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Ranking of mechanisms governing the phytoavailability of cadmium in agricultural soils using a mechanistic model

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Abstract

Aims The objective of this study was to rank the mechanisms influencing the phytoavailability of cadmium (Cd) in agricultural soils.

Methods We developed a model that simulates the transport by diffusion and convection, the kinetics of sorption and complexation in solution and the root uptake of Cd. The ranking of mechanisms was performed by simulating the Cd^{2+} uptake by 1 cm^2 root for 30 days for French agricultural soil characteristics.

Results The initial Cd^{2+} concentration was the most influential parameter followed by the soil buffer power for Cd^{2+} and by the soil water content and impedance

factor. The Cd^{2+} was generally strongly depleted at the root surface and the convection was almost negligible. In general, the Cd complex dissociation contributed little to the uptake due to a strong kinetics limitation. Conversely, the kinetics of sorption was little influential. **Conclusions** The initial concentration and diffusion of Cd^{2+} were the dominant processes governing the phytoavailability in non-polluted soils. A model considering only the transport and sorption of Cd^{2+} without kinetics would be adequate to predict the phytoavailability. The particular situations where these simplifications do not hold (relative error >10 %) corresponded to a high supply of labile Cd complex toward plant roots.

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Introduction

Cadmium (Cd) is a very toxic element, which naturally occurs in agricultural soils due to the parent material, sometimes in relatively high concentrations (Baize et al. 1999). Furthermore, this element is added to cultivated soils as a contaminant of agricultural inputs, in particular phosphate fertilizers and recycled wastes such as manure, compost, sewage sludges etc. Finally, Cd also enters cultivated soils as the results of atmospheric fallouts, from a natural origin or derived from human activities (Alloway and Steinnes 1999). Plant roots absorb Cd^{2+} from the soil solution (Cataldo et al. 1983; Redjala et al. 2009) and the contaminant is subsequently found in edible plant parts, which causes potential risk to humans due to the contamination of the food chain (Leblanc et al. 2004).

Plant roots mainly absorb Cd as free hydrated ion, Cd^{2+} , at a rate which depends on its concentration at the root surface, according to a Michaelis-Menten kinetics (Cataldo et al. 1983; Redjala et al. 2009). In agricultural soils, Cd^{2+} in solution is a minor fraction of the total soil Cd. Indeed, a large fraction of the soil Cd is generally adsorbed onto the solid phase including clay and organic matter (Mesquita and Silva 2002; Sauvé et al. 2000a, b). In the soil solution, in addition to the free Cd^{2+} ion, Cd also exists as complexes, mainly formed with soluble organic ligands (Cornu et al. 2009, 2011). The concentration of Cd^{2+} at the root surface is governed by sorption and complexation reactions and by the transport of Cd toward the root surface by diffusion and mass flow (Schneider 2008; Sterckeman et al. 2004).

In literature, some empirical relationships were proposed to link the concentration of Cd in plants with the soil variables assumed to govern the phytoavailability of the metal, i.e., generally the concentration of the total or labile Cd as experimentally defined by specific extractions, the pH, the soil organic matter and to a lesser extend the clay content (Hough et al. 2004; Tudoreanu and Phillips

2004). These correlation models can be good for some specific situations but due to the poor description of mechanisms, they are rarely reliable when extrapolating their predictions to contexts that are different from the ones used for their calibration. Therefore, mechanistic models appear as valuable alternative approach to predict Cd uptake more generically. A general model describing transport, sorption onto the solid phase and uptake by plant roots of one chemical species of nutrient has been developed in the 70's (Barber 1962; Barber and Cushman 1981; Nye and Marriott 1969). Specific improvements of the Barber's model have been performed to address specific questions. For instance, the modeling of the effect of root exudation/degradation on the solubilization of trace elements and phosphorus has been modeled with no kinetics (Ptashnyk et al. 2011; Schnepf et al. 2012) or with kinetics for dissolution but not for the complex dissociation (Seuntjens et al. 2004). Upscaling (Szegedi et al. 2008) or coupling with root architecture (Schnepf et al. 2012) have also been performed. The Barber's model was applied to the absorption of nutrients by branched systems including mycorrhiza (Schnepf et al. 2011) or roots with root hairs (Keyes et al. 2013).

Attempts have been made to extend the Barber's model to Cd uptake by crops but the predictions were not satisfactory (Mullins et al. 1986; Sterckeman et al. 2004). One possible reason for this may lie in the fact that the Barber's approach considers only one chemical species. Consequently, the model cannot correctly describe that Cd complexes formed with soluble organic ligands (Schneider 2008; Schneider and Nguyen 2011) can dissociate at the root surface and can buffer the concentration of Cd^{2+} , which is the only species assumed to be absorbed by plant roots (Panfili et al. 2009). The buffering capacity of Cd complex depends on their lability (Degryse et al. 2006) and therefore the kinetics of complexation might be important to consider. The contribution of Cd-complexes to the root uptake by considering the kinetics has been very recently carried out for an exogenous ligand added to polluted soil to enhance Cd extraction by plant roots in the context of phytoremediation (Lin et al. 2014). In the context of non-polluted agricultural soils where contrary to polluted soils, the Cd concentration is generally low

(Baize et al. 2007), the buffering of Cd^{2+} at the root surface by Cd complexes formed with the soil dissolved organic matter may be significant.

The objectives of this study were 1) to use a Cd phytoavailability model that simulates the transport by diffusion and convection, the kinetics of sorption and of complexation in solution with the soil organic matter and the root uptake of the free metal, 2) to rank the mechanisms by a sensitivity analysis of the model including the interactions between the mechanisms and focusing on agricultural non-polluted soils, 3) to assess the relative importance of sorption and complexation on the Cd phytoavailability, 4) to examine if the description of kinetics for sorption and complexation is necessary or if equilibrium could be assumed.

Materials and methods

The phytoavailability model

Barber's model (Barber 1995; Barber and Cushman 1981) was one mechanistic model widely used to simulate major and trace element transport and uptake by plant root in soil. The governing equation of Barber's model in cylindrical geometry adapted to consider adsorption-desorption kinetics (Roose et al. 2001) are as follows:

$$\begin{aligned} \theta \frac{\partial C_M}{\partial t} &= \frac{1}{r} \frac{\partial}{\partial r} \left(r f \theta D_M \frac{\partial C_M}{\partial r} + r_0 v_0 C_M \right) + (k_{des}^M S_M - \theta k_{ads}^M C_M) \\ \frac{dS_M}{dt} &= \theta k_{ads}^M C_M - k_{des}^M S_M \end{aligned} \quad (1)$$

In Eq. (1), θ is the soil volumetric water content (cm^3 soil water cm^{-3} soil), C_M is the metal concentration in soil solution ($\mu\text{mol cm}^{-3}$ solution), t is the time (s), r is the radial distance from the root axis (cm), f is the impedance factor (cm^2 soil cm^{-2} solution), D_M is the diffusion coefficient of the element in water ($\text{cm}^2 \text{s}^{-1}$), r_0 is the root radius (cm), v_0 is the water flux at the root surface (cm^3 water cm^{-2} root surface area s^{-1}), k_{ads}^M is the rate constant of adsorption from liquid phase onto solid phase for the metal (s^{-1}), k_{des}^M is the rate constant of desorption from solid phase to liquid phase for the metal (s^{-1}), S_M is the concentration

of the metal sorbed onto solid phase ($\mu\text{mol cm}^{-3}$ soil). The initial concentrations and boundary flux conditions of the above equations are as follows:

$$\left\{ \begin{array}{lll} C_M = C_{M0} & S_M = S_{M0} & r_0 \leq r \leq r_1 \quad t = 0 \\ J_M = -\frac{I_{\max} C_M}{K_m + C_M} & & r = r_0 \quad t \geq 0 \\ J_M = 0 & & r = r_1 \quad t \geq 0 \end{array} \right\} \quad (2)$$

In Eq. (2), C_{M0} is the initial metal concentration in the soil solution ($\mu\text{mol cm}^{-3}$ solution), S_{M0} is the initial concentration of the metal sorbed onto solid phase ($\mu\text{mol cm}^{-3}$ soil), $I_{\max}$ is the maximum uptake rate of the metal by the root ($\mu\text{mol cm}^{-2} \text{s}^{-1}$), K_m is the Michaelis affinity constant ($\mu\text{mol cm}^{-3}$ solution), i.e., the concentration of M in the soil solution when the uptake flux is half of $I_{\max}$, r_1 is the half distance between two root segments (cm soil).

