EDTA-ENHANCED TRANSPORT OF COPPER FROM CONTAMINATED SOIL AND ITS IMPLICATIONS

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Abstract

An understanding of the interacting physical and chemical processes involved is necessary for efficient and environmentally responsible remediation of copper-contaminated soils through EDTA-enhanced mobilisation, using either *ex situ* or *in situ* methods. In order to study these processes, leaching experiments were performed on repacked columns and intact cores, with various initial and boundary conditions, in two contrasting soils containing varying amounts of copper. One soil was an alluvial Manawatu fine sandy loam, which was low in organic matter, and the other a volcanic Opotiki sandy loam with a higher organic matter content.

In both soils, the EDTA moved without any observable adsorption when the soil pH was above 5.0. But, uncontaminated Opotiki soil with a pH of 4.5, did adsorb EDTA to some extent. Leaching with an excess of 0.01 *M* EDTA, extracted all but 40 mg kg^{-1} of the copper that was initially present in the repacked Manawatu soil and all but 90 mg kg^{-1} of the copper from the Opotiki repacked soil. In the intact Opotiki soil cores the EDTA reduced the copper concentration in the top 25 mm of the intact core from 240 to 80 mg kg^{-1}. EDTA not only leached the copper from the soil, but also a substantial amount of iron.

Opotiki soil with pulses of EDTA left in it for up to a month before leaching showed a time-dependent drop in the amount of copper leached, and a corresponding increase in the amount of iron leached. Increased EDTA residence time in the Manawatu soil prior to leaching in general also showed a time-dependent increase in iron leached. With increasing EDTA residence time in the soil, the mass of copper leached dropped markedly in the low-Cu Manawatu soil. However, the copper remained in the soil solution, and so prone to leaching, for at least a month in the medium and high-Cu Manawatu soils. These results are consistent with $CuEDTA^{2-}$ being gradually transformed to the more stable $Fe(III)EDTA^{-}$ and Cu^{2+} in all cases.

Copper contaminated Opotiki repacked soil columns and intact cores growing the grass *Agrostis tenuis* on were used to investigate the relative importance of plant uptake and leaching of copper. Application of 1800 μmol of EDTA to 0.9 kg of the contaminated soil in a repacked column increased the leaf copper concentration from 30 μg g^{-1} to 300 μg g^{-1}. The same amount of EDTA applied to 1.0 kg of soil in the intact

cores, increased the herbage copper concentration to 60 μg g^{-1}. Leaching the columns and cores with water about a month after the EDTA application removed 25 to 169 times more copper than was taken up by the herbage.

The convection dispersion equation (CDE), coupled with a source/sink term accounting for time-dependent reactions taking chemical species into or out of solution, was used to model the EDTA-enhanced transport of copper in contaminated soils. In general, the model successfully described the copper concentration in the leachate and soil, despite the quite different amounts and concentrations of EDTA applied, and the varying lengths of time it was left in the soil before leaching. However, the values for the key parameters had to be adjusted appropriately, with faster rate constants for the Manawatu soil than the Opotiki soil. The observed differences in behavior between the repacked and intact Opotiki soil could be simulated by increasing the dispersivity from 3 to 23 mm, while leaving unchanged the parameters describing the chemistry.

The results on the kinetics of the EDTA and the soil copper reaction, and for the stability of the $CuEDTA^{2-}$ and its interaction with physical processes, suggest that *in situ* remediation of copper contaminated soils is possible. However, the applied EDTA should be leached immediately or within few days. It would also require that the residence time of soil water moving through the profile to the water table was in excess of a month. EDTA-enhanced phytoremediation of copper might be possible if leaching can be avoided. If drainage occurs the copper moving below the root zone is likely to be at least an order of magnitude greater than that taken up by the vegetation.

