A critical assessment of chelant-enhanced metal phytoextraction

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Supporting Information

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Modeling extraction of Pb in the presence of chelants from soil

We use Pb as an example because data on the extractability of this metal from soils in the presence and absence of chelating agents are available (1). The soil had been polluted in the field with Pb (723 mg kg^{-1}) by application of sewage sludge. The extraction of Pb was measured over the pH range from 3 to 9 in the absence of chelants and in the presence of EDTA and EDDS. Dissolved Pb as well as dissolved Ca and Fe were measured.

Soil-bound Pb can be modeled using two pH-dependent binding sites. This concept of using a “soil-ligand” to model the solubility of metals in soils was introduced by Lindsay (2). Whereas Pb-binding in the absence of chelants can be modeled successfully using one “soil-ligand”, this is not possible for the Pb solubilization in the presence of chelants. Two different binding sites with differing affinity and pH dependence were necessary to model the observed solubilization of Pb. Fitting parameters are the protonation of the site, the logK value of the “soil-ligand”-Pb complex and the total site concentration. The dependence on pH was fixed at the power of -1 and -2 for the two sites, representing different susceptibility of the site towards protonation. The total site concentration (4.5 mmol kg^{-1}) was chosen in slight excess of the total Pb content (3.5 mmol kg^{-1}) and arbitrarily distributed between the two sites with a ratio of 1:2. Fitting parameters were therefore mainly the log K values. The measured Ca concentration was also included in the model to account for competition between Ca and Pb for the chelant. The total chelant concentration was also corrected for the measured amount of solubilized Fe, indicative of formation of Fe(III)-complexes that decrease the amount of chelant available for complexing other metals. Table S1 presents the results of a manual fit of the observed data with these two sites. Figure S1a shows the final model fit for Pb solubility in the absence and presence of EDDS.

Modeling Ca extraction from a carbonate-free soil

Ca extraction from a carbonate-free soil containing only exchangeable Ca was modeled using the same approach as for Pb. Two binding sites $>X_3Ca$ and $>X_4Ca$ were used. The pH-dependent reactions are given in Table S1. Fig. S1b shows the experimental data for the solubilization of Ca as a function of pH together with the model fit.

Table S1. Model for Pb and Ca adsorption onto soil based on experimental results from Tandy et al. (1)

Species	Equation	Site concentration (mmol kg^{-1})
$>X_1Pb$	$[Pb][X_1][H]^{-1}10^{2.61}$	1.5
$>X_2Pb$	$[Pb][X_2][H]^{-2}10^{-1.32}$	3.0
$>X_3Ca$	$[Ca][X_3][H]^{-1}10^{-4.32}$	250
$>X_4Ca$	$[Ca][X_4][H]^{-0.5}10^{0.44}$	250

Table S2: Conditions of the four model calculations used to model the influence of Ca and Fe on Pb extraction from soil.

Pb	500 mg kg^{-1} (2.4 mmoles kg^{-1})
extraction	in suspension with 20 g l^{-1} soil
EDTA/ EDDS	50 μM
EDTA:Pb	1
logK values	source of all logK values for EDTA, EDDS, Pb and Ca: reference (3)
case 1	no Ca in the system
case 2	exchangeable Ca (200 mmoles kg^{-1})
case 3	soil with 10% $CaCO_3$, CO_2(g): $3.16.10^{-4}$ atm in extraction solution
case 4	case 2) and additionally the Fe-phase hydrous ferric oxide (HFO)

Table S3: Soil and plant parameters for the calculations used to predict plant uptake

soil Pb concentration	1000 mg kg^{-1}
depth of polluted soil	0.2 m
soil bulk density	1.2 g cm^{-3}
total Pb mass	2400 kg ha^{-1}
soil water content	0.3 cm^3 cm^{-3}
soil solution concentration if all Pb is mobilized	16 mM (3300 mg L^{-1})
evapotranspiration	5 mm d^{-1} (5 L m^{-2} d^{-1})
yield (dry matter)	30 t ha^{-1}

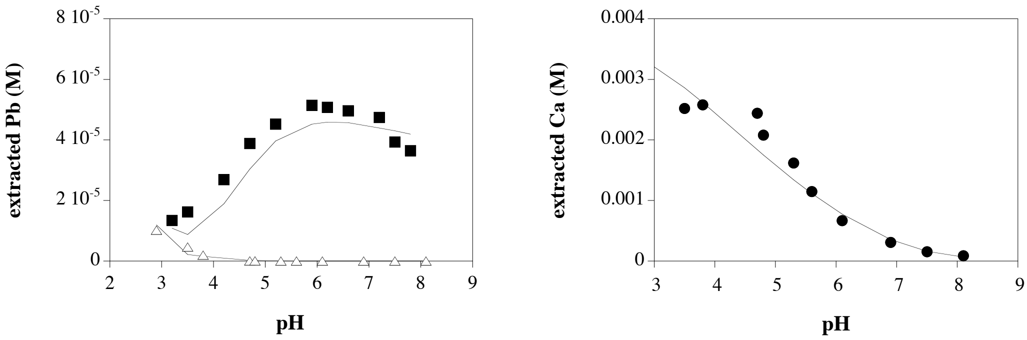

Fig. 1S: a) Measured and simulated Pb extraction in the absence (triangles) and presence of EDDS (squares) and b) Ca extraction from a non-calcareous soil (from Tandy et al. (1)). The simulations were obtained by fitting the equations shown in Table S1 to the experimental data.

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