Barber's approach considers only one chemical species in the soil solution. Therefore, to study Cd complexation, we consider three species: the free Cd^{2+} ion (M) assumed to be the only species absorbed by roots and which forms complex (ML) in the soil solution with an unique ligand (L), following the reaction:

The ligand was assumed to be representative of the dissolved endogenous soil organic matter, the concentration of which is at steady-state in the bulk soil. Therefore, no production/degradation equations were considered. Root exudation was also not accounted for. This complexation can be described by the following kinetics equations (Degryse et al. 2006; Schneider 2008; Schneider and Nguyen 2011):

$$\left\{ \begin{array}{l} \frac{dC_M}{dt} = k_d C_{ML} - k_a^{\text{cond}} C_M C_L \\ \frac{dC_L}{dt} = k_d C_{ML} - k_a^{\text{cond}} C_M C_L \\ \frac{dC_{ML}}{dt} = k_a^{\text{cond}} C_M C_L - k_d C_{ML} \end{array} \right\} \quad (4)$$

In Eq. (4), C_M , C_L , and C_{ML} are the concentrations ($\mu\text{mol cm}^{-3}$ solution) of Cd^{2+} , ligand, and Cd complex in the soil solution, respectively, k_a^{cond} is the second-order conditional association rate constant (cm^3 solution $\mu\text{mol}^{-1} \text{s}^{-1}$), k_d is the

first-order dissociation rate constant (s^{-1}). Completing Barber's model (Eq. 1) to account for the kinetics of complexation of Cd^{2+} with ligands in

the soil solution (Eq. 4) and for the kinetics of sorption of the three species gives the following set of equations:

$$\begin{aligned}
 \theta \frac{\partial C_M}{\partial t} &= \frac{1}{r} \frac{\partial}{\partial r} \left(rf \theta D_M \frac{\partial C_M}{\partial r} + r_0 v_0 C_M \right) + \theta (k_d C_{ML} - k_a^{\text{cond}} C_M C_L) + (k_{\text{des}}^M S_M - \theta k_{\text{ads}}^M C_M) \\
 \theta \frac{\partial C_L}{\partial t} &= \frac{1}{r} \frac{\partial}{\partial r} \left(rf \theta D_L \frac{\partial C_L}{\partial r} + r_0 v_0 C_L \right) + \theta (k_d C_{ML} - k_a^{\text{cond}} C_M C_L) + (k_{\text{des}}^L S_L - \theta k_{\text{ads}}^L C_L) \\
 \theta \frac{\partial C_{ML}}{\partial t} &= \frac{1}{r} \frac{\partial}{\partial r} \left(rf \theta D_{ML} \frac{\partial C_{ML}}{\partial r} + r_0 v_0 C_{ML} \right) + \theta (k_a^{\text{cond}} C_M C_L - k_d C_{ML}) + (k_{\text{des}}^{ML} S_{ML} - \theta k_{\text{ads}}^{ML} C_{ML}) \\
 \frac{dS_M}{dt} &= \theta k_{\text{ads}}^M C_M - k_{\text{des}}^M S_M \\
 \frac{dS_L}{dt} &= \theta k_{\text{ads}}^L C_L - k_{\text{des}}^L S_L \\
 \frac{dS_{ML}}{dt} &= \theta k_{\text{ads}}^{ML} C_{ML} - k_{\text{des}}^{ML} S_{ML}
 \end{aligned} \quad (5)$$

In Eq. (5), D_L and D_{ML} are the diffusion coefficients of the ligand and the Cd complex in water ($\text{cm}^2 \text{s}^{-1}$), respectively, k_{ads}^L and k_{ads}^{ML} are the rate constants of adsorption from liquid phase onto solid phase for the ligand and the Cd complex (s^{-1}), respectively, k_{des}^L and k_{des}^{ML} are the rate constants of desorption from solid phase to liquid phase for the ligand and the Cd complex (s^{-1}), S_L and S_{ML} are the concentration of the ligand and the Cd complex sorbed onto solid phase ($\mu\text{mol cm}^{-3}$ soil), respectively. At the root surface, only Cd^{2+} is absorbed following Michaelis-Menten kinetics (Chen et al. 2008; Panfili et al. 2009) and so, the boundary fluxes are:

$$\left\{ \begin{array}{l} J_M = -\frac{I_{\text{max}} C_M}{K_m + C_M} \\ J_L = 0 \\ J_{ML} = 0 \end{array} \right\} \quad r = r_0 \quad t \geq 0 \quad (6)$$

At the outer boundary of the domain, i.e., at the half distance between two root segments ($r=r_1$), the fluxes for Cd^{2+} , L and CdL are all set null. This enables representing the possible between-root competition for the uptake of Cd^{2+} .

$$\left\{ \begin{array}{l} J_M = 0 \\ J_L = 0 \\ J_{ML} = 0 \end{array} \right\} \quad r = r_1 \quad t \geq 0 \quad (7)$$

And the initial conditions are:

$$\left\{ \begin{array}{l} C_M = C_{M0} \\ C_L = C_{L0} \\ C_{ML} = C_{ML0} \\ S_M = S_{M0} \\ S_L = S_{L0} \\ S_{ML} = S_{ML0} \end{array} \right\} \quad r_0 \leq r \leq r_1 \quad t = 0 \quad (8)$$

In Eq. (8), C_{M0} , C_{L0} , and C_{ML0} are the initial concentrations of the free Cd^{2+} , ligand, and complex in the soil solution ($\mu\text{mol cm}^{-3}$ solution); S_{M0} , S_{L0} , and S_{ML0} are the initial concentrations of the sorbed Cd^{2+} , ligand, and complex in soil ($\mu\text{mol cm}^{-3}$ soil). Then, the cumulative uptake of Cd^{2+} per unit root segment (U_{cum} , $\mu\text{mol cm}^{-2}$) for the duration T (s) is given by:

$$U_{\text{cum}} = \int_0^T \frac{I_{\text{max}} C_M}{K_m + C_M} dt \quad r = r_0 \quad (9)$$

The effects of the different parameters on the phytoavailability of the metal in non-polluted agricultural soils were assessed by simulating the uptake of Cd^{2+} by 1 cm^2 root for 30 days.

Model parameters domain for non-polluted agricultural soils

The initial concentrations of the free Cd^{2+} and of the complex as well as their buffer powers are not

commonly determined in the literature and therefore, little data are available to help determining their relevant ranges of variations, which were therefore derived from parameters more commonly measured in the field.

Actual values of total Cd content (HF extraction; TM_0), pH , and soil organic carbon (SOC) for French agricultural soils were derived from available national databases: RMQS (RMQS © 2013), BDETM (BDETM © 2013), and ASPITET (Baize et al. 2007). Extreme cases where $TM_0 > 2 \text{ mg kg}^{-1}$ or $SOC > 8 \text{ g } 100 \text{ g}^{-1}$ soil were discarded (less than 1 % of the data). The resulting dataset had 8707 unique triplets (TM_0 , pH , SOC). The correlation coefficients between pH and TM_0 , and between SOC and TM_0 , are 0.30 and 0.39, respectively.

We assumed that the kinetics of sorption for Cd^{2+} , for the ligand and complex, and of complexation between Cd^{2+} and the ligand were at equilibrium at the beginning of simulations. The soil/solution partitioning coefficient for total Cd (K_d^{TOT} , $\text{cm}^3 \text{ solution g}^{-1} \text{ soil}$) was determined using the following statistical model (Degryse et al. 2009):

$$\log_{10}(K_d^{\text{TOT}}) = -1.04 + 0.55pH + 0.70\log_{10}(SOC) \quad (10)$$

Then the initial concentration of total Cd in the soil solution (C_M^{TOTO} , $\mu\text{mol cm}^{-3} \text{ solution}$) was calculated as follows:

$$C_M^{\text{TOTO}} = \frac{TM_0}{m_{\text{Cd}} K_d^{\text{TOT}}} \quad (11)$$

Where, m_{Cd} is the atomic weight of Cd ($112.411 \text{ g mol}^{-1}$).

