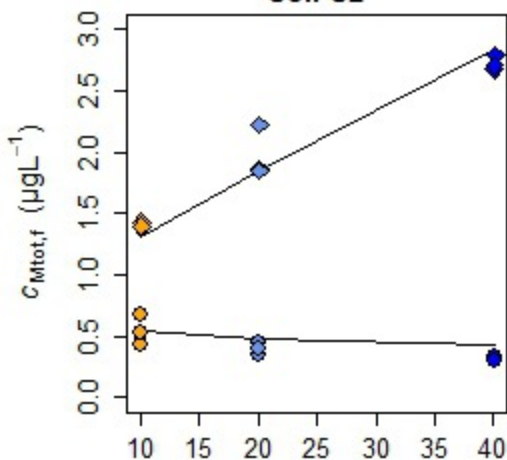
Soil S5



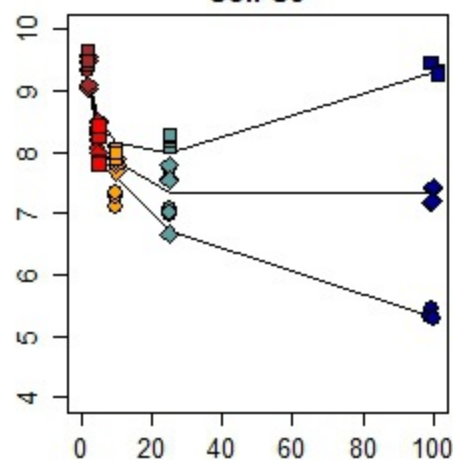
Soil S6



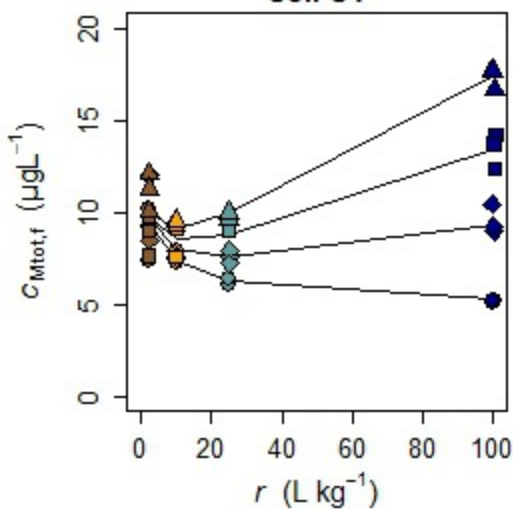
Soil S2



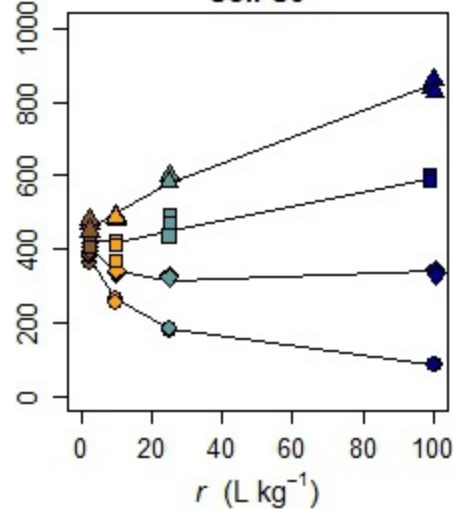
Soil S3



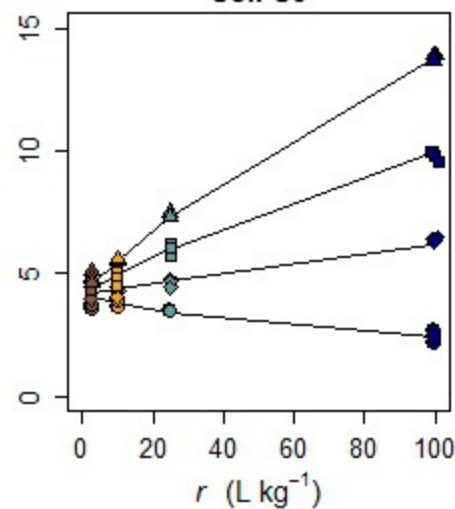
Soil S4



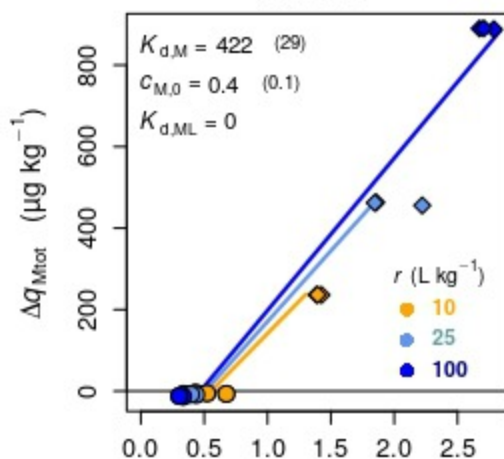
Soil S5



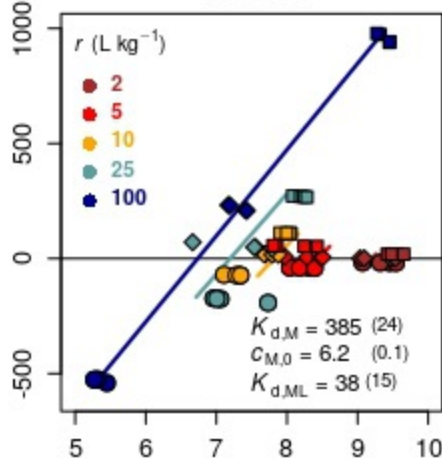
Soil S6



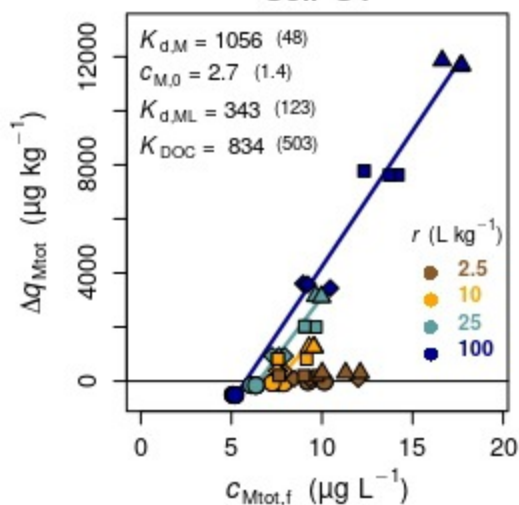
Soil S2



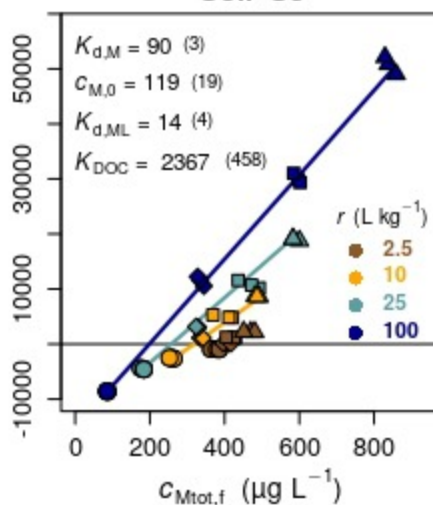
Soil S3



Soil S4



Soil S5



Soil S6

