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Abstract, tables and figures

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Labile Cd complexes increase Cd availability to plants

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Abstract: Dissolved trace metals are present in the environment as free ions and as complexes. Commonly used models to predict metal bioavailability consider the free ion as the major bioavailable species. However, increases in metal availability in the presence of metal complexes have repeatedly been found. We measured the uptake of cadmium (Cd) by spinach (*Spinacia oleracea*) from solution in absence or presence of synthetic ligands. At the same free ion concentration, uptake of Cd ranged over almost 3 orders of magnitude, and was largest in treatments with fast dissociating, *i.e.* labile, complexes. Similar results were found for the diffusional fluxes in these solutions, as measured with the DGT technique. The observed effect of Cd complexes on the plant uptake was in agreement with model calculations in which plant uptake was assumed to be governed by the diffusional flux. These results strongly suggest that Cd uptake is rate-limited by diffusion of the free ion to the root surface, even in stirred solutions. As a result, dissolved Cd complexes can increase Cd uptake, resulting in apparent exceptions from the free ion activity model. The magnitude of this increase depends both on the concentration and the lability of the complexes. The free ion concept should therefore be reconsidered when transport limitations of the metal ion to the uptake site prevail.

One-sentence synopsis: Labile complexes contribute to plant uptake of Cd in solution by increasing diffusional flux of Cd to the root surface.

TABLE 1. Stability constant (K_{CdL}) of the Cd-ligand complexes, dissociation rate constant (k_d) and the degree of lability (ξ) as determined from plant uptake at total concentrations of Cd and ligand as listed. The free Cd concentration, $[Cd^{2+}]$, was 1 nM in all solutions ^a

ligand	logK_{CdL} (M^{-1})	k_d (s^{-1})	Cd_{tot}^b (μM)	L_{tot}^b (μM)	ξ^b (%)
EDDA	10.0	$>10^{-2}$	0.011	100	40
NTA	11.1	$>10^{-2}$	0.1 – 6	100 – 3000	19 – 3.0
HEDTA	15.5	1.5×10^{-3}	1.0 – 100	3.0 – 280	1.2–0.12
EDTA	18.2	1.8×10^{-4}	25	100	0.15
EGTA	18.2	1.6×10^{-4}	1.0 – 100	5.9 – 500	0.26 – 0.09
CDTA	21.6	9.9×10^{-6}	1.0 – 100	1.4 – 138	0.11 – 0.04

^a The metal speciation was calculated with GEOCHEM-PC (32). ^b If a range is given for ξ and for the metal and ligand concentrations, Cd uptake was measured in 4 different solutions with concentrations ranging between the values given in the table.

Figure 1 Dissociation kinetics of Cd-ligand complexes, measured with the competitive ligand exchange method in solutions containing 2 mM $\text{Ca}(\text{NO}_3)_2$ and 2 mM MES (pH=6). Only the data for up to 4 hours after the start of the experiment are shown. The lines show the exponential regression (eq 2: $c_{\text{ML}}(t) = c_{\text{ML}}^0 \cdot \exp(-k_d \cdot t)$).

Figure 1

Figure 2 Uptake of Cd by spinach as a function of total Cd concentration in solution, at constant Cd^{2+} concentration of 1 nM in the presence of Cd complexes varying in dissociation kinetics (Table 1). The Free Ion Activity Model (dotted line) predicts identical uptake in all solutions. The departure from the FIAM is smallest in presence of complexes with the smallest dissociation rate (Cd–CDTA), and is largest for the most labile complexes (Cd–EDDA, Cd–NTA). The solutions contained 2 mM $\text{Ca}(\text{NO}_3)_2$ and 2 mM MES (pH=6). Uptake in the ligand-free solution was measured both in stirred and stagnant solutions. The full lines indicate the simulated uptake in presence of complexes with given dissociation rate constant, assuming that the uptake is governed by diffusion ($D=5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $\delta=400 \text{ μm}$). Values are means $\pm$ s.e.m. ($n \geq 3$).

Figure 2

Figure 3 Relationship between the degree of lability of Cd complexes as determined

from plant uptake (ξ , eq 7: $\xi = \left(\frac{C_{d_{pl}}}{C_{d_{pl}^{contr}}} - 1 \right) \cdot \frac{[Cd^{2+}]}{[CdL]}$) and from DGT measurements

(ξ_{DGT} , eq 8: $\xi_{DGT} = \left(\frac{c_{DGT}}{c_{DGT}^{contr}} - 1 \right) \cdot \frac{[Cd^{2+}]}{[CdL]} = \frac{c_{DGT} - [Cd^{2+}]}{[CdL]}$). The solutions used for the

measurements were the same as in Figure 2. The full line shows the linear regression with

the intercept (that is not significantly different from zero) forced to zero ($\log \xi = 1.70$

$\log \xi_{DGT}$; $r^2 = 0.92$). The dotted line is the 1:1 line.

Figure 3

Figure 4 Observed versus predicted ratios of Cd uptake in a ligand-buffered solution to that in a control (ligand-free) solution with the same free Cd^{2+} concentration. The predictions were made with numerical simulations assuming that Cd uptake is limited by

diffusion, or with an analytical approximation (eq 15: $\frac{\text{Cd}_{\text{pl}}}{\text{Cd}_{\text{pl}}^{\text{contr}}} \approx \frac{\delta}{\mu}$, with $\delta=400 \mu\text{m}$ and

$$\mu \text{ calculated according to eq. 13: } \mu = \sqrt{\frac{D_{\text{M}}}{k_{\text{a}} \cdot [\text{L}_{\text{free}}]_{\text{b}}}} = \sqrt{\frac{D_{\text{M}}}{k_{\text{d}} \cdot \frac{[\text{M}]_{\text{b}}}{[\text{ML}]_{\text{b}}}}).$$

Figure 4

Figure 5 Modeled steady state concentration profiles of Cd^{2+} (full line) and the Cd-ligand complex (dotted line) for a fast-dissociating complex (panels a,b) and a slowly dissociating complex (panels c,d) at different degrees of buffering. The vertical dotted line gives the thickness of the reaction layer, μ , calculated with eq 13:

$$\mu = \sqrt{\frac{D_M}{k_a \cdot [\text{L}_{\text{free}}]_b}} = \sqrt{\frac{D_M}{k_d} \cdot \frac{[\text{M}]_b}{[\text{ML}]_b}}$$

Figure 5