In order to calculate the speciation of Cd in the soil solution, we assumed that Cd was complexed by the humic acids (HA) and fulvic acids (FA) of the dissolved organic carbon (DOC) with H and Ca being the competitor cations. The proportion of HA in DOC (p_{CHA}) was considered to depend on soil pH. Data from You et al. (1999) were used to fit an empirical logistic model for the p_{CHA} as a function of soil pH with 1 as a maximum:

$$p_{\text{CHA}} = \frac{1}{1 + 9984e^{-1.26pH}} \quad (12)$$

Based on Haynes (2005), the DOC concentration measured in the 2:1 (V:W; L kg^{-1}) soil extraction, i.e., $DOC_{2:1}$, can be assumed to be a fraction of the total soil

organic carbon. Then, the concentration of $DOC_{2:1}$ ($\text{mg C L}^{-1} \text{ solution}$) is calculated as:

$$DOC_{2:1} (\text{mg L}^{-1}) = 1000 \times \frac{SOC(\%)}{100} \times \frac{F_{\text{DOC/SOC}}}{100} \times 1000 \times \frac{1}{2} \quad (13)$$

Where, $F_{\text{DOC/SOC}}$ is the DOC:SOC ratio ($\text{g DOC } 100 \text{ g}^{-1} \text{ SOC}$) ranging from 0.05 to 0.4 $\text{g DOC } 100 \text{ g}^{-1} \text{ SOC}$ (Haynes 2005). Considering a linear sorption, the partitioning coefficient of DOC (K_d^{L}) is given by (Ponizovsky et al. 2006):

$$\begin{aligned} K_d^{\text{L}} (\text{L solution kg}^{-1} \text{ soil}) &= \frac{SOC_{2:1}^{\text{SF}} (\text{g C kg}^{-1} \text{ soil})}{DOC_{2:1} (\text{g C L}^{-1} \text{ solution})} \\ &= \frac{SOC^{\text{SF}} (\text{g C kg}^{-1} \text{ soil})}{DOC (\text{g C L}^{-1} \text{ solution})} \end{aligned} \quad (14)$$

In Eq. (14), $SOC_{2:1}^{\text{SF}}$ is the concentration of soluble fraction of SOC sorbed onto the solid phase at equilibrium with the solution at the 2:1 liter:kilogram ratio, SOC^{SF} is the concentration of soluble fraction of SOC sorbed onto the solid phase at natural soil moisture condition. Considering mass conservation, the partitioning coefficient of DOC was used to calculate the DOC concentration at the soil water content:

$$K_d^{\text{L}} DOC - K_d^{\text{L}} DOC_{2:1} = DOC_{2:1} \times 2 - DOC \frac{\theta}{\rho} \quad (15)$$

Rewriting the above equation we obtain:

$$DOC (\text{mg L}^{-1}) = DOC_{2:1} \frac{K_d^{\text{L}} + 2}{K_d^{\text{L}} + \frac{\theta}{\rho}} \quad (16)$$

In Eqs. (15–16), ρ is the soil density (g cm^{-3}), which ranged between 1.3 and 1.7 g cm^{-3} (Bruand et al. 2004). The soil volumetric water content θ was allowed to vary between 0.05 and 0.45 $\text{cm}^3 \text{ water cm}^{-3} \text{ soil}$. Considering the different textures of the French agricultural soils, this corresponds to the wilting point and to the water holding capacity, respectively (Bruand et al. 2004).

The speciation calculations were done with Cheaqs Pro (Release P2013.2; <http://www.cheaqs.eu/>) with C_M^{TOTO} , pH , Ca concentration, DOC, p_{CHA} as input parameters. The Ca^{2+} concentration ranged from 0.1 to

10 mM and the charges of Ca^{2+} were equilibrated with NO_3^- . In Cheaqs Pro, organic complexation is calculated by using WHAM VII (Tipping et al. 2011). The WHAM model implemented in Cheaqs Pro considers that a cation is associated to FA or HA by specific associations (with a stability constant corresponding to site affinity) to form mono, bi and tri dentate complexes, and by nonspecific associations (double diffusion layer DDL).

$$C_{\text{ML}0} = \left[\frac{(CdFA_{\text{mono}} + CdFA_{\text{bi}} + CdFA_{\text{tri}} + CdFADDL) + (CdHA_{\text{mono}} + CdHA_{\text{bi}} + CdHA_{\text{tri}} + CdHADDL)}{(CdFA_{\text{mono}} + CdFA_{\text{bi}} + CdFA_{\text{tri}} + CdFADDL) + (CdHA_{\text{mono}} + CdHA_{\text{bi}} + CdHA_{\text{tri}} + CdHADDL)} \right] \times 1000 \quad (17)$$

In Eq. (17), $CdFA$ and $CdHA$ corresponds to mono, bi and tri dentates Cd complexes with FA and HA, respectively (mol L^{-1}).

From the output of Cheaqs Pro, the site densities of FA and HA are 6.01 mmol g^{-1} FA and 3.60 mmol g^{-1} HA, respectively. Then total ligand concentration can be calculated as follows:

$$C_L^{\text{TOT0}} = [6.01 \times 10^{-3}(1-p_{\text{CHA}}) + 3.60 \times 10^{-3}p_{\text{CHA}}] \text{DOC} \times 1000 \quad (18)$$

And the initial concentrations of free ligand and Cd in soil solution can be calculated as follows:

$$C_{\text{L}0} = C_L^{\text{TOT0}} - C_{\text{ML}0} \quad (19)$$

$$C_{\text{M}0} = C_M^{\text{TOT0}} - C_{\text{ML}0} \quad (20)$$

With the assumption that the complexation kinetics is at equilibrium at the beginning of simulation, the second-order conditional association rate constant k_a^{cond} is given by the following formula:

$$k_a^{\text{cond}} = \frac{C_{\text{ML}0}k_d}{C_{\text{M}0}C_{\text{L}0}} = \frac{(1-F_{\text{M}0})k_d}{F_{\text{M}0}C_{\text{L}0}} \quad (21)$$

In Eq. (21), $F_{\text{M}0}$ is the initial free Cd^{2+} ion fraction in the soil solution. The range of the first-order dissociation rate constant for the complex (k_d) was set as 10^{-6} to 10^{-2} s^{-1} (Degryse et al. 2006; Schneider and Nguyen 2011).

The soil/solution partitioning coefficient of the total Cd (K_d^{TOT}) can be rewritten from the soil/solution partitioning coefficient of Cd^{2+} (K_d^{M} , $\text{cm}^3 \text{ solution g}^{-1}$ soil) and of CdL (K_d^{ML} , $\text{cm}^3 \text{ solution g}^{-1}$ soil) as:

$$\begin{aligned} K_d^{\text{TOT}} &= \frac{K_d^{\text{M}}C_{\text{M}0} + K_d^{\text{ML}}C_{\text{ML}0}}{C_M^{\text{TOT0}}} \\ &= F_{\text{M}0}K_d^{\text{M}} + (1-F_{\text{M}0})K_d^{\text{ML}} \end{aligned} \quad (22)$$

Then the soil/solution partitioning coefficient of Cd^{2+} (K_d^{M}) can be derived as follows:

$$K_d^{\text{M}} = \frac{K_d^{\text{TOT}} - (1-F_{\text{M}0})K_d^{\text{ML}}}{F_{\text{M}0}} \quad (23)$$

The range of K_d^{L} ($1\text{--}50 \text{ cm}^3 \text{ solution g}^{-1}$ soil) was derived from values reported in the literature for the soil/solution partitioning coefficients of the soil organic matter (Ponizovsky et al. 2006; Yin et al. 2002; You et al. 1999). We assumed that the soil/solution partitioning coefficients of the ligand and the complex were the same in the model ($K_d^{\text{ML}} = K_d^{\text{L}}$).

