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1 A method to determine the soil-solution distribution
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4 cadmium

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13

14 Abstract

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

34 **Keywords** : Complexation; Distribution coefficient; Modeling, Sorption-desorption; Trace
35 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

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

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

117 **2 Materials and Methods**

118 **2.1 Considerations about the distribution coefficient**

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

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

120 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

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

153 For a given soil, q_0 is constant for the different SD experiments whereas q_f varies. So,
 154 $d(\Delta q) = d(q_f - q_0) = dq_f$ and Eq. 2 can be written as :

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

155 **2.2 Modeling of the distribution coefficient by taking into ac-** 156 **count the speciation in the soil solution**

157 **2.2.1 Conceptual model and assumptions**

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

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

166 The initial state is a mass m (kg) of air-dried soil with a volume V_r (L) of residual solution.
 167 The soil contents in M , ML , L reversibly sorbed onto the solid phase are $q_{M,0}$, $q_{ML,0}$, $q_{L,0}$
 168 (mol kg^{-1}), respectively, which are in equilibrium at the time of sampling with the con-
 169 centrations of the corresponding species in the residual solution $c_{M,0}$, $c_{ML,0}$, $c_{L,0}$ (M),
 170 respectively. The total initial content/concentration for M is $q_{Mtot,0} = (q_{M,0} + q_{ML,0})$ and
 171 $c_{Mtot,0} = (c_{M,0} + c_{ML,0})$ and for L, $q_{Ltot,0} = (q_{L,0} + q_{ML,0})$ and $c_{Ltot,0} = (c_{L,0} + c_{ML,0})$.

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

175 are in equilibrium with the concentrations of the corresponding species in the solution
 176 $c_{M,f}$, $c_{ML,f}$, $c_{L,f}$, respectively. The proportion of metal irreversibly sorbed is neglected
 177 at the time scale of SD experiments. The total final contents/concentrations for M is
 178 $q_{Mtot,f} = (q_{M,f} + q_{ML,f})$ and $c_{Mtot,f} = (c_{M,f} + c_{ML,f})$ and for L $q_{Ltot,f} = (q_{L,f} + q_{ML,f})$ and
 179 $c_{Ltot,f} = (c_{L,f} + c_{ML,f})$.

180 The mass balance for the total metal writes :

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

181 and for L_{tot}

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

182 **Assumption 2.** : The volume of added solution V is much greater than V_r so that
 183 $(V + V_r) \simeq V$

184 **Assumption 3.** : The ligand is always in excess compared to the complex, both in
 185 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
 186 $(q_{L,\{0,f\}} \gg q_{ML,\{0,f\}})$ so $q_{L,\{0,f\}} \simeq q_{Ltot,\{0,f\}}$

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

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

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

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

188 So

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

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

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

189 **Assumption 5.** : The amounts of M , of L and of ML in V_r are negligible compared
 190 to the corresponding amounts initially sorbed onto the solid phase : $V_r c_{M,0} \ll m q_{M,0}$,
 191 $V_r c_{L,0} \ll m q_{L,0}$, $V_r c_{ML,0} \ll m q_{ML,0}$, respectively. This means $\frac{q_{M,0}}{c_{M,0}} = K_{d,M} \gg \frac{V_r}{m}$,
 192 $\frac{q_{L,0}}{c_{L,0}} = K_{d,L} \gg \frac{V_r}{m}$ 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
 193 generally below 5%, the condition is $\{K_{d,M}; K_{d,L}; K_{d,ML}\} \gg 0.05 \text{ L kg}^{-1}$. Starting from
 194 a wet soil with $\frac{V_r}{m}$ around 0.3 L kg^{-1} , the condition becomes $\{K_{d,M}; K_{d,L}; K_{d,ML}\} \gg 0.3$
 195 L kg^{-1} .

196 From assumptions 2 and 5 , Eq. 4 becomes :

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

197 and additionally with assumption 3, Eq. 5 becomes :

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

198 where $r = V/m$.

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

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

200 From Eq. 11 and Eq. 13 :

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

201

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

202

203 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 :

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

219 and from Eq. 19 :

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

220 2.2.2 Distribution coefficient for the total metal

221 The distribution coefficient for the total metal is

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

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

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

225 The sorption of M and ML being linear, $K_{d,M}$ and $K_{d,ML}$ are constant (assumption 4).
 226 Moreover, $F_{M,f}$ and therefore $F_{ML,f}$ only depend on r (Eqs. 19 and 20). As a consequence,
 227 for a given r , the distribution coefficient $K_{d,Mtot}$ for the total metal ($M + ML$) is constant.
 228 From (Eq. 24), it means that plotting $r(c_{M,i} - c_{Mtot,f}) = \Delta q_{Mtot}$ against $c_{Mtot,f}$ should
 229 produce one linear relationship by r value, the slope of which is $K_{d,Mtot,f}$. The intercept
 230 with the y -axis is the initial content of sorbed metal $q_{Mtot,0} = K_{d,Mtot,f} c_{Mtot,0}$ so that
 231 $\Delta q_{Mtot} = 0$ when the added solution has a concentration of total metal $c_{M,i} = c_{Mtot,0}$.
 232 The initial content of sorbed metal is the so-called mobile pool for fast reactions of SD. It
 233 is a constant for a given soil and it has a great environmental importance. Its estimation
 234 by modeling is of great interest because it is difficult to determine experimentally.

235 To summarize :

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

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})

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

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

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

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

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

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

263 where

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

264 The experimental final concentrations of the DOC in the SD experiments are utilized
 265 to fit Eq. 30 to estimate $K_{d,DOC}$ and $c_{DOC,0}$. Then, from these two estimated values,
 266 Eq.22 is fitted to the experimental data of $c_{Mtot,f}$, assuming that $K_{d,L} = K_{d,DOC}$ and
 267 $K_0^* = K_{DOC,0}^* = K_{DOC}c_{DOC,0}$ (Eq. 32), which gives the estimates of $K_{d,M}$, $K_{d,ML}$, $c_{M,0}$
 268 and K_{DOC} .

269 **2.2.5 Partitioning and speciation of the metal at low r values corresponding** 270 **to the soil moisture in field conditions**

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

276 $K_{d,L}$, K_0^* or $K_{DOC,0}^*$, $K_{d,L}$ or $K_{d,DOC}$ and $F_{M,f}$ the concentrations of the total metal and
277 of the free ion can be estimated at any r values by Eqs. 21, 22 and 23 by setting $c_{M,i} = 0$.
278 It can be noticed that if the SD experiments are performed from the moist soil instead of
279 an air-dried soil, then, $c_{M,0}$ becomes the concentration of the free metal at the targeted
280 soil water content. Working with moist soil has the advantage of limiting the microbial
281 flush that can occur during the equilibration of the soil with the added solution.