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a	a constant in equations (1- 20, 1-21)	-
b	a constant in equation (1-21)	-
c	tortuosity factor	-
f	reduction factor	-
h	matric potential	[m]
k_1	rate constant for reaction between $EDTA_0$ and extractable copper	$[s^{-1}]$
k_2	rate constant for reaction between $EDTA_0$ and extractable iron	$[s^{-1}]$
k_3	rate constant for reaction between CuEDTA and extractable iron	$[s^{-1}]$
k_4	rate constant for reaction between $EDTA_0$ and slowly extractable iron	$[s^{-1}]$
k_5	rate constant for reaction between CuEDTA and slowly extractable iron	$[s^{-1}]$
n	order of reaction	-
q_s	solute flux density	[kg or mol m^{-2} s^{-1}]
q_w	water flux density	[m s^{-1}]
$q_{w,\,in}$	flux into the top of the soil layer	[m s^{-1}]
$q_{w,\,out}$	flux out of the bottom of the soil layer	[m s^{-1}]
t	time	[s]
t_p	solute introduction time	[s]
v	pore water velocity	[m s^{-1}]
z	depth	[m]
z_c	characteristic length	[m]

C	soil solution solute concentration	[kg or mol m^{-3}]
C_c	characteristic concentration	[kg or mol m^{-3}]
C_0	applied solute concentration	[kg or mol m^{-3}]
C_1	solute concentration in the pre-leaching solution	[kg or mol m^{-3}]
C_2	solute concentration in the pre-leaching solution	[kg or mol m^{-3}]
C_{crit}	critical concentration of Cu triggering exclusion by roots	[kg or mol m^{-3}]
C_f	flux solute concentration	[kg or mol m^{-3}]
C_r	resident soluteconcentration	[kg or mol m^{-3}]
D_0	molecular diffusion coefficient in solution	[m^2 s^{-1}]
D_h	hydrodynamic dispersion coefficient	[m^2 s^{-1}]
D_i	effective diffusion coefficient	[m^2 s^{-1}]
D_w	soil water diffusivity	[m^2 s^{-1}]
H	hydraulic potential	[m]
I	cumulative infiltration	[mm or m]
$K(\theta)$	unsaturated hydraulic conductivity	[m s^{-1}]
K_d	distribution constant	[m^3 kg^{-1}]
$K_{Me\text{-}Y}$	metal-EDTA formation constant	-
K_S	saturated hydraulic conductivity	[m h^{-1} or m s^{-1}]
L	length of the column	[m or mm]
M	total solute concentration	[kg or mol m^{-3}]
M_{Cu}	EDTA-extractable copper	[mol kg^{-1}]
M_{Fe}	EDTA-extractable iron (rapidly reacting)	[mol kg^{-1}]
M_{Fe}^*	slowly reacting iron fraction	[mol kg^{-1}]
P	pressure potential	[m]
R	dimensionless retardation factor	-

S	sink/source term accounting for any chemical reactions bringing that chemical species into or out of solution	[mol m^{-3} of soil s^{-1}]
S_{Cu}	source/sink term for $CuEDTA^{2-}$	[mol m^{-3} of soil s^{-1}]
S_{Fe}	source/sink term for $FeEDTA^{-}$	[mol m^{-3} of soil s^{-1}]
S_o	source/sink term for $EDTA_0$	[mol m^{-3} of soil s^{-1}]
S_s	amount of solute adsorbed	[kg or mol kg^{-1}]
T	dimensionless time ($v\ t/z_c$)	-
U_{max}	maximum water uptake from the the column/core	[s^{-1}]
U_s	copper uptake by roots	[mol m^{-3} of soil s^{-1}]
U_{tot}	total root water uptake rate	[m s^{-1}]
U_w	sink term for root water uptake	[s^{-1}]
Y	ligand	-
Z	gravitational potential in equation (1-1)	[m]
Z	dimensionless depth (z/z_c)	-

α	mol fraction of a particular EDTA species	-
θ	volumetric water content	[$m^3\ m^{-3}$]
θ_m	mobile water fraction	[$m^3\ m^{-3}$]
θ_{im}	immobile water fraction	[$m^3\ m^{-3}$]
θ_i	initial water content	[$m^3\ m^{-3}$]
θ_{FC}	water content at field capacity	[$m^3\ m^{-3}$]
λ	dispersivity	[m or mm]
ρ_b	soil bulk density	[Mg m^{-3}]
τ	λ/z_c	-

Abbreviations

BTC	breakthrough curve
CDE	convection-dispersion equation
CEC	cation exchange capacity
$CuEDTA^{2-}$	copper-EDTA complex
DOC	dissolved organic carbon
EDTA	ethyline diamine tetraacetic acid
$EDTA_0$	Influent solution (mixture of EDTA, halide tracer and KOH)
$Fe(III)EDTA^-$	ferric-EDTA complex
Me	any metal
Me-EDTA	any metal-EDTA complex
MIM	mobile-immobile model
Na_2H_2EDTA	disodium ethyline diamine tetra acetic acid
PV	pore volumes