Then the soil buffer powers for Cd^{2+} , for the ligand and the complex were calculated as follows (Barber 1995):

$$\begin{cases} b_{\text{M}} = \rho K_d^{\text{M}} \\ b_{\text{L}} = \rho K_d^{\text{L}} \\ b_{\text{ML}} = b_{\text{L}} \end{cases} \quad (24)$$

For the desorption rate constant of Cd^{2+} ($k_{\text{des}}^{\text{M}}$), we defined the range of variation from literature values (Chaturvedi et al. 2006; Chen et al. 2006; Cornu et al. 2007; Ernstberger et al. 2002; Tsang et al. 2007); 10^{-6} to $5.5 \times 10^{-4} \text{ s}^{-1}$. This range was also chosen for the desorption rate constant of the ligand and of the complex ($k_{\text{des}}^{\text{L}} = k_{\text{des}}^{\text{ML}}$).

Then, the adsorption rate constants for Cd^{2+} , for the ligand and the complex can be calculated by:

$$\begin{cases} k_{\text{ads}}^{\text{M}} = \frac{b_{\text{M}}k_{\text{des}}^{\text{M}}}{\theta} \\ k_{\text{ads}}^{\text{L}} = \frac{b_{\text{L}}k_{\text{des}}^{\text{L}}}{\theta} \\ k_{\text{ads}}^{\text{ML}} = k_{\text{ads}}^{\text{L}} \end{cases} \quad (25)$$

The diffusion coefficient of Cd^{2+} in water, D_{M} was fixed at $7.07 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Lide 2004). We assumed that the diffusion coefficient of the complex in water was equal to that of the free ligand D_{L} but lower or equal to that of Cd^{2+} (D_{M}); then, $D_{\text{ML}} = D_{\text{L}}$ ranged between 10^{-8} and $7.07 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Pinheiro et al. 1994).

For the plant parameters, the I_{max} and K_{m} ranges were derived from different studies reviewed by Lux et al. (2011) for agricultural crops including wheat, maize, soybean. Cadmium hyperaccumulators were not

Table 1 Parameter domain of the Cd phytoavailability model in non-polluted agricultural soils

Parameters	Descriptions	Min	Max	$\log_{10}(\text{Min})^\dagger$	$\log_{10}(\text{Max})^\dagger$	Units
$D_M^\ddagger$	diffusion coefficient of Cd^{2+} in water	7.07×10^{-6}				$\text{cm}^2 \text{s}^{-1}$
$T^\ddagger$	uptake duration	2592000				s
$TM_0^{\dagger\dagger}$	initial content of total Cd in soil	0.01	2			$\mu\text{g g}^{-1}$
$pH^{\dagger\dagger}$	soil pH value	4.4	9.14			
$SOC^{\dagger\dagger}$	soil organic carbon content	0.0017	7.9			$\text{g } 100 \text{ g}^{-1}$
Ca	calcium concentration in solution	0.1	10	-1	1	$\mu\text{mol cm}^{-3}$
$F_{\text{DOC}/\text{SOC}}$	dissolved organic carbon fraction	0.05	0.4			$\text{g } 100 \text{ g}^{-1}$
θ	soil volumetric water content	0.05	0.45			$\text{cm}^3 \text{cm}^{-3}$
f	soil impedance factor	0.01	0.55			$\text{cm}^2 \text{cm}^{-2}$
D_L	diffusion coefficient of ligand in water	10^{-8}	7.07×10^{-6}	-8	-5.151	$\text{cm}^2 \text{s}^{-1}$
ρ	soil bulk density	1.3	1.7			g cm^{-3}
K_d^L	soil/solution partitioning coefficient of ligand	1	50			$\text{cm}^3 \text{g}^{-1}$
k_{des}^M	desorption rate constant of Cd^{2+}	10^{-6}	5.5×10^{-4}	-6	-3.260	s^{-1}
k_{des}^L	desorption rate constant of ligand	10^{-6}	5.5×10^{-4}	-6	-3.260	s^{-1}
k_d	dissociation rate constant of complex in solution	10^{-6}	10^{-2}	-6	-2	s^{-1}
I_{max}	maximum absorption rate of Cd^{2+} by plant root	10^{-8}	10^{-6}	-8	-6	$\mu\text{mol cm}^{-2} \text{s}^{-1}$
K_m	affinity coefficient	10^{-6}	10^{-3}	-6	-3	$\mu\text{mol cm}^{-3}$
v_0	water velocity at root surface	10^{-9}	5×10^{-6}	-9	-5.301	cm s^{-1}
r_0	plant root radius	0.005	0.05			cm
r_1	half distance between plant roots	0.1	1			cm

† Maximum and minimum values were applied in $\log_{10}$ -transformed form

‡ D_M and T were constants in the model

†† TM_0 , pH , SOC were actual values from public data bases

considered. The ranges for the water flux at the root surface v_0 and for the root radius r_0 were also derived from values summarized in the literature for crop species (Adhikari and Rattan 2000; Barber 1995; Williams and Yanai 1996). Finally, the half distance between two root axes (r_1) was calculated from the root length density range for agriculture crops $R_d=0.3$ to $20 \text{ cm root cm}^{-3}$ soil (Metselaar and De Jong van Lier 2011; Williams and Yanai 1996) following the formula:

$$r_1 = \frac{1}{\sqrt{\pi R_d}} \quad (26)$$

The impedance factor f was chosen in the range of 0.01 to 0.55, with boundary limitations linked to θ based on data from (Chou et al. 2012; Tinker and Nye 2000):

$$0.009 + 0.059\theta + 1.039\theta^2 \leq f \leq 0.038 + 1.023\theta + 0.237\theta^2 \quad (27)$$

All parameter ranges are summarized in Table 1. The ranges for the parameters were chosen to be representative of the uncontaminated French agricultural soils.

The design of virtual experiments and data processing

In total, there were 18 parameters allowed to vary as summarized in Table 1. Three of them (TM_0 , pH , SOC) were directly derived from actual values of the data-bases. The remaining 15 were sampled using quasi-random sampling with low discrepancy sequences from a uniform distribution (Saltelli et al. 2004). The parameters whose ranges covered more than two orders of magnitude were sampled within the $\log_{10}$ -transformation of their ranges to ensure an uniform distribution of the sampling values over different orders of magnitude. In order to guarantee that the simulated situations were realistic, we discarded all the combinations of parameter values that did not fulfill the following constraint.

$$5 \leq K_d^M \leq 10^6 \text{ cm}^3 \text{ solution g}^{-1} \text{ soil} \quad (28)$$

To analyze the contribution of the complex to uptake and the kinetics limitation of sorption and complexation, four models were ran for each combination of

parameters: the full model (Eqs. 5–8) and the no-complex model (Eqs. 1–2), both of them with kinetics (the kinetics constants for sorption and complexation were allowed to vary within their ranges (Table 1)), or at equilibrium by setting the kinetics constants $k_{\text{des}}^{\text{M}}$, $k_{\text{des}}^{\text{L}}$, and $k_{\text{des}}^{\text{ML}}$ all at 1000 s^{-1} , and k_{d} at 10^5 s^{-1} , respectively. These values were determined from preliminary tests aiming at having equilibrium indices equal to 1 (see below).

Some derived variables were calculated to help understanding the outputs of phytoavailability models. The relative importance of convection and diffusion fluxes of Cd^{2+} at the root surface was assessed by calculating the dimensionless Péclet number (Roose et al. 2001):

$$Pe = \frac{v_0 r_0}{f \theta D_M} \quad (29)$$

If Pe is lower than 1, then the convection is less important compared with the diffusion of Cd^{2+} in soil.

The mean equilibrium index for the sorption kinetics of Cd^{2+} at root surface for the absorption duration (E_{CdS}) is calculated as follows:

$$E_{\text{CdS}} = \frac{\int_0^T \left(\frac{C_{\text{MS}}}{C_{\text{M}}} \right) dt}{T \frac{\theta k_{\text{ads}}^{\text{M}}}{k_{\text{des}}^{\text{M}}}} \quad r = r_0 \quad (30)$$

If E_{CdS} is equal to 1, then the exchange of Cd^{2+} between solid phase and solution is not limited by the sorption kinetics.