282 **2.3 Experiments**

283 **2.3.1 Soils**

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

298 The soil samples were air-dried and sieved at 2 mm before use. The following char-
299 acteristics were determined with standardized methods by the Laboratoire d'Analyses
300 des Sols of INRA (Arras, France, [https://www6.hautsdefrance.inra.fr/las/Methodes-d-](https://www6.hautsdefrance.inra.fr/las/Methodes-d-analyse/Sols)
301 [analyse/Sols](https://www6.hautsdefrance.inra.fr/las/Methodes-d-analyse/Sols)): particle size distribution (pipette method, NF X 31-107), organic carbon
302 content (SOC, dry combustion method, NF ISO 10694), pH_{H_2O} (NF ISO 10390), total
303 carbonates (CaCO_3 , volumetric method, NF ISO 10693), cation exchange capacity (CEC,
304 Metson's method, NF X 31-130), and total Cd concentrations (HF - HClO_4 solubilization,

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

306 **2.3.2 Sorption-desorption experiments**

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

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

336 **2.3.3 Calculations and statistical analyses**

337 Data processing and analyses were performed with R (R Code Team, 2013). The Eq. 19,
338 21, 22 and 30 were fitted to the experimental observations by the “port” algorithm of the
339 non-linear least-squares *nls()* function (stats package). Confidence intervals ($p=0.05$) of
340 predicted values (*e.g.* $c_{Mtot,f}$ from Eq. 22 , $K_{d,Mtot,f}$ from Eq. 24) were derived from
341 Monte Carlo simulations (100 000 replicates) using the estimated parameters values and
342 their asymptotic standard errors returned by the *nls()* function.

343 **3 Results**

344 **3.1 Influence of the Ca concentration of the solution added to** 345 **the soil on the sorption-desorption results**

346 As predicted by the modeling (section 2.2.2), the change in the sorbed metal ($\Delta q_{Mtot,f}$)
347 calculated from Eq. 12 plotted against the concentration of the total metal in the solution
348 at equilibrium was linear (Eq. 26) for each Ca concentration (Fig. 1a). The intercepts of
349 the linear relationships with the y-axis, which give the initial mobile pool of sorbed Cd
350 for the dried soil ($q_{Mtot,0}$) was not affected by the Ca concentrations. This makes sense
351 because at the time scale of the SD experiments, this pool being related to the dry soil
352 before the contact with the Ca solution, it is not depending on the latter. By contrast,
353 the slope of the relationships, which gives $K_{d,Mtot,f}$ decreased when the Ca concentration
354 increased. An inverse relationship between $K_{d,Mtot,f}$ and the final Ca concentration in
355 solution ($c_{Ca,f}$) fitted relatively well the data (Fig. 1b). This means that the initial
356 concentration of total Cd in the residual soil solution in equilibrium with $q_{M,0}$ increased
357 with $c_{Ca,f}$ (Fig. S5a in SI). The final pH of the suspensions was independent of $c_{M,i}$ but
358 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

389 $\{K_{d,L}; K_0^*\}$ were applied in Eq. 22, which was then fitted to the observed concentra-
 390 tion of total Cd in solution ($c_{Mtot,f}$). This allowed to estimate $K_{d,M}$, $K_{d,ML}$, $c_{M,0}$ and
 391 K_{DOC} . In the DOC-based approach (see section 2.2.4, soils S4 to S6), the estimated
 392 $\{c_{DOC,0}; K_{d,DOC}\}$ were applied in Eq.22 to estimate $K_{d,M}$, $K_{d,ML}$, and $c_{M,0}$ by replacing
 393 K_0^* by $K_{d,DOC} c_{DOC,0}$ (Table 4). The influence of r on $c_{Mtot,f}$ depended on both the range
 394 of r and on the soil (Figure 4). When $r \geq 10 \text{ L kg}^{-1}$, the relationship between $c_{Mtot,f}$
 395 and r was more or less linear, with a slope that was negative when $c_{M,i} = 0$ and that
 396 increased with $c_{M,i}$. When $r \leq 10 \text{ L kg}^{-1}$, the slope was still negative when $c_{M,i} = 0$ and
 397 $c_{Mtot,f}$ generally increased when r tended towards 0. For soil S4, and particularly for
 398 soil S3, whatever the value of $c_{M,i}$, the relationship was curved with a local slope that
 399 becomes more negative as r decreases. This complex relationship between $c_{Mtot,f}$ and r
 400 was well illustrated by Eq. 22. Indeed, the linear regression between the observed and
 401 the predicted $c_{Mtot,f}$ indicated a very good fit ($R^2 > 0.91$) and no significant bias (slope
 402 and intercept never significantly different from 1 and 0, respectively, Figure S7 in SI) .
 403 Figure 5 shows the relationships between Δq_{Mtot} and $c_{Mtot,f}$ for the five soils, *i.e.* the
 404 observed SD curves. As predicted by the modeling (see section 2.2.2), for a given r value,
 405 the relationship between Δq_{Mtot} and $c_{Mtot,f}$ was linear. Because $K_{d,M} > K_{d,ML}$ (Table 4)
 406 and because $F_{M,f}$ increases with increasing r values (Eq. 19), the model of Eq. 25 also
 407 predicts an increase of $K_{d,Mtot,f}$ (the slope) if r increases. This was confirmed by the
 408 experimental observations (Fig. 5).

409 3.3 Values of the estimated parameters

$$410 \quad \{K_{d,L}; K_0^*; c_{DOC,0}; K_{d,DOC}; K_{d,M}; K_{d,ML}; c_{M,0}\}$$

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

417 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

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

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

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

491 For the other soils, the modeling of $F_{M,f}$ (Eq. 19), of $c_{DOC,f}$ (Eq. 30) and thereafter of
492 $c_{Mtot,f}$ (Eq. 22) generally predicted well the experimental observations (Figs. 2, 3 and 4).
493 This does not question the validity of the different assumptions except part of assumption
494 3, which states that $ML \ll L$ both in the solution and sorbed onto the solid phase. The
495 observations that $c_{ML,0} \ll c_{DOC,0}$ and $q_{ML,0} \ll q_{DOC,0}$ give a high degree of confidence
496 to assumption 3 in the case where the ligand is considered to be a significant part of the
497 DOC. By contrast, if the mean ligand is inorganic or is a minor fraction of the DOC,
498 assumption 3 can be questioned.

499 **4.3** $K_{d,M}$, $K_{d,ML}$ and $K_{d,L}$

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

514 **4.4** Effect of complexation on the SD curves

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

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

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

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

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

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

562 4.5 A simplified procedure for estimating the parameters

563 There is a great interest in easily determining $K_{d,Mtot}$, $K_{d,M}$ and $K_{d,ML}$ in environmental
 564 and agricultural sciences for studying the transfers and bioavailability of metals (Lin et al.,
 565 2016; Schneider et al., 2018). As demonstrated in this work, due to complexation, $K_{d,M}$
 566 cannot be approximated by $K_{d,Mtot}$. Furthermore, because $K_{d,Mtot}$ depends on r , SD
 567 experiments usually performed at a unique r value (commonly 10 L kg^{-1}) poorly reflects
 568 the values of $K_{d,Mtot}$ and $K_{d,M}$ at the field soil moisture. Our approach allows estimating
 569 $K_{d,Mtot}$, $K_{d,M}$, $K_{d,ML}$, $c_{M,0}$ and $c_{ML,0}$, including for field soil moisture by extrapolating
 570 the relationship between $K_{d,Mtot}$ and r at the appropriate r value (Fig. S9 in SI). An
 571 alternative would be to study moist soils instead of air-dried soils. This could avoid
 572 problems due to re-wetting, including the microbial flush.

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

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

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

- 589 • Experiments 3 (*E3*) is a desorption experiment performed at a very high r_{high} value,
 590 1000 L kg⁻¹ for instance, with a M -free solution ($c_{M,i,3} = 0$) containing only Ca and
 591 Mg at the concentrations determined in *E1*.
- 592 • Experiments 4 (*E4*) is a sorption experiment, also performed at r_{high} , with a
 593 solution containing Ca and Mg as previously, together with M at a concentration
 594 $c_{M,i,4}$ that must also be chosen so that the amount of added M is a fraction (< 1) of
 595 the initial total M content in the soil. Therefore, $c_{M,i,4} \ll c_{M,i,2}$ because $r_{low} \ll r_{high}$.

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

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

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

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

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

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

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

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

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

603 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}
604 becomes

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

605 and then

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

606 5 Conclusions

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

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624 The authors declare that they have no conflict of interest.

References

- 625 Barber, S. A. (1995). *Soil nutrient bioavailability: a mechanistic approach*. Purdue
626 University, USA. John Wiley and Sons John Wiley and Sons.
- 628 Boekhold, A. E., Temminghoff, E. J. M., and Van der Zee, S. E. a. T. M. (1993). Influence
629 of electrolyte composition and pH on cadmium sorption by an acid sandy soil. *Journal*
630 *of Soil Science*, 44(1):85–96.
- 631 Christensen, T. H. (1984). Cadmium soil sorption at low concentrations: I. Effect of time,
632 cadmium load, pH, and calcium. *Water Air Soil Pollut*, 21(1-4):105–114.
- 633 Christensen, T. H. (1985). Cadmium soil sorption at low concentrations. IV. Effect of
634 waste leachates on distribution coefficients. *Water Air Soil Pollut*, 26(3):265–274.
- 635 Christensen, T. H. (1989). Cadmium soil sorption at low concentrations. VII: Effect of
636 stable solid waste leachate complexes. *Water Air Soil Pollut*, 44(1-2):43–56.
- 637 Custos, J.-M., Moyne, C., Treillon, T., and Sterckeman, T. (2014). Contribution of Cd-
638 EDTA complexes to cadmium uptake by maize: a modelling approach. *Plant Soil*,
639 374(1-2):497–512.
- 640 de Vries, W. and Groenenberg, J. E. (2009). Evaluation of approaches to calculate critical
641 metal loads for forest ecosystems. *Environ. Pollut.*, 157(12):3422–3432.
- 642 de Vries, W., McLaughlin, M. J., and Groenenberg, J. E. (2011). Transfer func-
643 tions for solid-solution partitioning of cadmium for Australian soils. *Environ. Pollut.*,
644 159(12):3583–3594.
- 645 Degryse, F., Smolders, E., and Parker, D. R. (2009). Partitioning of metals (Cd, Co, Cu,
646 Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications – a review.
647 *European Journal of Soil Science*, 60(4):590–612.
- 648 Di Toro, D. M., Mahony, J. D., Kirchgraber, P. R., O’Byrne, A. L., Pasquale, L. R.,
649 and Piccirilli, D. C. (1986). Effects of nonreversibility, particle concentration, and ionic
650 strength on heavy-metal sorption. *Environ. Sci. Technol.*, 20(1):55–61.

- 651 Elliott, H. A. and Denny, C. M. (1982). Soil Adsorption of Cadmium From Solutions
652 Containing Organic Ligands 1. *Journal of Environmental Quality*, 11(4):658–663.
- 653 Fardeau, J. C., Morel, C., and Boniface, R. (1991). Cinétiques de transfert des ions
654 phosphate du sol vers la solution du sol : paramètres caractéristiques. *Agronomie*,
655 11(9):787–797.
- 656 Filipović, V., Cambier, P., Filipović, L., Coquet, Y., Pot, V., Bodineau, G., Jaulin, A.,
657 Mercier, V., Houot, S., and Benoit, P. (2016). Modeling Copper and Cadmium Mo-
658 bility in an Albeluvisol Amended with Urban Waste Composts. *Vadose Zone Journal*,
659 15(12):0.
- 660 García-Miragaya, J. and Page, A. L. (1978). Sorption of trace quantities of cadmium
661 by soils with different chemical and mineralogical composition. *Water Air Soil Pollut*,
662 9(3):289–299.
- 663 Gérard, E., Echevarria, G., Sterckeman, T., and Morel, J. L. (2000). Cadmium Avail-
664 ability to Three Plant Species Varying in Cadmium Accumulation Pattern. *Journal of*
665 *Environmental Quality*, 29(4):1117–1123.
- 666 Gray, C. W., McLaren, R. G., Roberts, A. H. C., and Condon, L. M. (1999). Cadmium
667 phytoavailability in some New Zealand soils. *Aust. J. Soil Res.*, 37(3):461–477.
- 668 Harter, R. D. and Naidu, R. (2001). An Assessment of Environmental and Solution
669 Parameter Impact on Trace-Metal Sorption by Soils. *Soil Science Society of America*
670 *Journal*, 65(3):597–612.
- 671 Kabata-Pendias, A. (2004). Soil–plant transfer of trace elements—an environmental issue.
672 *Geoderma*, 122(2):143–149.
- 673 Lee, S.-Z., Allen, H. E., Huang, C. P., Sparks, D. L., Sanders, P. F., and Peijnenburg,
674 W. J. (1996). Predicting Soil- Water Partition Coefficients for Cadmium. *Environmental*
675 *science & technology*, 30(12):3418–3424.
- 676 Legind, C. N., Rein, A., Serre, J., Brochier, V., Haudin, C.-S., Cambier, P., Houot, S.,
677 and Trapp, S. (2012). Simultaneous Simulations of Uptake in Plants and Leaching

678 to Groundwater of Cadmium and Lead for Arable Land Amended with Compost or
679 Farmyard Manure. *PLoS ONE*, 7(10).

680 Lin, Z., Schneider, A., Nguyen, C., and Sterckeman, T. (2014). Can ligand addition to
681 soil enhance Cd phytoextraction? A mechanistic model study. *Environ Sci Pollut Res*,
682 21(22):12811–12826.

683 Lin, Z., Schneider, A., Sterckeman, T., and Nguyen, C. (2016). Ranking of mechanisms
684 governing the phytoavailability of cadmium in agricultural soils using a mechanistic
685 model. *Plant Soil*, pages 89–107.

686 Neal, R. H. and Sposito, G. (1986). Effects of soluble organic matter and sewage sludge
687 amendments on cadmium sorption by soils at low cadmium concentrations. *Soil Science*,
688 142(3):164.

689 Neff, J. C. and Asner, G. P. (2001). Dissolved Organic Carbon in Terrestrial Ecosystems:
690 Synthesis and a Model. *Ecosystems*, 4(1):29–48.

691 O'Connor, D. J. and Connolly, J. P. (1980). The effect of concentration of adsorbing
692 solids on the partition coefficient. *Water Research*, 14(10):1517–1523.