The mean equilibrium index for the complexation kinetics at the root surface for the absorption duration (E_{CdL}) is calculated as follows:

$$E_{\text{CdL}} = \frac{\int_0^T \left(\frac{C_{\text{ML}}}{C_{\text{M}} C_{\text{L}}} \right) dt}{T \frac{k_{\text{a}}^{\text{cond}}}{k_{\text{d}}}} \quad r = r_0 \quad (31)$$

If E_{CdL} is equal to 1, then the complexation kinetics is always at equilibrium at the root surface during the uptake, and C_{ML} is coupled with C_{M} and C_{L} for the diffusion.

The mean net volumic rate of Cd^{2+} desorption at the root surface (v_{des} , $\mu\text{mol cm}^{-3} \text{ soil s}^{-1}$) is calculated as follows:

$$v_{\text{des}} = \frac{\int_0^T (k_{\text{des}}^{\text{M}} C_{\text{MS}} - \theta k_{\text{ads}}^{\text{M}} C_{\text{M}}) dt}{T} \quad r = r_0 \quad (32)$$

The mean net volumic rate of CdL dissociation at the root surface (v_{dis} , $\mu\text{mol cm}^{-3} \text{ soil s}^{-1}$) is calculated as follows:

$$v_{\text{dis}} = \frac{\int_0^T \theta (k_{\text{d}} C_{\text{ML}} - k_{\text{a}}^{\text{cond}} C_{\text{M}} C_{\text{L}}) dt}{T} \quad r = r_0 \quad (33)$$

The contribution of complex to the uptake (ϕ , %) was calculated by the relative difference in the uptake between the full model (U_{cum} , $\mu\text{mol cm}^{-2}$) and the no-complex model ($U_{\text{cum_no_complex}}$, $\mu\text{mol cm}^{-2}$):

$$\phi = \frac{U_{\text{cum}} - U_{\text{cum_no_complex}}}{U_{\text{cum}}} \times 100 \quad (34)$$

The phytoavailability models were numerically solved by using FlexPDE Professional 6.32 (PDE Solutions Inc. 2012). The 8707 triplets (total soil Cd, pH, and SOC) were replicated 12 times in combination with different values for the other parameters to reach a total of 104 484 cases to be simulated. About 4.6 % simulations were discarded due to non-convergence of the solution, and about 0.55 % simulations were discarded due to negative contribution of the complex dissociation to the Cd uptake; the negative contribution were attributed to numerical errors because they should have not occurred as the initial Cd^{2+} concentration was the same for the models with and without complexation. The final number of simulations of the phytoavailability model was 99 087. Data processing and analyses were performed with R (R Core Team 2013).

Results

Ranking of the model input parameters

The ranking of the parameters are presented by Fig. 1 as standardized regression coefficients (Gan et al. 2014). By construction, some input parameters are correlated (Table S1 in Supplementary materials). For example, the initial Cd^{2+} concentration ($C_{\text{M}0}$) is correlated with the initial Cd complex concentration ($C_{\text{ML}0}$), the Cd^{2+} soil/solution partitioning coefficient (K_{d}^{M}), and the association rate constant for complex ($k_{\text{a}}^{\text{cond}}$); the soil volumetric water content (θ) and the soil impedance factor (f)

Fig. 1 Rankings of model parameters (**a**) and primary parameters (**b**) based on their standardized coefficients for the $\log_{10}$ -cumulative Cd uptake multiple regression. In the Fig. 1a, C_{M0} is the initial concentration of Cd^{2+} in solution, K_d^M the soil/solution partitioning coefficient of Cd^{2+} , θ the soil water content, f the soil impedance factor, K_m the affinity coefficient, I_{max} the maximum absorption rate of Cd^{2+} by plant root, r_0 the root radius, k_{ads}^L and k_{des}^L the adsorption and desorption rate constants of ligand, respectively, v_0 the water velocity at the root surface, C_{MLO} the initial concentration of CdL in the soil solution, k_d and k_a^{cond} the dissociation and

conditional association rate constants of CdL in solution, respectively, D_L the diffusion coefficient of the ligand in water, k_{des}^M the desorption rate constant of Cd^{2+} , and r_1 the half root distance between roots. In the Fig. 1b, pH is the soil pH value, TM_0 the initial content of total Cd in soil, SOC the soil organic carbon content, Ca the calcium concentration in the soil solution, $F_{\text{DOC/SOC}}$ the fraction of dissolved organic carbon to soil organic carbon, K_d^L the soil/solution partitioning coefficient of the ligand, and ρ the soil bulk density

are also correlated (see **Materials and methods**). Only parameters which cannot be derived by the others are presented in the figure. Figure 1a shows the ranking of the model parameters (Eqs. 5–8) and Fig. 1b is similar but it shows the primary parameters used to derive some of the model parameters. The model parameters allowed to better understand the relative importance of the different mechanisms while the ranking of the primary parameters was more adapted to traditional field measurements.

The most influential model parameters in Fig. 1a were C_{M0} , K_d^M , θ and f . Altogether, these parameters govern the diffusion flux of Cd^{2+} toward the root surface. The most influential primary parameters in Fig. 1b were the soil pH, the total Cd content (TM_0), the soil organic carbon content (SOC), the calcium concentration in the soil solution (Ca), and the dissolved organic carbon ($F_{\text{DOC/SOC}}$). These parameters governed the initial concentration of Cd^{2+} in the soil solution and its sorption onto the solid phase (see **Materials and methods**). As shown by Fig. S1 in the Supplementary materials, high initial concentrations of soluble Cd^{2+} corresponded to low pH, which favored the solubility of Cd, to low $F_{\text{DOC/SOC}}$, which disfavored the DOC and consequently

the formation of CdL (the latter being also disfavored by low pH (Sauvé et al. 2000b)), to high Ca concentrations (competition with Cd for complexation) and to low percentages of DOC as humic acids (pC_{HA} , Eq. 12).

After this first group of parameters related to the diffusion of Cd^{2+} in soil, the most influential parameters were the root capacity for absorbing Cd^{2+} (I_{max} and K_m) and the root radius (r_0) (Fig. 1a). The root radius also influences the diffusion fluxes towards the root by geometry considerations. These plant parameters were much less influential than the diffusion of Cd^{2+} meaning that for most of the situations studied here, the uptake was limited by the availability of Cd^{2+} and not by the root absorption capacity. The least influential parameters were related to the diffusion of CdL and of L (k_{ads}^L , k_{des}^L , K_d^L , D_L), the water flux (v_0), the kinetics rate constants for CdL (k_a^{cond} , k_d), the desorption rate constants for Cd^{2+} (k_{des}^M), and the between-roots competition (r_1).

Free Cd^{2+} concentration and Cd^{2+} convection at the root surface

The speciation calculations indicated that the initial concentration of Cd^{2+} (C_{M0}) ranged between $1.1 \times$

10^{-10} and $9.4 \times 10^{-4} \mu\text{mol cm}^{-3}$ with a median value of $2.7 \times 10^{-7} \mu\text{mol cm}^{-3}$ (0.27 nM). This corresponded to a free Cd^{2+} ion fraction (F_{M0}) between 8.4×10^{-5} and 1.0 with a median value of 0.12 (12 % of the total soluble Cd). This illustrated that most of the soluble Cd was complexed with the dissolved organic matter. The statistics for other derived parameters are presented in Table S2 in the Supplementary materials.

Figure 2 shows the Cd^{2+} concentration at the root surface averaged for the duration of the simulated uptake and expressed as a percentage of the initial concentration. Cd^{2+} was strongly depleted at the root surface since the average Cd^{2+} concentration had a median of 1.4 % and for 68 % of the simulations, it was less than 5 % of the initial concentration. This important depletion, which can be assimilated to a zero sink approximation, was not correlated with the magnitude of the uptake. It was characterized by a relatively high root absorption capacity (high I_{max} and low K_{m}), and to a lower extend by a low soil water content and a low soil/solution partitioning for Cd^{2+} (K_{d}^{M}) (Fig. S2 in the Supplementary materials). Except this, the zero sink approximation was not depending on the range of other input parameters.