693 Ponizovsky, A. A., Metzler, D. M., Allen, H. E., and Ackerman, A. J. (2006). The
694 effect of moisture content on the release of organic matter and copper to soil solutions.
695 *Geoderma*, 135(0):204–215.

696 Posch, M. and de Vries, W. (2009). Dynamic modelling of metals - Time scales and target
697 loads. *Environ. Modell. Softw.*, 24(1):86–95.

698 Ren, Z.-L., Tella, M., Bravin, M. N., Comans, R. N., Dai, J., Garnier, J.-M., Sivry, Y.,
699 Doelsch, E., Straathof, A., and Benedetti, M. F. (2015). Effect of dissolved organic
700 matter composition on metal speciation in soil solutions. *Chemical Geology*, 398:61–69.

701 Schneider, A. (1997). Release and fixation of potassium by a loamy soil as affected by
702 initial water content and potassium status of soil samples. *European Journal of Soil
703 Science*, 48(2):263–271.

- 704 Schneider, A. (2003). Characterisation of soil potassium supply as derived from sorption-
705 desorption experiments. *Plant and Soil*, 251(2):331–341.
- 706 Schneider, A. (2006). Adaptation of the Ion Exchange Method for the Determination
707 of the Free Ionic Fraction of Cadmium in Solution. *Journal of Environment Quality*,
708 35(1):394.
- 709 Schneider, A. (2008). An Exchange Method To Investigate the Kinetics of Cd Complex-
710 ation in Soil Solutions. *Environ. Sci. Technol.*, 42(11):4076–4082.
- 711 Schneider, A., Lin, Z., Sterckeman, T., and Nguyen, C. (2018). Comparison between
712 numeric and approximate analytic solutions for the prediction of soil metal uptake by
713 roots. Example of cadmium. *Science of The Total Environment*, 619–620:1194–1205.
- 714 Schneider, A., Mollier, A., and Morel, C. (2003). Modeling the kinetics of the solution
715 phosphate concentration during sorption and desorption experiments. *Soil Science*,
716 168(9):627–636.
- 717 Schneider, A. and Morel, C. (2000). Relationship between the isotopically exchangeable
718 and resin-extractable phosphate of deficient to heavily fertilized soil. *European Journal*
719 *of Soil Science*, 51(4):709–715.
- 720 Selim, H. (2013). Chapter Five - Transport and Retention of Heavy Metal in Soils:
721 Competitive Sorption. In Sparks, D. L., editor, *Advances in Agronomy*, volume Volume
722 119, pages 275–308. Academic Press.
- 723 Shi, Z., Allen, H. E., Di Toro, D. M., Lee, S.-Z., Flores Meza, D. M., and Lofts, S. (2007).
724 Predicting cadmium adsorption on soils using WHAM VI. *Chemosphere*, 69(4):605–612.
- 725 Singh, A. and Pandeya, S. (1998). Modelling uptake of cadmium by plants in sludge-
726 treated soils. *Bioresource Technology*, 66(1):51–58.
- 727 Sivry, Y., Riotte, J., Munoz, M., Sappin-Didier, V., and Dupre, B. (2006). Study of labile
728 Cd pool in contaminated soil using stable isotope analysis, radioactive isotope dilution
729 and sequential extraction. *Geochimica Et Cosmochimica Acta*, 70(18, S):A594.

- 730 Staunton, S. (2004). Sensitivity analysis of the distribution coefficient, K_d , of nickel with
731 changing soil chemical properties. *Geoderma*, 122(2):281–290.
- 732 Sterckeman, T., Perriguey, J., Cael, M., Schwartz, C., and Morel, J. (2004). Apply-
733 ing a mechanistic model to cadmium uptake by *Zea mays* and *Thlaspi caerulescens*:
734 Consequences for the assessment of the soil quantity and capacity factors. *Plant Soil*,
735 262(1-2):289–302.
- 736 Temminghoff, E. J. M., Zee, S., and Haan, F. A. M. (1995). Speciation and calcium
737 competition effects on cadmium sorption by sandy soil at various pHs. *European Journal*
738 *of Soil Science*, 46(4):649–655.
- 739 Tiller, K. G., Honeysett, J. L., and De, V. M. (1972). Soil zinc and its uptake by plants. I.
740 Isotopic exchange equilibria and the application of tracer techniques. II. Soil chemistry
741 in relation to prediction of availability. *Soil Res.*, 10(2):151–164.
- 742 Vandenbruwane, J., De Neve, S., Qualls, R. G., Sleutel, S., and Hofman, G. (2007). Com-
743 parison of different isotherm models for dissolved organic carbon (DOC) and nitrogen
744 (DON) sorption to mineral soil. *Geoderma*, 139(1):144–153.
- 745 Voegelin, A., Vulava, V. M., and Kretzschmar, R. (2001). Reaction-Based Model De-
746 scribing Competitive Sorption and Transport of Cd, Zn, and Ni in an Acidic Soil.
747 *Environmental Science & Technology*, 35(8):1651–1657.
- 748 Weng, L., Temminghoff, E. J. M., Lofts, S., Tipping, E., and Van Riemsdijk, W. H.
749 (2002). Complexation with dissolved organic matter and solubility control of heavy
750 metals in a sandy soil. *Environ. Sci. Technol.*, 36(22):4804–4810.
- 751 Yin, Y., Impellitteri, C. A., You, S.-J., and Allen, H. E. (2002). The importance of organic
752 matter distribution and extract soil:solution ratio on the desorption of heavy metals
753 from soils. *Science of The Total Environment*, 287(1–2):107–119.
- 754 Zhou, L. X. and Wong, J. W. C. (2001). Effect of Dissolved Organic Matter from Sludge
755 and Sludge Compost on Soil Copper Sorption. *Journal of Environmental Quality*,
756 30(3):878–883.

757 Table 1 : Description of the different variables of the modeling with their respective
758 units. The terms 'initial' and 'final' correspond to sorption/desorption (SD) experiments,
759 namely before and after the addition of the solution to the air-dried soils. M, L, ML
760 and DOC stands for the free metal, the free ligand, the metal complex and the dissolved
761 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
762 $F_{M,f}, F_{ML,f}$	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	$L \text{ kg}^{-1}$

763

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	$c_{Ca,i}$ mM	$c_{SS,Cd}$ $\mu\text{g L}^{-1}$	r L kg^{-1}	$c_{M,i}$ nM	n^d	N^e
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

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 ($c_{ML,0}$, $q_{DOC,0}$, $q_{M,0}$, $q_{ML,0}$).