There were no situations where Cd^{2+} accumulated at the root surface (Fig. 2). The highest mean Cd^{2+} concentrations at the root surface (above 0.95 quantile) ranged between 56 and 98 % of the initial concentration and generally corresponded to low uptakes. For these situations (Fig. S3 in the Supplementary materials), the root uptake capacity was low (low I_{max} and high K_{m}), the potential buffering of Cd^{2+} by both the solid phase and the complex dissociation was high: high K_{d}^{M} , and high stability constant for CdL ($K_{\text{S}}^{\text{cond}}$). Additionally, the conditions for diffusion were favorable (high θ and f) but the water flux was not particularly higher than for the general cases (Fig. S3).

The distribution of the Péclet number (Eq. 29) is presented by Fig. 3. The values ranged from 4×10^{-6} to 22.7 with a median of 6.2×10^{-3} . For 56 % of the simulations, the Péclet number values corresponded to diffusion being 100 times convections. These results indicate that regarding the supply of Cd^{2+} to the root surface, the convection was negligible compared to diffusion for most of the cases studied (Fig. S4 in the Supplementary materials). When the convection was significant, the situations corresponded to a low root uptake capacity (I_{max} , K_{m}) and a high water flux (v_0) (Fig. S5 in the Supplementary materials).

Cd^{2+} desorption and Cd complex dissociation at root surface

The mean equilibrium indices for the sorption and complexation kinetics at the root surface, i.e., E_{CdS} and E_{CdL} (Eqs. 30 and 31) are shown in Fig. 4. The minimum values of E_{CdS} and E_{CdL} were 1.00003 and 1.00508, respectively. Equilibrium indices greater than one mean that compared to equilibrium conditions, the concentrations of the sorbed or complexed Cd^{2+} were relatively too high compared to that of free Cd^{2+} at root surface. The figure shows that the departure from equilibrium was more marked for complexation than for sorption (Fig. 4). For the sorption kinetics, there were only 20.4 % simulations where $E_{\text{CdS}} > 10$; while for the complexation kinetics, there were 72.5 % simulations which showed strong departure from equilibrium ($E_{\text{CdL}} > 10$). Desorption kinetics was close to equilibrium ($E_{\text{CdS}} < 1.05$) for around 29 % simulations while for the complex kinetics, approximate equilibrium ($E_{\text{CdL}} < 1.05$) was observed for only 0.3 % of the simulations.

For sorption, disequilibrium corresponded to cases of a relatively high root uptake capacity, a relatively low soil diffusivity (low f and θ) and to both a low K_{d}^{M} and a low kinetics of sorption (low $k_{\text{ads}}^{\text{M}}$ and $k_{\text{des}}^{\text{M}}$) (Fig. S6 in the supplementary materials). Hence, when the root absorption was high, the buffering of Cd^{2+} at the root surface by the rate of Cd^{2+} desorption from the soil matrix was too low. The reason for that was the low desorption rate constants because to reach equilibrium, $k_{\text{des}}^{\text{M}}$ had to be increased to 1000 s^{-1} (not shown).

For complexation, disequilibrium cases also corresponded to situations where the soil supply of Cd^{2+} was limiting the uptake (compared to plant absorption capacities), i.e., a high root capacity for Cd^{2+} uptake and to a lesser extend to a low CdL dissociation rate constant and a low soil water content (θ) (Fig. S7 in the supplementary materials). Apart these parameters, the others were little or not discriminant. The departure from equilibrium arose from the difficulty of maintaining Cd^{2+} concentration at equilibrium with CdL while root absorbs Cd^{2+} . CdL dissociation was therefore limiting but this was not due to a limitation in CdL availability since its concentration at the root surface was on average the initial one (median of 100.4 % of the initial concentration, not shown). Consequently, the limitation of CdL dissociation comes from the low values of k_{d} . The virtual values of k_{d} necessary to maintain equilibrium for complexation were very high since, to reach

Fig. 2 Cd cumulative uptake ($\mu\text{mol cm}^{-2}$) against Cd^{2+} depletion at the root surface expressed as a percentage of the initial concentration (%)

equilibrium, k_d values of 10^5 s^{-1} were necessary (not shown). This explains why within the range tested (max 10^{-2} s^{-1}), k_d was little discriminant of the departure from equilibrium for CdL dissociation (Fig. S7).

The departure from equilibrium for the sorption and complexation kinetics had a significant effect on the

uptake (Fig. 5), which was increased by 21 % (median value) if equilibrium was forced by setting kinetics rate constants at very high values. The influence of kinetics was weak for very low and very high uptakes. Fig. S8 (Supplementary materials) shows the uptake simulated by the no-complex model with and without kinetic for

Fig. 3 Kernel density functions of the Péclet number illustrating the relative importance between convection and diffusion

Fig. 4 Kernel density functions of mean equilibrium indices for complexation (comp.) and for sorption (sorp.) kinetics at root surface. The statistics of the two indices are given in the inset

sorption. It can be seen that considering or not the sorption kinetics gave very similar simulated uptake. This shows that when there is no complex, the sorption kinetics is of little importance.

Figure 6 (x axis) shows the mean net volumic rates of Cd^{2+} desorption (v_{des} ; Eq. 32) against CdL dissociation

Fig. 5 Cd cumulative uptake with sorption and complexation kinetics at equilibrium ($\mu\text{mol cm}^{-2}$) against Cd cumulative uptake with sorption and complexation kinetics ($\mu\text{mol cm}^{-2}$)

Fig. 6 Contribution of CdL to the uptake (%) against the ratio between the mean net volumic rates ($\mu\text{mol cm}^{-3} \text{ soil s}^{-1}$) of CdL dissociation (dissoc.) and of Cd^{2+} desorption (desorp.) at root surface

(v_{dis} ; Eq. 33) at the root surface during the root absorption. The two mean net volumic rates were always both positive (not shown), which was consistent with the fact that the two equilibrium indices (E_{CdL} and E_{CdS}) were always greater than one. For 78.9 % simulations, values of v_{des} were greater than those of v_{dis} .

Contribution of Cd complex to uptake and the free Cd^{2+} model approximation

The contribution of complex to Cd^{2+} uptake (Eq. 34) is presented in Fig. 6 (y axis). In the no complex model (Eqs. 1–2), the Cd^{2+} desorption is virtually enhanced compared to the desorption in the full model (Eqs. 5–8) because it partially compensated the lack of buffering by the complex formalized in the full model. Therefore, the complex contribution estimated by our calculations might be underestimated.

The contribution of CdL ranged from 0 to 96 % (with CdL/without CdL=25) with a median of 1.6 % and a third quartile of 7.0 %. For 69.5 % of the simulations, CdL contribution was less than 5 % of the uptake (with CdL/without CdL=1.05). The contribution of CdL did not show any relationship with the uptake nor with the dissociation or with the desorption rates (not shown). However, the relative importance of the volumic dissociation and desorption rates ($v_{\text{dis}}, v_{\text{des}}$) strongly correlated with the contribution of CdL to the uptake (Fig. 6). When the volumic rate of CdL dissociation was lower

Fig. 7 Kernel density functions of influential parameters for all simulations (solid lines) and simulations where contribution of CdL to the uptake was greater than 10 % of the uptake (grey areas). In the figure, C_{ML0} is the initial concentration of CdL in the soil solution, k_a^{cond} and k_d the conditional association and the dissociation rate constants of CdL in the soil solution, k_{des}^M the desorption

rate constant of Cd^{2+} , I_{max} the maximum absorption rate of Cd^{2+} by plant roots, K_m the affinity coefficient, v_0 the water velocity at the root surface, r_0 the root radius, D_L the diffusion coefficient of the ligand in water, K_d^M the soil/solution partitioning coefficient of Cd^{2+} , and K_S^{cond} the conditional stability constant of CdL ($=k_a^{\text{cond}}/k_d$)

than the volumic rate of Cd^{2+} desorption, the contribution of CdL to the uptake had a median of 0.7 % and a 95 percentile of 9.3 %. When the rate of CdL dissociation was greater than the rate of Cd^{2+} desorption, the complex contribution had a median of 17.7 % and a 95 percentile of 55.3 %. Hence, not surprisingly, CdL contribution was low when CdL dissociation was dominated by desorption rates and conversely.