Soil	$K_{d,L}$ L kg ⁻¹	K_0^*	K_{DOC} M ⁻¹	c_{DOC} mg L ⁻¹	$c_{DOC,0}$ mg L ⁻¹	$K_{d,M}$ L kg ⁻¹		$c_{M,0}$ μg Cd L ⁻¹	$c_{ML,0}^c$	$q_{DOC,0}^d$	$q_{M,0}$ mg kg ⁻¹	$q_{ML,0}$
						$K_{d,M}$	$K_{d,ML}$					
S2	9	0.7	-	-	422	0	0.4	0.3	-	-	0.2	0.0
779 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	120	2.8	3.0
S5	8 ^a	2.8 ^b	2367	14	90	14	119.0	328.0	113	113	10.6	4.6
S6	3 ^a	59.0 ^b	10421	68	1256	511	0.1	4.1	196	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

784 **7 Figure captions**
785 Figure 1: Effect of the background Ca concentration on the sorption/desorption (SD)
786 experiments. Fig 1a: Variation of the mobile pool of total Cd (Δq_{Mtot}) as a function
787 of the concentration of total Cd in solution ($c_{Mtot,f}$, points) and linear regressions (lines)
788 with slopes ($K_{d,Mtot}$) and intercept ($-q_{Mtot,0}$) given inset (standard errors in parentheses).
789 Fig 1b: $K_{d,Mtot}$ as a function of the Ca concentration in solution at the end of the SD
790 experiments ($c_{Ca,f}$); the vertical bars are the confidence intervals ($P = 0.05$); the curve
791 is the inverse relationship ($y = a/x$) fitted to the data the equation of which is given in
792 inset.

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

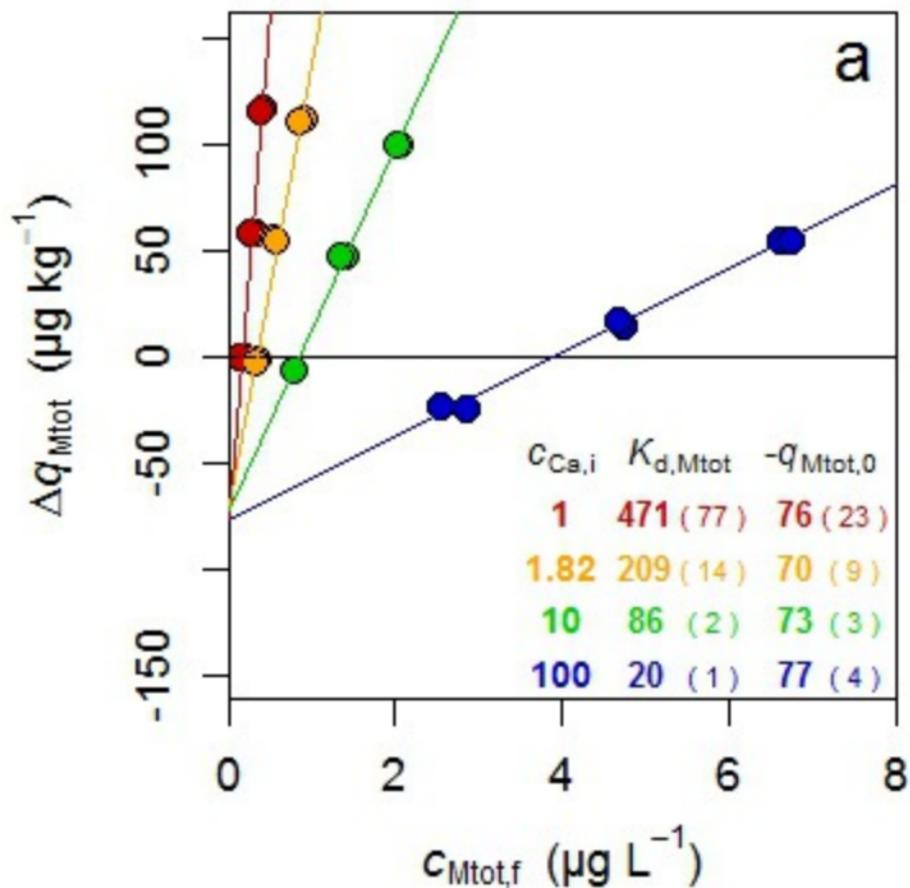
800 Figure 3: Observed final DOC concentration ($c_{DOC,f}$) as a function of the solution vol-
801 ume:soil mass ratio (r) for soils S4-S6. The colors indicate the tested soil solution:soil
802 mass ratio (r) and the different symbols show the different tested values of $c_{M,i}$ (circles :
803 $c_{M,i}=0$, diamond and square symbols for increasing non null $c_{M,i}$; see Table 3). The thick
804 line is the model of Eq. 16 fitted to the data; the thin lines are for the corresponding
805 confidence interval ($P = 0.05$) of the predicted values; the estimated values of $K_{d,DOC}$
806 ($L\ kg^{-1}$) and of $c_{DOC,0}$ ($mg\ L^{-1}$) are given in each graph as well as their standard error
807 (in parentheses).

808 Figure 4: Observed (points) and modeled (Eq. 22, lines) $c_{Mtot,f}$ values as a function of
809 the solution volume:soil mass ratio (r). The colors indicate the tested soil solution:soil
810 mass ratio (r) and the different symbols show the different tested values of $c_{M,i}$ (circles :
811 $c_{M,i}=0$, diamond and square symbols for increasing non null $c_{M,i}$; see Table 3).

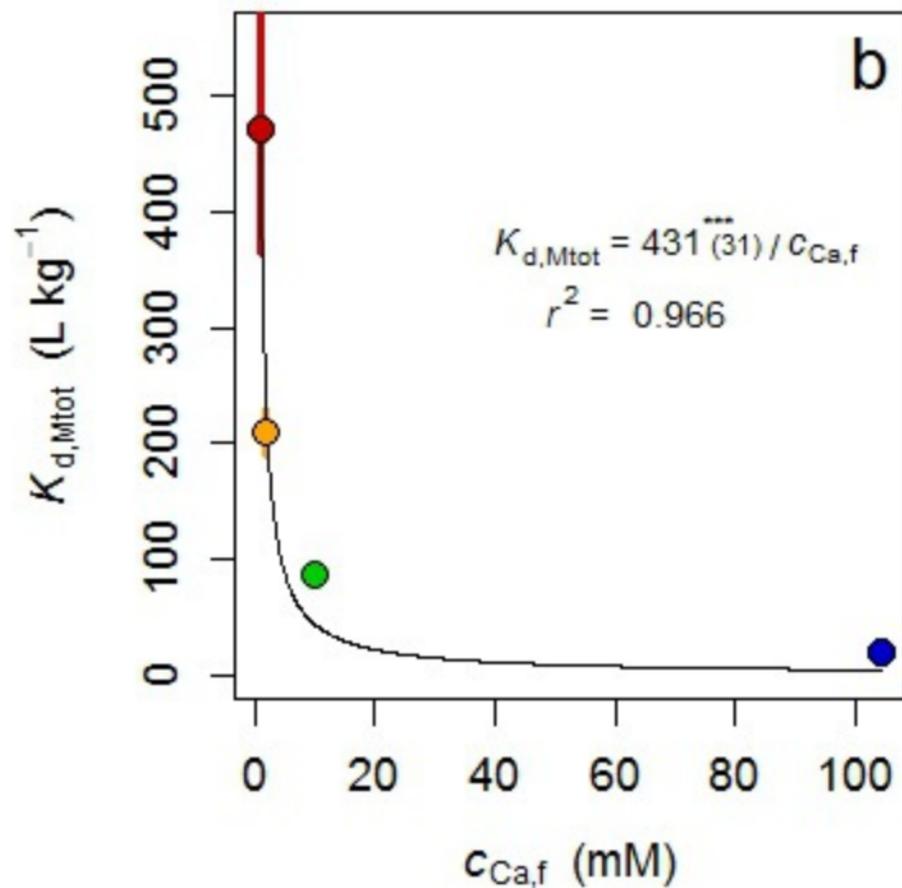
812 Figure 5: Observed (points) and modeled (lines) SD curves of total Cd. The points

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).

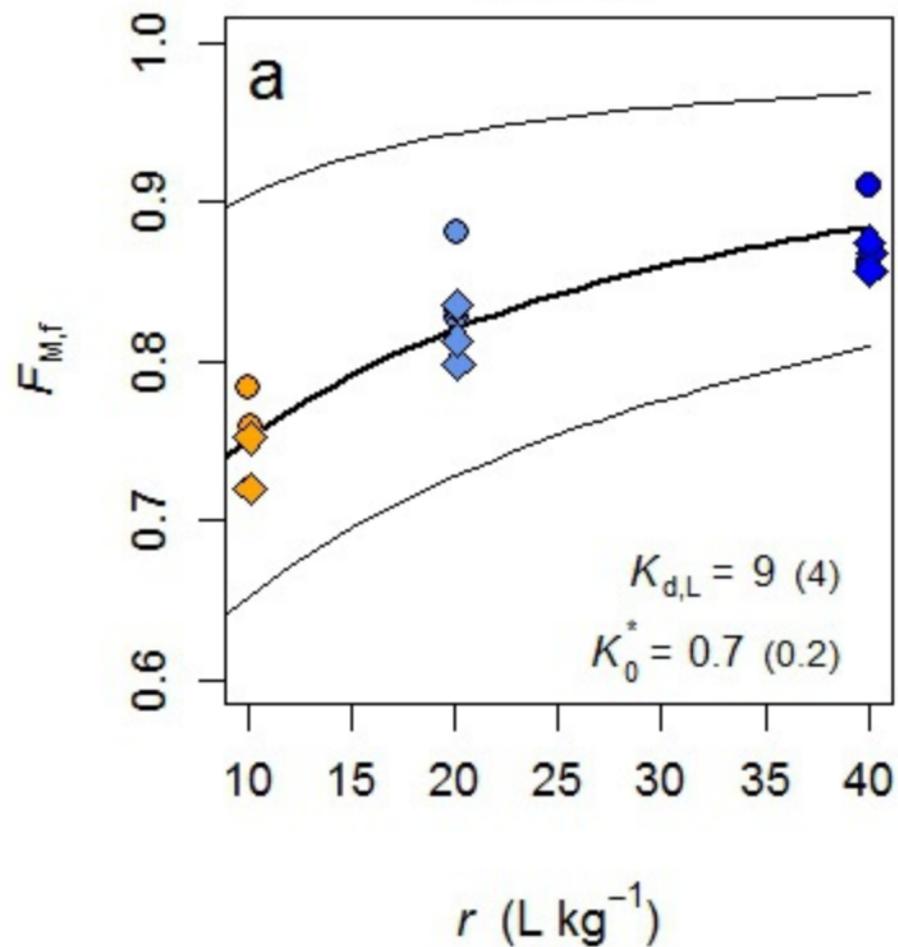
Soil S1



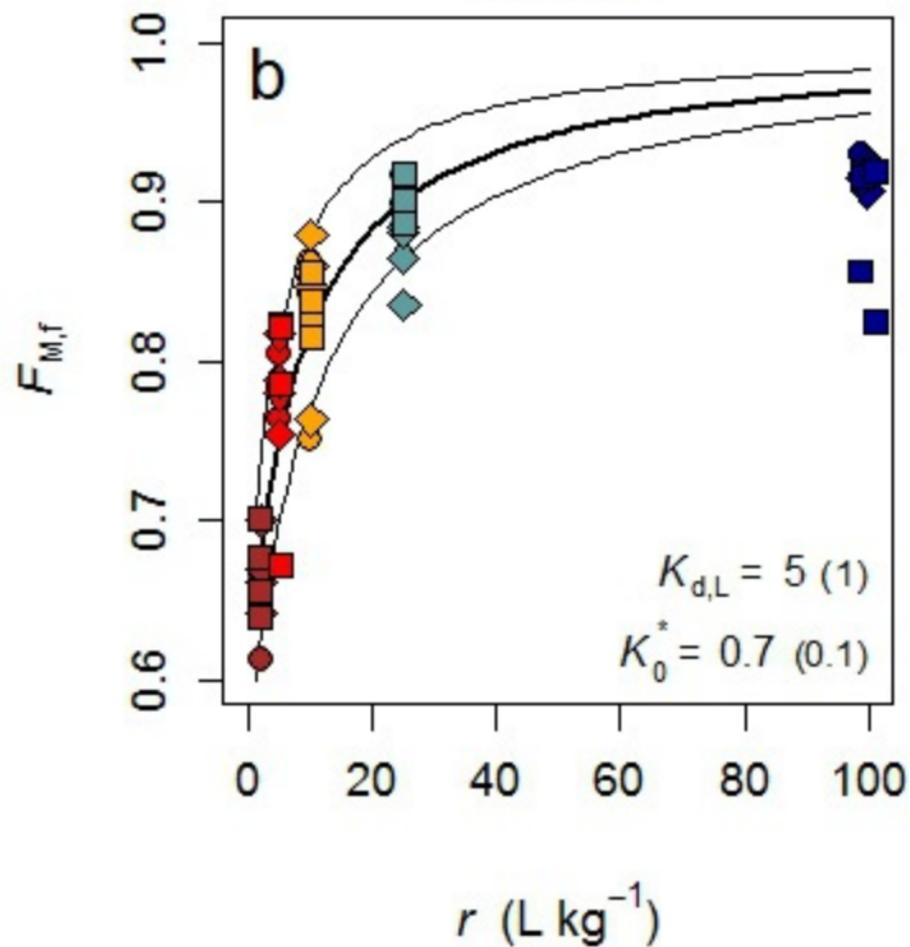
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