The highest values of CdL contribution to the uptake (>10 %) were characterized by a high lability of the complex (high k_a^{cond} and k_d) (Fig. 7). The stability constant K_S^{cond} and therefore the initial concentration of CdL (C_{ML0}) were also greater than the average. The flux of water towards the root was also clearly more important as it transport CdL towards the root. The moderate low the diffusivity of the soil (f and θ) suggests that the diffusion of Cd^{2+} was limited compared to the higher root uptake capacity (higher I_{max} and lower K_m). The

condition of high complex concentration (consequently high contribution) corresponded to high DOC concentrations (high $F_{\text{DOC}/\text{SOC}}$ values) with a high proportion of fulvic acids (low percentage of humic acids p_{CHA}), with a low concentration of Ca in solution and moderate acid soil conditions (moderate lower pH) (Fig. S9 in the supplementary materials).

Considering that on average the complex contribution to the uptake was low and that the sorption kinetics was little limiting the uptake, we compared the full model (sorption and complexation with both kinetics, Eqs. 5–8) with a simplified model considering only the transports of Cd^{2+} and its sorption on the solid phase at equilibrium (Eqs. 1–2; $k_d=1000 \text{ s}^{-1}$), i.e., the free ion model. The agreement between the full model and the free ion model was good with very little bias (Fig. 8). The error was low with a median of 0.8 % and a third quartile of 6 %. The cases where the error was >10 % corresponded to

Fig. 8 Cd cumulative uptake ($\mu\text{mol cm}^{-2}$) simulated by the full model (kinetics for complexation and sorption) against the cumulative uptake simulated by a model without complex and sorption at equilibrium (free ion model)

situations where the CdL contribution was above 15 % (not shown), which means high supply of labile CdL (Fig. 7). Consequently, for the domain studied, a model not considering the complex and the sorption kinetics was a satisfactory proxy for estimating the availability of Cd^{2+} .

Discussion

Diffusion of Cd^{2+} in soil is the main process governing the uptake of Cd^{2+}

For most of the cases, the concentration of Cd^{2+} at the root surface was very low (median value 0.27 nM; Fig. 2). For 98 % of the simulations, the initial concentration of Cd^{2+} was below 20 nM (not shown), which is consistent with what was reported in the literature for Cd^{2+} in non-polluted agricultural soils (Sauvé et al. 2000b). Initial Cd^{2+} is very low because Cd easily sorbs onto the soil matrix and forms complexes in solution, particularly with the soluble organic matter. In our results, the dissolved organic carbon (DOC) concentration was between 1.1×10^{-2} and 234 mg L^{-1} , and the 3st quarter value was 21.9 mg L^{-1} (Table S2); this range was a little lower than reported ranges (21–528 mg L^{-1}) in the literature (Li et al. 2013; Yin et al. 2002). The free ion fraction (F_{M0}) ranged

between 8.4×10^{-5} and 1.0 with a median value 0.12 and was comparable with 0 to 0.6 (median value 0.2) in Sauvé et al. (2000b) and *c.a.* 0.3–1.0 in Degryse et al. (2009). Our F_{M0} was lower than that in Degryse et al. (2009) because we did not consider too low pH like in their work (3–8) and the F_{M0} decreased with pH generally.

In our model, the diffusion gradient of Cd^{2+} results from the balance between the sink strength of the root for uptake (I_{max} , K_{m}) and from the supply of the soil including the diffusivity (f , θ), the water velocity (v_0), the initial concentration of Cd^{2+} , r_0 for geometric considerations, the kinetics of exchanges between sorbed and soluble Cd and the complexation kinetics of Cd in the solution. The simulations showed that actually, the initial concentration of Cd^{2+} and its buffer power (calculated through adsorption and desorption rate constants, $k_{\text{ads}}^{\text{M}}$ and $k_{\text{des}}^{\text{M}}$) were by far the most influential, followed by the soil diffusivity (f and θ) (Fig. 1a). Therefore, the supply of Cd^{2+} to the root generally determined the uptake in agricultural soils, which is well established experimentally and which corresponds to the good predictive value of the free ion activity model (Parker and Pedler 1997).

The relative importance between convection and diffusion, i.e., the Péclet number was in general very low, showing that diffusion was the dominant process for the supply of the root surface with Cd^{2+} . Diffusion was not only the main process influencing Cd uptake but it was for most of the cases the limiting factor. Indeed, the root capacity for absorption (I_{max} , K_{m}) was not very influential, meaning that it was generally not limiting the uptake. Consequently, a moderate uncertainty in the values of I_{max} and K_{m} or moderate changes in these parameters due to the plant functioning are expected to have little influence on the simulated uptake for most of the cases. This could explain why, for example, the 3 times increase in the root power from the basis toward the tip of sunflower roots (Laporte et al. 2013, 2014) was not experimentally observed to impact the Cd uptake of plants with different root architecture (different numbers of root tips) (Laporte et al. 2015). The low influence of I_{max} and K_{m} on the uptake is related to the nanomolar range for initial concentration of Cd^{2+} . In the literature, observed differences in Cd uptake between plant species cultivated on the same soil can generally be explained by the higher initial availability of Cd^{2+} (Stritsis et al. 2014) but it cannot be excluded that variations in root architecture impacting soil exploration (de Dorlodot et al. 2007) or root-deduced changes in the rhizosphere including pH could also explain these differences (Hinsinger et al. 2009).

Because of the low Péclet number (Fig. 3) and of the very low Cd^{2+} concentration at the root surface (Fig. 2), neglecting convection or considering a null concentration of Cd^{2+} at the root surface makes sense for many simulations. However, cases where these hypotheses do not hold may be of significant importance in the field. For example, the simulations indicated that significant contribution of convection to uptake is expected for low root capacity uptake and high water flux (Fig. S5 in the supplementary materials). This can actually be the case for maize, an important crop species that can have water flux of 10^{-6} to $10^{-5} \text{ cm s}^{-1}$ (Varney and Canny 1993) and I_{max} around $10^{-8} \mu\text{mol cm}^{-2} \text{ s}^{-1}$ (Lux et al. 2011).

Neglecting convection and assuming a steady state has been attained at the root surface are hypotheses of great interest for building simple models for predicting the uptake. The uptake of Cd^{2+} could then be calculated from the time integration of a diffusion flux of Cd^{2+} within a diffusion layer of thickness δ with a null concentration at the root surface and with the initial concentration at δ . This kind of model would give an analytical solution for the time integration, which is much more convenient than the numerical integration of the partial differential equations developed in our model. The difficulty is to estimate δ , which depends on the diffusivity of the soil (f and θ), on r_0 , and on the buffer power for Cd^{2+} .

Cd^{2+} in solution is generally buffered by desorption with little influence of kinetics

The importance of Cd^{2+} diffusion in soil also includes the buffering of the Cd^{2+} by the desorption from the solid phase as illustrated by the ranking of the partitioning coefficient K_d^M in Fig. 1a. The relatively low contribution of the Cd complex to root uptake as well as the mean net volumic rate of dissociation vs desorption at the root surface (Fig. 6) showed that generally the buffering of Cd^{2+} came from sorbed Cd^{2+} pool; and little from the dissociation of the complex.

Although the buffer power for Cd^{2+} is a key parameter, the kinetics of sorption/desorption was much less influential. In the no-complex model, forced equilibrium for sorption kinetics did not result in a large increase of the uptake (Fig. S8); the desorption rate constant (k_{des}^M) was likely enough high, making the desorption of sorbed Cd able to maintain quasi-equilibrium conditions when the root absorbed Cd^{2+} . We tested rate constants for desorption from 10^{-6} to $5 \times 10^{-4} \text{ s}^{-1}$. The upper range correspond to acid soils with low sorption capacity (Ernstberger et al.

2005; Wang et al. 2009) and were the highest values we were able to find for soils in the literature.