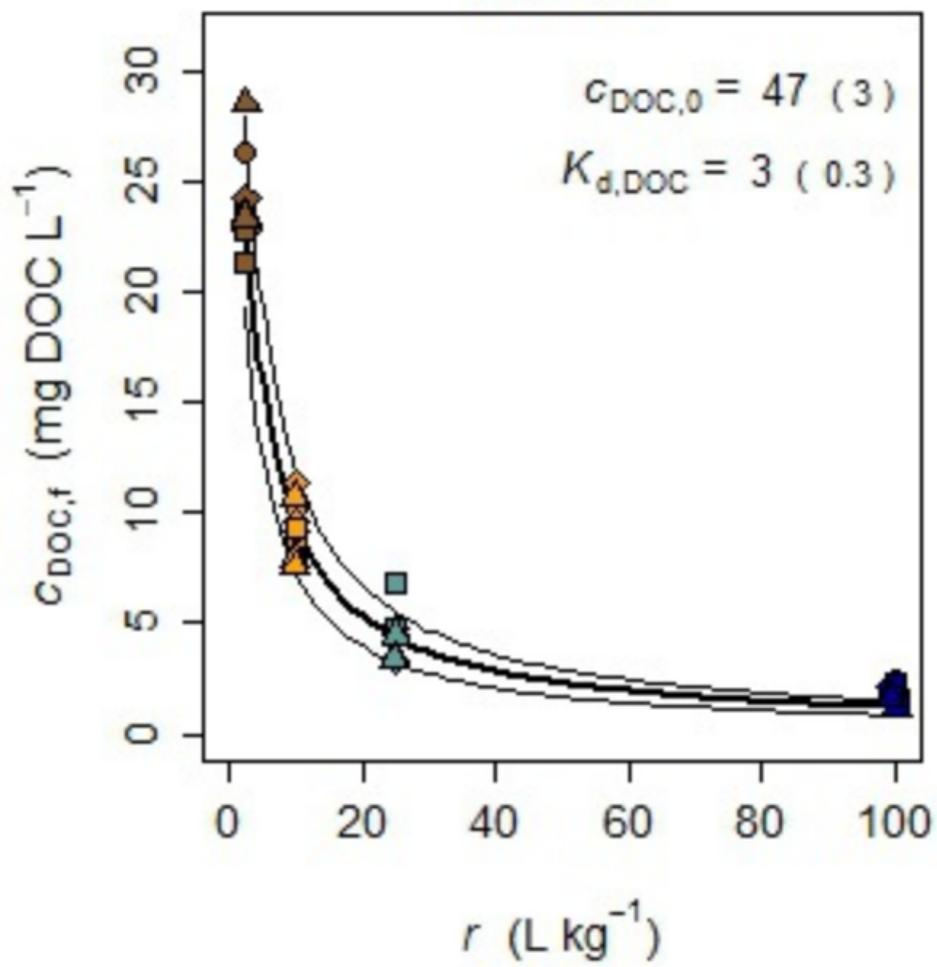
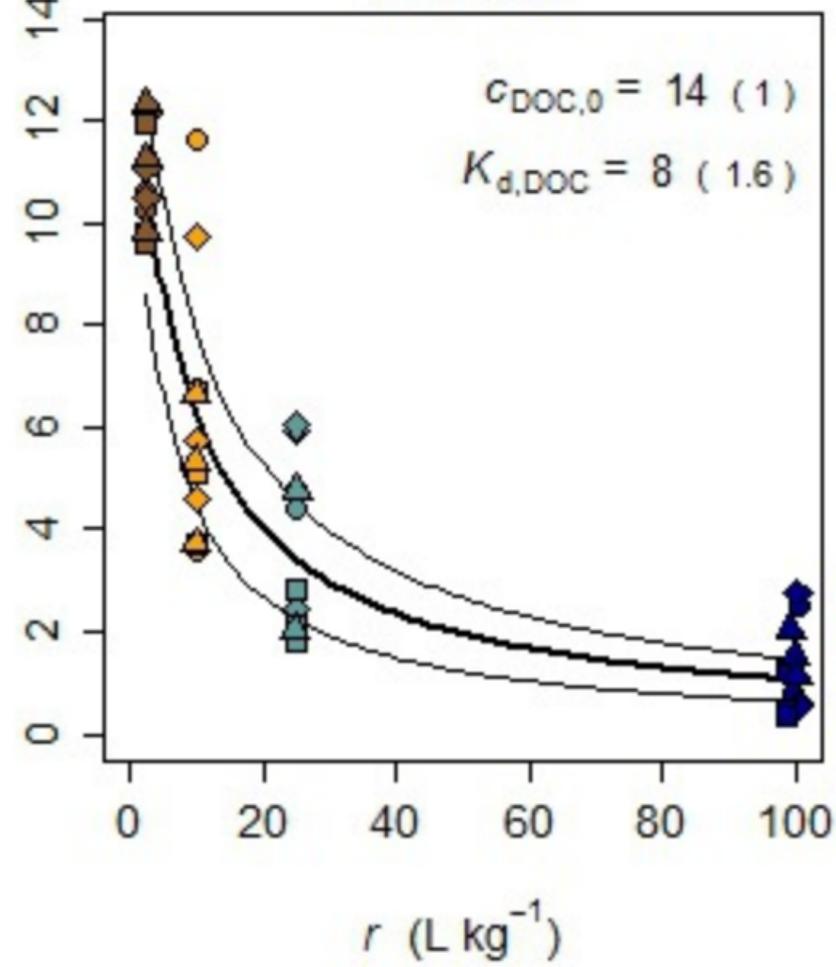
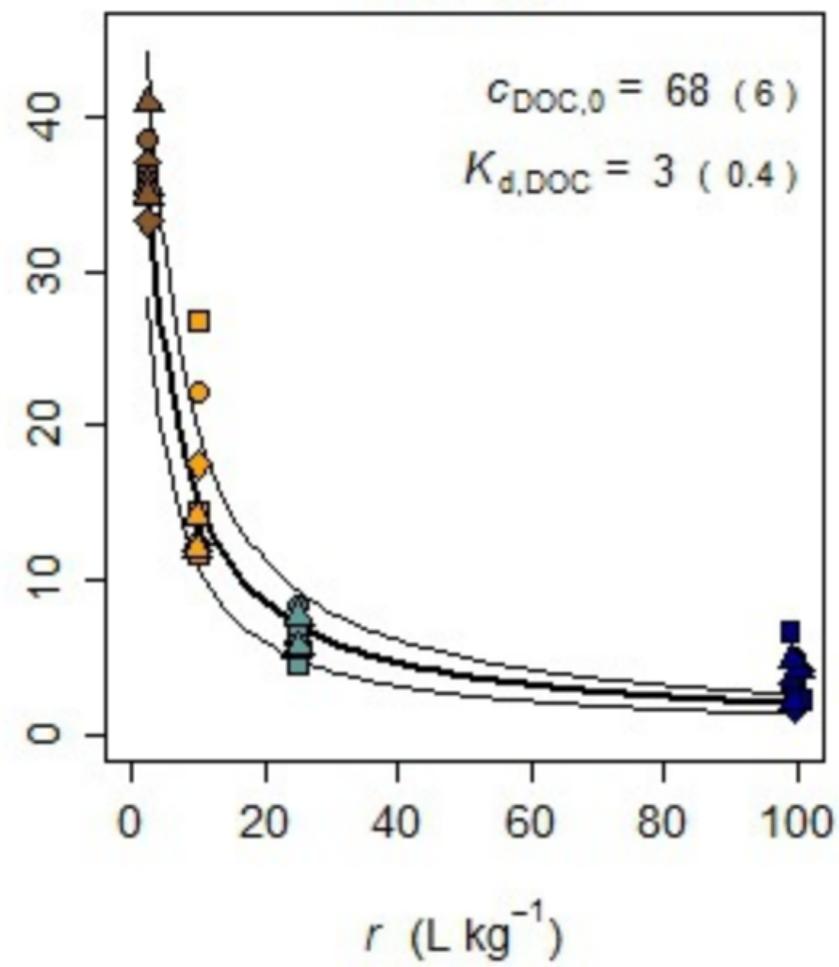


Soil S2

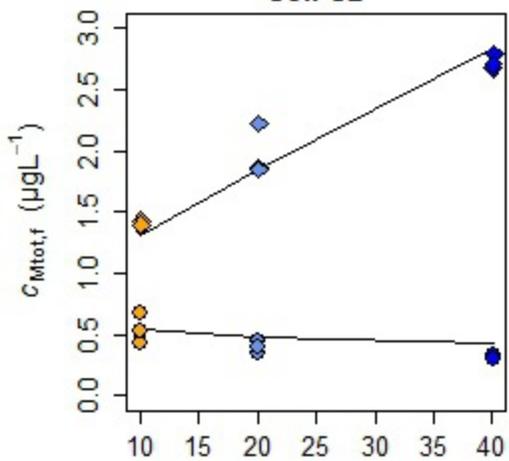


Soil S3

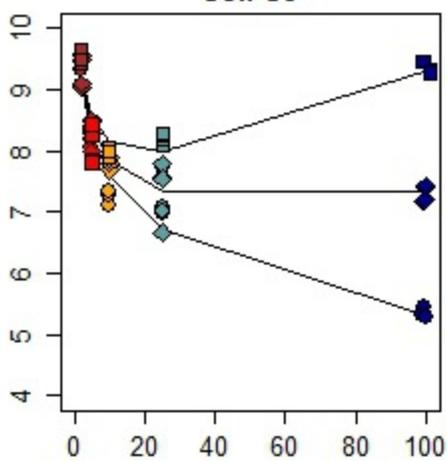


Soil S4**Soil S5****Soil S6**

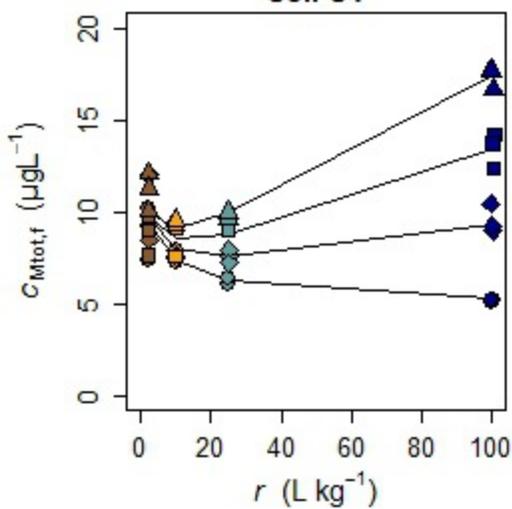
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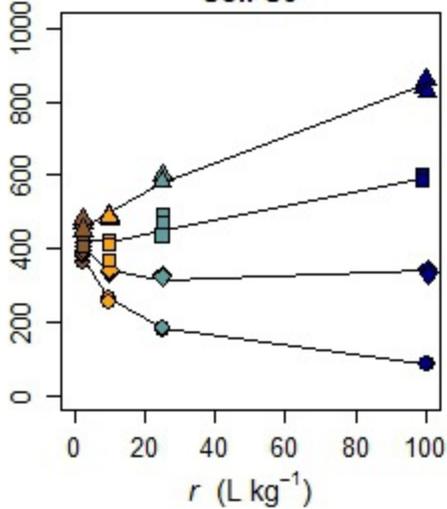
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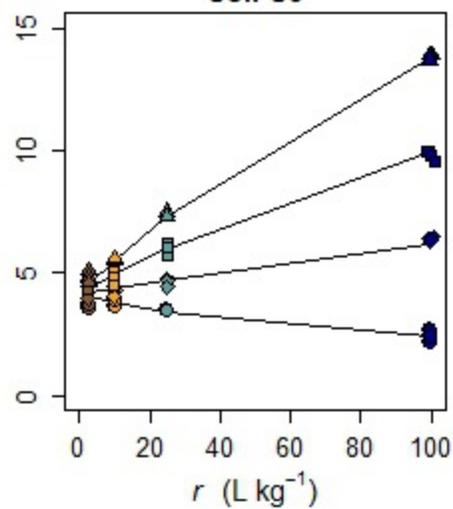
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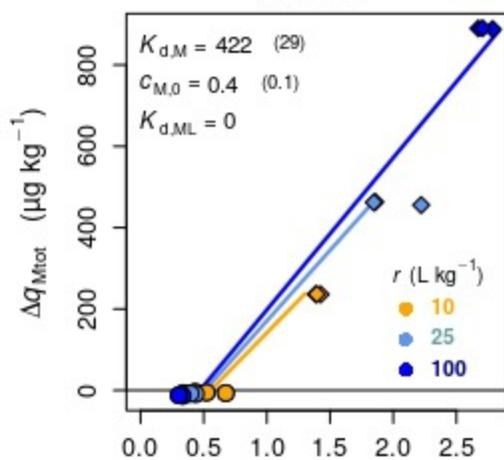
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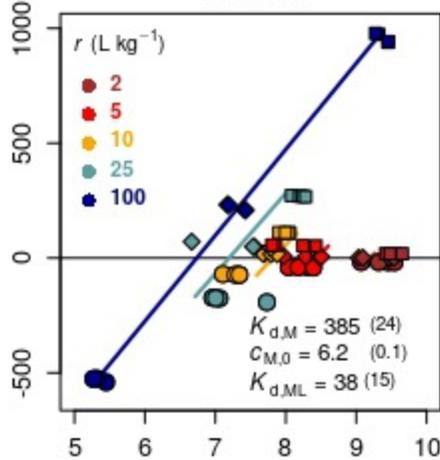
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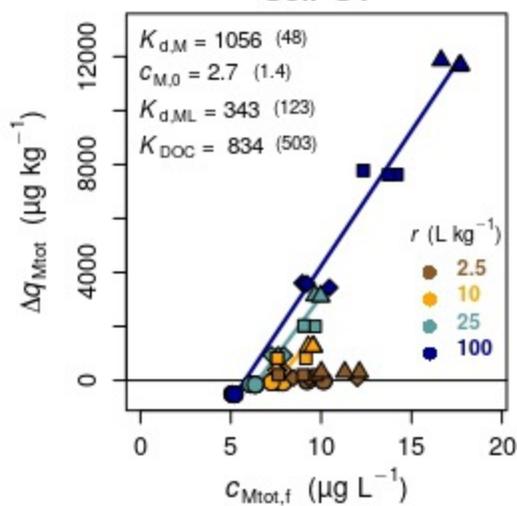
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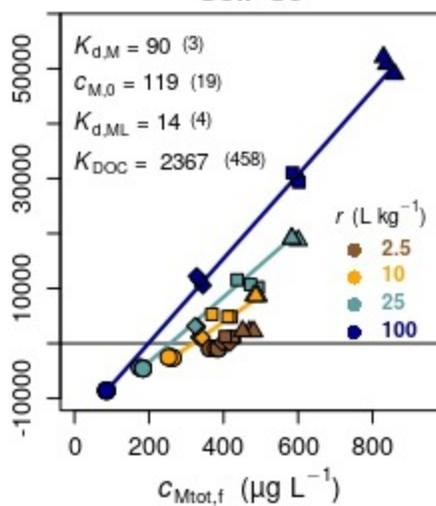
Soil S3



Soil S4



Soil S5



Soil S6