Without Cd complex in solution, the sorption kinetics showed almost negligible influence on the uptake (Fig. S8). In the presence of a complex, the kinetics of desorption is expected to be even less influential as the complex dissociation also contributes to buffer Cd^{2+} and the solid phase is then less mobilized. Additionally, when the buffer power for Cd^{2+} is accounted for by considering the pH, the SOC, the concentration of total Cd and Ca in solution, the desorption rate constant k_{des}^M is little influential (Fig. 1b). Therefore, as shown by the very good agreement between the full model with kinetics and the free ion model without sorption kinetics, the sorption kinetics was generally not necessary and sorption/desorption could be simplified by a constant buffer power in the model. The particular cases where this does not hold correspond to situations where the root absorption was high, and where the kinetics constant for sorption and desorption were very low (Fig. S6).

Strong complexation kinetic limitation and low complex contribution to uptake

The complexation kinetics showed much stronger disequilibrium than the sorption kinetics (Fig. 4). To simulate equilibrium, a k_d (rate constant for CdL dissociation) of 10^5 s^{-1} was required. Considering that the sorption kinetics is of little influence (Fig. S8), the significant increase of uptake when the full model is forced to equilibrium (Fig. 5) can be attributed to the forced equilibrium for the complexation kinetics. As the CdL concentration at the root surface was not depleted (median of 100.4 % of the initial concentration), this increase of uptake indicates the strong limitation of the complex dissociation kinetics. The dissociation of CdL in soil solution was not enough rapid to supply the roots with Cd^{2+} indicating that generally, the lability of the complex (Degryse et al. 2006) was low to compete with the buffering by desorption from solid phase.

For 69.5 % simulations not including the complex in the model did not result in an important error (<5 %) when simulating Cd^{2+} uptake (not shown). These simulations corresponded to low rate constants for association and dissociation (meaning relatively inert complex in the soil solution), high soil/solution partitioning for Cd^{2+} , and low water flux. The increase in uptake by the presence of CdL observed in our work was lower than those reported elsewhere in hydroponics (Degryse et al.

2012; Panfili et al. 2009). Indeed, strong increase in uptake due to CdL has been demonstrated in system with no buffer power from a solid phase (Degryse et al. 2006; Panfili et al. 2009). When a sorbing phase exists, both desorption and CdL dissociation can buffer Cd^{2+} at the root surface. We observed that the mean net volumic rates of Cd^{2+} desorption was generally dominating that of CdL dissociation. The concentration of sorbed Cd was on average 946 and 44 times that of CdL in solution at the beginning and for the whole duration of root absorption, respectively. This makes the sorbed pool a greater reserve for buffering the free Cd^{2+} compared to CdL. Additionally, the strong limitation of complexation kinetics discussed above also resulted in the low contribution of the complex. Consistent with this, the situations where the complex contribution was found high corresponded to high k_a^{cond} and k_d (Fig. 7), meaning highly labile complex for which the kinetics limitation was lower. Hence, at the root surface, the higher concentration of sorbed Cd^{2+} compared to CdL together with a strong kinetic limitation in CdL dissociation resulted in a high rate of desorption compared to CdL dissociation explaining the general low contribution of the complex to the uptake.

Our work concentrated on the endogenous dissolved soil organic matter and did not include exudation for simplification. In the literature, exudation of low molecular weight organic acids (LMWOA) has been hypothesized to increase the phytoavailability of Cd (Cieřliński et al. 1998; Nigam et al. 2001). However, in soil conditions, the mechanisms responsible for that are not easy to elucidate. Correlations between LMWOA concentration in the rhizosphere and plant Cd uptake can be explained by an increase in Cd phytoavailability due to an acidification associated with the organic acid exudation (Jones 1998). When supplied to the plant, LMWOA-Cd complexes can increase the uptake in nutrient solution because there is no solid phase to compete for the buffering of Cd^{2+} (Panfili et al. 2009). In soil, the increase in the plant Cd uptake reported in the literature (Nigam et al. 2001) can be explained by the fact that LMWOA-Cd complexes are supplied at very high concentrations, making the Cd complexes the main source of Cd.

The ligands exuded by roots form complexes with Cd^{2+} , which should result in a decrease in the free ion concentration, all the more so as the buffer power is low (Lin et al. 2014). In soils with a low buffering capacity for Cd^{2+} , root exudation is thus expected to decrease the uptake. In soils with a high buffering capacity for Cd^{2+} ,

the free ion concentration should decrease little while the Cd complex concentration increases. If the Cd complexes are absorbed as it is assumed for phytosiderophores (Ptashnyk et al. 2011), the uptake should increase. Otherwise, the additional Cd complex might increase the uptake only if they can buffer Cd^{2+} more strongly than the solid phase does, which is questionable considering the kinetic limitation suggested by our results.

Assessing the phytoavailability of Cd^{2+} in agricultural soils

Considering that the contribution of CdL was low (Fig. 6) and that the sorption kinetics was little influential (Fig. S8), a free ion activity model assuming that CdL was totally inert and only considering Cd^{2+} transport and buffering at equilibrium was a good approximation for assessing the phytoavailability of Cd in agricultural soils within the ranges of the soil characteristics studied here (Fig. 8). This simplified model can be used to compare and rank different soils differing quite substantially. The effort is to be concentrated on the estimation of the initial Cd^{2+} concentration and on the soil buffer power for the free ion as these parameters are not frequently determined in current soil analyses. Here, the initial concentration of Cd^{2+} and its buffer power were derived from the pH, the total concentration of Cd in the soil, the SOC, the concentration of soluble Ca^{2+} and the DOC ($F_{\text{DOC/SOC}}$) by using statistical models for the soil/solution partitioning of Cd and speciation calculations. This can be an approach for deriving the initial concentration of Cd^{2+} and its buffer power from parameters commonly measured in the field assuming that the underlying statistical model for the soil/solution partitioning are correctly calibrated. Otherwise, it is recommendable to directly measure these parameters from the soil to be characterized. The initial Cd^{2+} concentration can be determined by specific electrode or by resin-based methods (Cornu et al. 2009, 2011; Schneider et al. 2009) while the buffer power for the free ion could be assessed by sorption/desorption experiments including the determination of the free ion fraction at equilibrium.

If one is interested in minimizing the prediction error risk for a particular soil+plant situation, the above-mentioned simplified free-ion model may not be appropriate. Then, the first step would be to examine if it is necessary to account for the complex contribution by examining limit values for the kinetics constant k_a^{cond} and k_d and for the water flux (Fig. 7). If the complex

has to be accounted for, the kinetics of complexation has to be included as it is expected to strongly influence the contribution of CdL. If the complex could be assumed as inert, the phytoavailability can be estimated from the simple transport model with buffer power of Cd^{2+} in soil.

Here, we concentrate on a phytoavailability modelling for soil diagnosis. From our approach and because the between-roots competition (r_1) was little influential, the uptake by a growing root system can be achieved by integrating the uptake along with a linear or exponential root growth model following the approach proposed by Barber (1995) or possibly by considering the root architecture (Schnepf et al. 2011) to account for spatial heterogeneity in Cd availability in the soil.

Conclusions

We analyzed a phytoavailability model for Cd^{2+} in agricultural soils that considers Cd speciation, transport and kinetics for sorption and for complexation with the soil endogenous dissolved organic matter. The model analysis relied on databases for some agricultural soil parameters.

Our results confirmed that for non-polluted agricultural soils, because the initial concentration of Cd^{2+} was low, it is the main factor governing the phytoavailability of Cd along with the diffusion properties of the soil and the soil buffer capacity at equilibrium. As a consequence, the root capacity for absorbing Cd^{2+} was generally not limiting the uptake and was little influential.

The model outputs indicated that the dissociation of the Cd complexed to the dissolved endogenous soil organic matter generally contributed little to the root uptake, due to the large reserve of sorbed Cd^{2+} and because of the strong limitation by the kinetics of the dissociation. The situations where the complex could contribute significantly have been identified. For most of the situations, a model only considering Cd^{2+} transport and buffering at equilibrium (free ion activity model in soil) would be a good approximation for assessing the phytoavailability of Cd in agricultural soils. This stresses the need for setting up methods for routinely estimating as accurately as possible the initial Cd^{2+} concentration in the soil solution and the associated soil buffer power for the free ion.

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